STRUCTURE-PROPERTY RELATIONSHIPS IN PAEs PREPARED FROM 2-(2,4-DIFLUOROPHENYL)BENZOXAZOLE DERIVATIVES

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

By

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Amy Slaybaugh ENTITLED Structure-Property Relationships in PAEs Prepared from 2-(2,4-difluorophenyl)benzoxazole Derivatives BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Slaybaugh, Amy. M.S., Department of Chemistry, Wright State University, 2018. Structure-Property Relationships In PAEs Prepared From 2-(2,4-difluorophenyl)benzoxazole Derivatives.

The synthesis of N-heterocycle functionalized poly(arylene ether)s, derived from 2-(2,4-difluorophenyl)benzoxazole, was explored. The platform monomer, 2-(2,4-difluorophenyl)benzoxazole (3), was prepared in one-step and characterized using NMR spectroscopy and elemental analysis. The “pre” approach involved introducing a carbazole moiety, using a copper catalyzed C-N coupling reaction, while the “post” approach required conversion of monomer 3 to the corresponding poly(arylene ether)s (PAE)s first, then performing the C-N coupling reaction. Both “pre” and “post” approaches utilized bisphenol-A (BPA) and 4,4’-difluorophenylsulfone (DPS) as comonomers as well as 4,4’-dihydroxydiphenyl ether (DPE) and 4,4’difluorotriphenylphosphine oxide (dfTPPO). All of the materials had sufficient molecular weights (Mₙ) to allow good films to be cast. The polymers possessed excellent thermal stability as evidenced by 5% weight loss temperatures (Tₚₕₜₕ) above 400°C in nitrogen and air while glass transition temperatures (Tₜₚ) were all above 180°C. In general, the polymers containing TPPO and DPE had higher Tₜₚ values and Tₚₕₜₕ values.
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DEDICATION

Dedicated to my family for all the love and support they have given me.
1. INTRODUCTION

1.1 Lighting Overview

For general lighting purposes there are three main options: incandescent bulbs, fluorescent bulbs, and light emitting diodes (LED). Incandescent bulbs are commonly used for lights in a home. The bulbs produce light by using electricity to heat a filament until it is white hot. However, 90% of the electricity used is lost as heat. These bulbs typically last for 750-1,000 hours.\(^1\) Another type of incandescent bulb is a halogen bulb which is often known as a tungsten-halogen filament incandescent bulb. These bulbs contain a small halogen gas filled capsule that emits light. These bulbs are slightly more efficient than regular incandescent bulbs with a lifetime of approximately 2,000-3,000 hours of use.\(^1\) A more efficient alternative to incandescent lighting is fluorescent lighting. These bulbs contain a small amount of mercury that is excited to produce light. These bulbs are more efficient because energy, in the form of heat, is not lost as with incandescents.\(^1\) These bulbs come in two main forms, a long, thin tube or a compact spiral tube. These bulbs last approximately 10,000 hours.\(^1\) The most efficient lighting alternative is light emitting diodes, LEDs. These bulbs contain expensive metals that emit light when an electrical current is applied. LEDs have a vastly improved lifetime when compared to incandescent bulbs and fluorescent bulbs. LED bulbs last approximately 15,000 hours.\(^2\) The LED has become a versatile lighting source for applications from household lighting to TV, computer and smart phone displays.
1.2 LED

LEDs provide an efficient and bright light source for daily use lighting in homes as well as lighting for cars and industrial applications. A traditional LED utilizes inorganic semiconductors to conduct electricity to produce emission, typically via a p-n junction. This means a hole is injected from the anode and an electron is injected from the cathode. The electron will diffuse into the semiconductor and will recombine with the hole at the interface junction resulting in light emission. This process allows for the device structure to be simple with the only concern relating to electrode contacts on the p-n interface. A general device structure for LEDs (see Figure 1) consists of a sapphire substrate with two metal layers stacked on the substrate; a cathode on the p-layer metal and anode on the n-layer metal. The p-layer contains holes; a lack of electrons, while the n-layer contains an excess of electrons. These two layers are the main components of a semiconductor.
Figure 1. General Structure of LEDs.

LEDs available for consumer use have become a cheaper and more efficient replacement to traditional incandescent bulbs. Traditional 60 Watt incandescent bulbs have now been replaced by LEDs using 10.5 Watts to produce the same amount of light. The LED bulb has a lifetime of 15000 hours and produces 800 lumens of light. General Electric Company estimates that the LED bulb will have energy costs of approximately $1.26 per year. The traditional 60 Watt incandescent bulb, available from General Electric Company, produces approximately 820 lumens of light and has an estimated energy cost of $7.23 per year.

The downside to LEDs is their use of expensive metals to provide the light emission as at specific wavelengths. By varying the combination of expensive metals used in a device the desired color of emission can be achieved. For example, indium gallium nitride (InGaN) is used to produce a blue emitting LED. The use of expensive metals is accompanied by two significant issues, sustainability and affordability. The supply of these metals will eventually be depleted.

1.3 OLED

Organic light emitting diodes (OLEDs) with a low driving voltage, below 10 V, were first introduced in 1987. The driving voltage is the voltage required to produce light emission by injecting electrons into the organic material. OLEDs are self emitters
that do not require background light present in order to produce light and have the potential to consume less energy than traditional inorganic light emitting diodes (ILEDs). The organic layers have a thickness of approximately 100-200nm while the overall devices are only a few millimeters in thickness. The majority of the thickness is due to the substrate and encapsulation needed for device support and structure.

OLEDs produce light by passing an electrical current through the anode to the cathode. The electrical current will pass through the emitting layers (electron and hole transport layers) of the device, the result is the electron and hole combining and emitting a photon. The emission of a photon produces light through the substrate (Figure 2).

![Light emission for an OLED.](image)

**Figure 2.** Light emission for an OLED.

A blue fluorescent emitting OLED device can be achieved by using dopant emitters in a host-dopant system. An example of a blue emitting molecule can be found in Figure 3.

![Blue fluorescent emitting material.](image)

**Figure 3.** Blue fluorescent emitting material.
The compound above, in dichloromethane at a concentration of $10^{-5}$ M, exhibits a maximum absorption wavelength of 386 nm and a maximum fluorescence wavelength of 465 nm which was also the wavelength observed in the solid phase. The compound was used as a dopant in a host material, 2-methyl-9,10-di(naphthen-2-yl)anthracene (MADN), in varying concentrations to determine optimal values for wavelengths and efficiencies. When the compound was used in 5% doping concentration the maximum electroluminescence wavelength was 457 nm with maximum external quantum efficiency (EQE) of 3.3%. The concentration was increased to 10% doping concentration to achieve the same electroluminescence wavelength as the 5% concentration but had an increase in EQE to 5.1%. A final doping concentration of 15% was used to obtain a maximum electroluminescence wavelength of 456 nm with an EQE of 5.6%.

A blue phosphorescent OLED can be achieved by using an iridium based compound (Figure 4).

![Figure 4. Blue phosphorescent emitting molecule.](image)

The compound above exhibited an emission wavelength, when excited at 345 nm, of 440 nm and 470 nm in a solution of 2-MeTHF. The emission wavelength in the solid state, 10 wt% in a poly(methyl methacrylate) (PMMA) film, was 440 nm, 469 nm, 493
nm. The compound was incorporated into a device using 10%, 15%, and 20% doping concentrations. The wavelength observed was consistent for all three concentrations at 440 nm. The EQE improved with increasing concentration. The 10% doping concentration 4.90%, increased to 5.30% for the 15% doping concentration, and reached the highest EQE of the three with 7.00% for the 20% doping concentration.

OLEDs have been recently applied as various display types in consumer products. These display types include back-lighting displays, general purpose illumination, architectural lighting, industrial lighting, vehicular lighting, and various electrical sign displays. A promising development in the commercial use of OLEDs in displays is in the use of televisions. In 2009, Sony introduced the first television to use an OLED display. Despite the prospect of consuming less energy than LEDs, the long-term stability is poor. When comparing the structure of an OLED to an LED, the OLED contains a more complex structure due to the limited carrier mobility and the electrical conduction needed to produce emission.

1.4 Devices and Fabrication

OLED device structures (see Figure 5) generally start with a glass or plastic substrate with an anode layered on top. The next layer consists of a hole transport layer of organic material followed by an electron transport layer of organic material. The final layer of an OLED is a cathode. The anode is typically made of a transparent conductive oxide (TCO). A very common anode is indium tin oxide (ITO) because it has a low resistivity and a high morphological uniformity. These characteristics play an important role in the device performance because they allow for consistency throughout the device.
In an attempt to move away from the use of expensive metals for the anode, a conductive polymer, poly(3,4-ethylenedioxythiophene) (PEDOT) that has been doped with polystyrene sulfonate (PSS), has been explored. However, to successfully use the conductive polymer as an anode, the conductivity has to be enhanced due to the insulating PSS. The cathode is often aluminum because it is a readily available, can be purchased with a high purity, and low cost.

**Figure 5.** General illustration of OLED device.

By using plastic as the substrate the device can be flexible which will allow for a larger variety of lighting options, which is a major advantage over LEDs. The majority of the thickness of an OLED device comes from the substrate material. By using plastic as the substrate a thinner and more flexible display can be achieved. There are a number of methods available to fabricate an OLED, each with its own set of advantages and disadvantages. The first method is vacuum deposition or vacuum thermal evaporation (VTE). In VTE the organic material is heated in a vacuum chamber and is deposited when it condenses on a cooled substrate. An advantage to using this production method is that it is one of the cleanest methods for depositing onto substrates. The materials will be heated to a specific temperature and under certain vacuum conditions that allow for only pure materials to sublime. This purifies the material before being deposited onto the
substrate. A disadvantage to using the VTE method is the potential for material degradation if the sample is overheated during the process. A second option for fabrication is organic vapor phase deposition (OVPD). OVPD is performed in a low pressure, hot walled reaction chamber. A carrier gas is used to transport the evaporated organic material to a substrate where it will cool and condense as a film. An advantage to this method is the ability to achieve thick films with uniformity due to the careful introduction of the carrier gas. A disadvantage to using the OVPD production method is difficulty when scaling to large size substrates. The uniform distribution achieved from the carrier gas becomes increasingly difficult as the size of the substrate increases. A final fabrication option is inkjet printing. For this method, the organic material is sprayed onto the substrate in a similar manner as a printer spraying ink on paper. An advantage to this system is a minimized risk of contamination because the inkjet nozzle does not have to make contact with the substrate to deposit the organic material. A disadvantage to using inkjet printing is the production time for material to be deposited onto substrates.

1.4.1 Band Gap

In order to provide a full color display using OLEDs these devices require a combination of red-green-blue (RGB) emitters. The red and green emitting OLEDs have a far greater efficiency, life-time, stability, and performance than blue OLEDs. One of the main problems in obtaining blue emitting OLEDs is the large band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (see Figure 6). The large band gap required also makes the material susceptible to degradation via oxidation or other pathways.
In order to achieve a desired emission color, the band gap between the HOMO and LUMO energy levels must be controlled. The energy levels are obtained from the donor and acceptor materials used in the organic compounds. Generally, to achieve a blue emission of ~450 nm a band gap of ~2.8 eV is needed. In order to achieve a red emission of ~650 nm a band gap of ~1.9 eV is needed.

An example of a molecule that produces emission in the blue region can be found in Figure 7. The observed wavelength of emission was 404 nm when measured in toluene (1·10⁻⁴ M) and 423 nm when measured in a bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) film (10 wt%). Generally, the donor portion of the molecule is associated with the HOMO level and the acceptor portion is associated with the LUMO level.
The LUMO level in Figure 7 is associated with the diphenylsulfone portion whereas the HOMO level is associated with 3,6-di-tertbutylcarbazole branching off the diphenylsulfone.\textsuperscript{16}

An example of a molecule that emits in the green region can be found in Figure 8.\textsuperscript{18} The molecule showed an emission peak at 522nm from a phosphorescence emission spectrum as a film and an emission peak of 502 nm from a fluorescence spectrum in toluene.\textsuperscript{18}

![Molecule with wavelength emission in the green region.](image)

The LUMO level in Figure 8 is associated with the benzophenone portion whereas the HOMO level is associated with the carbazole derivatives.\textsuperscript{18}

An example of a molecule that emits in the red region can be found in Figure 9.\textsuperscript{19} The molecule showed an emission peak at 613 nm in toluene and 623 nm in CH\textsubscript{2}Cl\textsubscript{2}.\textsuperscript{19}
Figure 9. Molecule with wavelength emission in the red region.

The LUMO level in Figure 9 is associated with the thienopyridine core whereas the HOMO level is associated with the poly(phenylene) derivatives branching off the thienopyridine core.¹⁹

1.4.2 Thermally Activated Delayed Fluorescence, TADF

Thermally activated delayed fluorescence (TADF) is a specific method used to maximize emission efficiency for OLED devices. TADF systems are more desirable than traditional fluorescence and phosphorescence systems due to their triplet harvesting capabilities.¹⁵ In general, electroluminescent materials have two excitons formed, singlet and triplet. The singlets have a spin of $S=0$ while the triplets have a spin of $S=1$.¹⁵ As observed in Figure 10, fluorescence occurs at an efficiency of 25% by utilizing the singlet exciton where phosphorescence systems can produce 75% or more efficiency by utilizing the triplet excitons as well as singlets from intersystem crossing (ISC).
Figure 10. Fluorescence, Phosphorescence, and TADF emission pathways.

The goal of a TADF emitter is to convert the $S = 1$ excitons to $S = 0$ excitons for eventual light emission. This is accomplished by using reverse intersystem crossing (rISC) to harvest the triplets to achieve 100% efficiency (see Figure 10).\(^\text{15}\)

To achieve a TADF molecule, a donor-acceptor system is needed. If the HOMO and LUMO levels have a good separation, little overlap, a smaller $\Delta E (S-T)$, which is the difference in energy between the singlet and triplet states, will be obtained. The overlap between the two levels can be manipulated by altering the structures of the donor and acceptor.\(^\text{15}\) By using specific chromophores to control the $\pi$-conjugation length of a $\pi$ donor-acceptor system a TADF device can be used in the design of a blue emitting OLED.\(^\text{16}\) The donor systems used in this project are carbazole and carbazole–derivatives as well as arylamine derivatives (see Figure 11).\(^\text{15}\)
Figure 11. TADF donor systems.

There are various types of acceptor systems (see Figure 12) that can be used for a TADF system including sulfone derivatives, benzonitrile derivatives, and \( N \)-heterocyclic derivatives.

Figure 12. TADF acceptors.

The various combinations of donors and acceptors have been used to produce molecules emitting different wavelengths. For example, emitter molecules containing carbazole units emitted wavelengths around 480 nm while emitter molecules containing dimethylcarbazole units emitted wavelengths around 500 nm (see Figure 13). The difference in wavelengths can be attributed to the more electron rich methyl groups. The
photoluminescence quantum yield for the systems in Figure 13, range from 43% for DCzTrz at 31 μs, 100% for TCzTrz at 14 μs, and 99% for DczmCzTrz at 14 μs.²⁰,²¹

![Chemical structures of DCzTrz, TCzTrz, DczmCzTrz, and TrmCzTrz](image)

**Figure 13.** Donors and acceptors varying the connectivity to vary the emission wavelength.

When a molecule is placed in a device, EQE can be determined. For a multilayered OLED device containing the emitter material in Figure 7, the EQE was determined to be 9.9%.¹⁶

One characteristic important in TADF molecules is the twist angle of the donor unit from the acceptor unit. A larger twist angle will break conjugation from the donor and the acceptor which will lead to a more separated HOMO and LUMO. This also has the effect of hindering charge transfer. The more separated HOMO and LUMO will allow for a smaller ΔE (S–T), allowing for ISC and rISC to occur allowing for a TADF molecule to exist.¹⁵

### 1.4.3 Polymer OLEDs

TADF molecules can be incorporated into polymers using 4 types of polymers (see Figure 14): alternating connections of the donor and acceptor groups, TADF
molecules that have been separated by backbone units, donors being fixed to the backbone of the polymer with acceptor groups grafted as side chains, and TADF molecules as a pendant molecule in the backbone of the polymer.\textsuperscript{17}

![Diagram of TADF molecule types](image)

**Figure 14.** Types of TADF-based polymers.

In a TADF molecule, the donor and the acceptor are connected to allow for a small $\Delta E$ (S–T) which allows for reverse intersystem crossing for the triplet and singlet state electrons to occur. This concept can be applied to TADF polymers by alternating the donor and acceptor groups in the polymer backbone.\textsuperscript{17} An example of an alternating donor-acceptor polymer can be found in **Figure 15.**

![Diagram of alternating donor-acceptor molecules](image)

**Figure 15.** Alternating donor-acceptor molecules in TADF based polymer.
The above polymer, in an oxygen-free toluene solution, has maximum absorption wavelengths of 307 nm and 361 nm and a maximum emission wavelength of 472 nm. The polymer in the solid phase, 10 wt% doped into a mixed host of tris(4-carbazol-9-yl-phenyl)amine (TCTA) (65 wt%) and 4,4′-cyclohexyldenedi[ N, N -bis(4-methylphenyl)benzenamine] (TAPC) (25 wt%), has a maximum wavelength emission of 508 nm. When the polymer is incorporated into an OLED device, the maximum EQE achieved was approximately 8.1%.\textsuperscript{22}

A polymer with TADF molecules that have been separated by backbone units is synthesized using donor, acceptor, and polymeric backbone molecules (see Figure 16). A host system is synthesized using acceptor and backbone molecules. The emitter portion of the polymer is composed of the donor and acceptor molecules.\textsuperscript{23}

![Figure 16. TADF Molecules in Polymer Backbone.](image)

The above polymer, as a film cast from 2 wt% xylene solution, had an emission wavelength of approximately 550 nm. When the polymer was placed in an OLED device, the EQE was determined to be 10%.\textsuperscript{23}
A different method for achieving a TADF based polymer is to have the donor molecule as the backbone of the polymer with the acceptor group grafted as a side chain. An example of this type of TADF polymer can be found in Figure 17.\textsuperscript{24}

![Figure 17. TADF polymer with donor as backbone and acceptor group grafted as a sided chain.](image1)

The above polymer had a maximum wavelength emission of 510 nm in toluene and a maximum wavelength emission of 507 nm as a film. When placed in an OLED device, an emission wavelength of 521 nm was observed with an EQE of 12.63\%.\textsuperscript{24}

A final method for incorporating a TADF molecule into a polymer is to have the TADF molecule pendant so that it not a part of the polymeric backbone.\textsuperscript{17} An example of this type of polymer can be found in Figure 18.\textsuperscript{25}

![Figure 18. Pendant TADF based polymer.](image2)
As a film, the polymer above had a maximum wavelength emission of 535 nm. When the polymer is placed in an OLED device, the maximum wavelength emission is 533 nm with an EQE of 20.1%.\textsuperscript{25}

1.5 Poly(arylene ether), PAE

Poly(arylene ether)s, PAEs, are engineering thermoplastics with a structure consisting of aromatic rings connected by ether bonds. PAEs have high thermal stability and mechanical properties due to a high rigidity and electron rich aromatic rings. Some common PAE derivatives can be found in Figure 19.

\includegraphics[width=\textwidth]{Figure_19_PAEs.png}

**Figure 19.** PAEs.

UDEL and Radel are poly sulfones that have amorphous characteristics and are commonly used in appliances that perform at high temperatures and in electrical components because they have a low flammability.\textsuperscript{26} The amorphous characteristics could be attributed to a high chain stiffness preventing the polymer chains from being able to rotate and stack. Poly(ether ether ketone) (PEEK) is a semicrystalline polymer and is commonly used in electronics, automobile technology, and aerospace technology.\textsuperscript{27} Poly(phenylene oxide) (PPO), is an amorphous polymer and is a high
performance engineering thermoplastic. PPO is commonly used for electrical insulation and is generally synthesized as a polymer blend with polystyrene.²⁸

1.6 “Pre” and “Post” Functionalization

There are two functionalizing techniques, “pre” functionalization and “post” functionalization (see Figure 20) that can be used to incorporate functional groups into polymers.

![Figure 20. “Pre” and “Post” Functionalization Methods.](image)

By using the two functionalization methods it will be possible to attach a larger variety of functional groups to the monomers and polymers. The “pre” method, functional groups can be attached to the monomer before polymerization will occur. This method is suitable for functional groups that are capable of surviving polymerization conditions. If the functional group is unable to survive polymerization conditions then the “post” method will be utilized. With this method, a temporary functional group that can survive polymerization conditions will be placed on the monomer before polymerization. After polymerization has occurred, the temporary functional group will be removed and
the desired functional group will be attached to the system. The “post” method also allows for a polymer to be synthesized and then attach a variety of functional groups without having to synthesize various monomers.

1.7 Nucleophilic Aromatic Substitution, (NAS)

Nucleophilic aromatic substitution (NAS) involves the substitution of a leaving group by a nucleophile (see Scheme 1). When a halide group is attached ortho or para to an electron withdrawing group (EWG) on a benzene ring, the ring will become activated towards NAS chemistry. A partial positive charge is formed on the ipso carbon, which is then susceptible to attack by a nucleophile.29

The nucleophile will attack the electrophile, forming a Meisenheimer complex, which is a resonance stabilized anion. This process is slow and considered to be the rate determining step. The second step of the mechanism occurs when the aromaticity of the ring is reformed, which occurs when the negative charge on the ring forces out the leaving group. This step is considered to be fast because of the aromaticity being restored.29

Scheme 1. Mechanism for NAS reaction.

1.8 Previous work

Previous group work began with polymeric OLEDs using PAE systems for functionalization due to their good thermal properties as well as chemical and physical
Polymers were synthesized via nucleophilic polycondensation using commercially available monomers such as bisphenol A and 4,4’-difluorodiphenyl sulfone. The resulting polymers were linear polymers with monomer components in the backbone. Based off previous work by Tatli, who determined that by altering the position of the fluorines of difluorodiphenyl sulfone to a 3,5 stereoisomer, from the 4,4’ orientation, the backbone of the polymer, bearing a pendant 3-iodophenyl sulfonyl group, would not be altered during the functionalization process. Picker used a 3,5 difluorodiphenyl sulfone monomer to synthesize PAEs. The change in fluorine orientation places an iodo functional group in a pendent position allowing for more accessibility for modifying the functional group post polymerization (see Scheme 2).

Scheme 2. Synthesis of iodo functionalized PAES.

The polymers synthesized in Scheme 2 were used for “Post” functionalization with various amine groups. The “Post” functionalization was unsuccessful due to potential crosslinking of the polymer chains at the previous C-I bond.

The 3,5-difluorodiphenyl sulfone monomer was also utilized for modification before polymerization occurred. Picker used carbazole as the donor group for C-N coupling at the iodine location. The donor group was used to attempt to achieve wavelengths close to the blue emission range that could later be incorporated into a PAE system (see Scheme 3).
Scheme 3. Functionalization of 3,5-difluorodiphenyl sulfone.

The carbazole monomer was dissolved in dilute THF solution and tested for UV-VIS absorbance and fluorescence. The carbazole monomer showed weak absorbance in the UV region. Absorbance peaks were detected at 292, 323, and 336 nm. The obtained absorbance wavelengths were then used to study the fluorescence emission of the monomer. When the monomer was excited at 292, 323, and 336 nm for fluorescence testing, the resulting emission peak occurred around 440 nm for each excitation wavelength.  

Various carbazole polymers were synthesized using carbazole monomer, bisphenol-A and 4,4’-difluorodiphenyl sulfone. The polymers were excited at 336 nm and showed a peak emission wavelength at 430 nm during solution phase absorption and fluorescence. Attempts were made to cast the polymers into films, however, due to inconsistent film thickness UV-VIS data could not be obtained. Fluorescence for one of the polymers showed peaking at approximately 430 nm when excited at 365 nm. The various carbazole PAEs were also tested to determine molecular weights (Mₙ) and thermal properties (Tₜ₅₅ and Tₜ) (see Table 1).
Table 1. Polymer statistics for Carbazole PAEs: monomer ratios, molecular weights, degradation temperature, and glass transition temperature.

<table>
<thead>
<tr>
<th>Carbazole-Based Monomer</th>
<th>DFDPS</th>
<th>BPA</th>
<th>$M_n$ (g/mol)</th>
<th>$T_{d,5%}$ (°C)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>28,025</td>
<td>444</td>
<td>167</td>
</tr>
<tr>
<td>0.75</td>
<td>0.25</td>
<td>1</td>
<td>23,648</td>
<td>473</td>
<td>169</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>36,500</td>
<td>444</td>
<td>175</td>
</tr>
<tr>
<td>0.25</td>
<td>0.75</td>
<td>1</td>
<td>24,122</td>
<td>437</td>
<td>181</td>
</tr>
<tr>
<td>0.1</td>
<td>0.9</td>
<td>1</td>
<td>22,715</td>
<td>426</td>
<td>185</td>
</tr>
</tbody>
</table>

The OLED project was continued by Kemboi using benzoxazole (BOX) and benzothiazole groups (BTZ). Benzoxazole and benzothiazole groups served as the acceptor groups for the donor-acceptor systems. Continuing the same fluorine orientation asPicker, Kemboi used 3,5-difluorophenyl benzoxazole and 3,5-difluorophenyl benzothiazole monomers for polymerization and functionalization. The chromophores were synthesized using carbazole or indole (see Scheme 4) as the arylamine group.

\[ \text{Scheme 4. Kemboi chromophore synthesis using BOX and BTZ.} \]

The benzoxazole carbazole monomer was dissolved in dilute THF solution and tested for UV-VIS absorbance and fluorescence. The carbazole monomer showed absorbance in the UV region at approximately 339 nm. When the monomer was excited
at 310 nm for fluorescence testing, the resulting emission peak occurred around 460 nm.\textsuperscript{32}

Once the chromophores were synthesized and characterized, they were polymerized using 4,4’-biphenol and 4,4’difluorotriphenylphosphine oxide (dFTPPO). The polymers were synthesized using varying monomer mole ratios (see Scheme 5).\textsuperscript{31}

\begin{center}
\textbf{Scheme 5.} Kemboi polymer synthesis.
\end{center}

Various BOX-carbazole polymers were tested for absorbance and fluorescence in solution phase (dilute NMP) and as films. The various BOX-carbazoles showed absorptions from 262 nm to 344 nm. The polymers with 15% and 25% chromophore composition showed a maximum fluorescence peak emission at 473 nm. The 5% chromophore containing polymer showed the weakest fluorescence at approximately 400 nm and a secondary peak at approximately 460 nm. Films were also cast for the various BOX-carbazole polymers and tested for fluorescence emission. The BOX-carbazole polymer emitted at 432 nm. The various BOX-carbazole polymers were also tested to determine thermal properties ($T_d$-5\% and $T_g$) (see Table 2). Molecular weights were unable to be determined due to lack of solubility in the GPC solvent (THF/5\% acetic acid).\textsuperscript{32}
Table 2. Kemboi polymer data.

<table>
<thead>
<tr>
<th>Carbolze Based Monomer</th>
<th>TPPO</th>
<th>BP</th>
<th>$T_d$-5% ($^\circ$C)</th>
<th>$T_g$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>590</td>
<td>232</td>
</tr>
<tr>
<td>5%</td>
<td>95%</td>
<td>1</td>
<td>517</td>
<td>232</td>
</tr>
<tr>
<td>15%</td>
<td>85%</td>
<td>1</td>
<td>507</td>
<td>236</td>
</tr>
<tr>
<td>25%</td>
<td>75%</td>
<td>1</td>
<td>472</td>
<td>235</td>
</tr>
</tbody>
</table>

1.9 Current Project

The goal of this project is to construct a spectrally pure blue emission OLED from a π donor-acceptor type of chromophore. To accomplish this, the band gap can be tuned by using structural modifications to tailor the triplet and singlet energies to allow for TADF to be efficient. The goal of the tailoring is to achieve blue emission of 452 nm, which is governed by the singlet energy level. By using a difluorinated monomer (see Scheme 6) activated towards nucleophilic aromatic substitution (NAS) reactions by a benzoxazole group, polymerizable chromophores may be synthesized. In order to achieve these polymeric structures, both “pre” and “post” methods will be used. Comparisons between the “pre” and “post” systems will be made through UV-VIS, fluorescence, thermal properties, and MW analyses. The benzoxazole will act as the acceptor for chromophores designed for donor-acceptor systems. The donor groups will be aromatic amines which are electron rich. When these electron rich amines attach to the benzoxazole acceptor, a “push-pull” system will form. This system will lower the charge transfer energy from the acceptor to the donor, which lowers the $\Delta E$ (S–T).

Another method for enhancing the efficiency of emission of a blue OLED is by limiting self-quenching, which normally is a result of aggregation of chromophores. Aggregation can be lessened by preparing structures that are not able to pack closely together. In addition, controlling the local environment and polarity can influence the
emission lifetime and thermal stability of chromophores. The effects of local
environment and polarity will be studied by performing NAS polycondensation reactions,
with various bisphenols, to incorporate the chromophore into polymer matrices with
different local polarities.

Scheme 6. Current project.
2. EXPERIMENTAL

2.1 Instrumentation

A Bruker AVANCE 300 MHz instrument was used to acquire $^1$H (300 MHz) and $^{13}$C (75.5 MHz) Nuclear Magnetic Resonance (NMR) spectra. To perform GC/MS analysis a Hewlett-Packard (HP) 6890 Series GC, coupled with a HP 5973 Mass Selective Detector/Quadropole system was used. Thermogravimetric analyses (TGA) and Differential Scanning Calorimetry (DSC) were carried out on TA Instruments TGA Q500 (under nitrogen or air) and DSC Q200 (under nitrogen), respectively, at a heating rate of 10°C/min. Fluorescence data was acquired using an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer and UV-VIS data was acquired using an Agilent Cary 50 UV-VIS Spectrometer. Size Exclusion Chromatography (SEC) analysis was performed using a system consisting of a Viscotek Model VE3580 Refractive Index Detector (RI) and Viscotek Model 270 Dual Detector (viscometer and light scattering). Two Polymer Laboratories 5µm PL gel Mixed C columns (heated to 35°C) were used with tetrahydrofuran/5% (v/v) acetic acid as the eluent and a GPC max VE-2001 with pump operating at 1.0 mL/minute. Number average molecular weights, $M_n$, and dispersities were determined with the RI signal (calibrated with polystyrene standards from Scientific Polymer Product, INC). Melting points were determined using a MEL-TEMP instrument. Elemental analyses were obtained from Midwest Micro Labs, Inc., Indianapolis, IN.
2.2 Materials

The compounds \( N,N \)-dimethylglycine, carbazole, copper (I) iodide (CuI), potassium carbonate, cesium carbonate, Bisphenol-A, chloroform-\( d \) (CDCl\(_3\)), dimethyl sulfoxide-\( d_6 \) (DMSO-\( d_6 \)), \( N \)-methylpyrrolidinone (NMP), \( m \)-cresol, polyphosphoric acid (PPA), phenothiazine, and DMSO were purchased from Sigma Aldrich. \( N,N \)-Dimethylglycine, \( m \)-cresol, phenothiazine, CDCl\(_3\), and DMSO-\( d_6 \) were used as received. Carbazole was recrystallized from chloroform. Copper (I) iodide was activated by washing in a Soxhlet extractor with hot tetrahydrofuran (THF). Potassium carbonate and cesium carbonate were dried in an oven at 130°C. NMP and DMSO were dried over CaH\(_2\) and distilled under nitrogen prior to use. Bisphenol-A was recrystallized from toluene and dried \textit{in vacuo} prior to use. The compounds 2-amino-4-bromophenol, bis-(4-fluorophenyl) sulfone, and 2,4-difluorobenzoic acid were purchased from Oakwood Chemicals and were used as received. The compound 4,4’difluorotriphenylphosphine oxide was purchased from Daychem Laboratories and used as received. Ascorbic acid, sodium bicarbonate, isopropanol, THF, and magnesium sulfate were purchased from Fisher Chemical and used as received. The compound triphenyl phosphine was purchased from Supelco, INC and used as received. The compound sodium bisulfite was purchased from BDH and used as received. Ethanol was purchased from Decon Laboratories, Inc and was used as received. Chloroform was purchased from Millipore and was used as received. 4,4’-Dihydroxydiphenyl ether was purchased from TCI and was recrystallized from toluene prior to use. Tris(dibenzylideneacetone)dipalladium(0) was purchased from Alfa Aesar and was used as received.
2.3 Synthesis of BOX-Br, 3

To a 250 mL round bottomed flask (RBF), equipped with a condenser, stir bar and nitrogen gas inlet, were added 2-amino-4-bromophenol (5.00 g, 26.6 mmol), 2,4-difluorobenzoic acid (5.40 g, 34.6 mmol), and poly phosphoric acid (49.4 g, 146 mmol), PPA. The flask was evacuated and backfilled with nitrogen. Using a thermostatted hotplate with a mineral oil bath, the reaction was heated and stirred at 90°C and then increased to 130°C. After approximately 24 hours at 130°C, GC/MS analysis of an aliquot showed the presence of the desired product. The solution was added dropwise to a beaker of vigorously stirred DI water and the resulting solids were isolated via filtration. The red-brown solid was dissolved in toluene and washed with water followed by saturated solution of sodium bicarbonate, water, and brine solution. The toluene layer was dried with magnesium sulfate and evaporated in the rotary evaporator and a red-pink solid remained. The obtained solid was recrystallized from ethanol and water to yield a bright pink solid, which was then dissolved in chloroform and stirred with decolorizing carbon to yield 4.7 grams (57%) of a light pink solid. Elemental Analysis: Calculated: C-50.35%; H-1.95%; Found: C-49.96%; H-2.12%. 1H NMR (CDCl₃; δ): 7.01 (m), 7.45 (d), 7.47 (d), 7.90 (m), 8.19 (m) 13C NMR (CDCl₃; δ): 105.5 (t), 111.6 (dd), 111.8 (s), 112.2 (dd), 117.5 (s), 123.2 (s), 128.5 (s), 132 (dd), 143.2 (s), 149.3 (s), 159.8 (dd), 163.0 (dd), 163.2 (dd).

2.4 Synthesis of BOX-CBz, 5

To a 25 mL Schlenk flask, equipped with a stir bar and a nitrogen gas inlet, were added 3 (0.50 g, 1.61 mmol), carbazole (0.404 g, 2.42 mmol), CuI (0.092 g, 0.483 mmol),
\(N,N\)-dimethylglycine (0.099 g, 0.967 mmol), ascorbic acid (0.085 g, 0.484 mmol), and \(\text{K}_2\text{CO}_3\) (0.367 g, 2.66 mmol). The flask was then evacuated and backfilled with nitrogen and 1.2 mL of DMSO was added. Using a mineral oil bath and a thermostatted hotplate the reaction was heated to 90°C for 48 hours. After that time, GC/MS analysis of an aliquot showed the presence of the desired product. The solution was added dropwise to a beaker of vigorously stirred DI water and the resulting solids were isolated via filtration. The resulting solids were dissolved in chloroform and washed with water, a 5% HCl solution, saturated sodium bisulfite solution, and a brine solution. The water layers were extracted with chloroform and organic layers were combined and dried over magnesium sulfate. The organic layer was evaporated using house vacuum and dissolved in a 50:50 ethanol:chloroform layer. The chloroform was evaporated by house vacuum allowing 5 to crystallize leaving residual impurities (carbazole and 3) in solution. The resulting crystals were isolated via vacuum filtration and recrystallized using ethanol-chloroform mixture to afford 0.321 grams (50.2%) of a tan solid. Elemental Analysis: Calculated: C-75.75; H-3.56; Found:[C: 74.81%, H: 3.68%]. \(^1\)H NMR (CDCl\(_3\); \(\delta\)): 7.10 (m), 7.35 (m), 7.45 (m), 7.60 (dd), 7.85 (d), 8.05 (d), 8.20 (d), 8.31 (m) \(^{13}\)C NMR (CDCl\(_3\); \(\delta\)): 105.5 (t), 109.6 (s), 111.6 (s), 111.7 (dd), 112.3 (dd), 119.2 (s), 120.1 (s), 120.4 (s), 123.4 (s), 124.9 (s), 126.1 (s), 132.0 (dd), 134.6 (s), 141.2 (s), 142.9 (s), 149.4 (s), 159.8 (dd), 163.0 (dd), 163.2 (dd).

2.5 Model Reaction: (2-(2,4-di-\(m\)-cresol)-6-bromo-benzoxazole), 7

To a 10 mL RBF, equipped with a stir bar and a condenser with a nitrogen gas inlet, were added 3 (0.100 g, 0.323 mmol), \(m\)-cresol (0.069 g, 0.645 mmol), \(\text{K}_2\text{CO}_3\)
(0.134 g, 0.975 mmol), and NMP (0.50 mL). Using a silicone oil bath and a thermostatted hotplate, the reaction was heated to 120°C for 24 hours. Upon completion, the reaction mixture was precipitated from 300 mL of vigorously stirred DI water. The product was isolated via extraction using chloroform, washed with 1M KOH and dried over magnesium sulfate. The solvent was removed using the rotary evaporator. The desired product was obtained as 0.121 grams (77%) of a light-red solid. $^1$H NMR (CDCl$_3$; δ): 2.3 (s), 6.7 (d), 6.8 (dd), 6.9 (m), 7.2 (m), 7.4 (dd), 7.9 (dd), 8.2 (d) $^{13}$C NMR (CDCl$_3$; δ): 21.3 (s), 21.4 (s), 109.1 (s), 111.7 (s), 112.5 (s), 116.8 (s), 117.0 (s), 119.9 (s), 120.5 (s), 122.8 (s), 124.8 (s), 125.4 (s), 127.6 (s), 129.6 (s), 129.7 (s), 132.6 (s), 140.1 (s), 140.2 (s), 143.5 (s), 149.6 (s), 155.3 (s), 156.3 (s), 157.8 (s), 161.8 (s), 162.4 (s).

2.6 “Post” Functionalization Model Reaction, 8

To a 25 mL Schlenk flask, equipped with a stir bar and a nitrogen gas inlet, were added 7 (0.100 g, 0.206 mmol), carbazole (0.172 g, 1.03 mmol), CuI (3.91 mg, 0.021 mmol), N,N-dimethylglycine (4.24 mg, 0.041 mmol), and K$_2$CO$_3$ (0.156 g, 1.13 mmol). The flask was then evacuated and backfilled with nitrogen and 0.62 mL of DMSO was added. Using a mineral oil bath and a thermostatted hotplate the reaction was heated to 90°C for 48 hours. The solution was added dropwise to a beaker of vigorously stirred DI water and the resulting solids were isolated via filtration.

2.7 Polymerization of BoxBr with BPA and 4,4’-DiF-DPS, 11a-c

For polymerizations using 3 with bisphenol A, the procedure for 11c (25% of 3) is shown as an example. To a 10 mL round bottomed flask, equipped with a stir bar and a
condenser with a nitrogen gas inlet, were added 3 (0.116 g, 0.375 mmol), bisphenol A (0.342 g, 1.50 mmol), 4,4’-difluorophenylsulfone (0.285 g, 1.13 mmol), K$_2$CO$_3$ (0.622 g, 4.50 mmol), and NMP (2.3 mL). Using a silicone oil bath and a thermostatted hotplate, the reaction was heated to 120°C for 23 hours. The reaction was precipitated from vigorously stirred water and the resulting solids were isolated using vacuum filtration. The solids were re-precipitated by dissolving in THF and adding dropwise into isopropanol. The resulting white, flaky solids were isolated using vacuum filtration and dried in a drying pistol to afford 0.255 grams (34.3%) of the desired polymer. $^1$H NMR (CDCl$_3$; δ): 1.7 (s), 6.7 (d), 6.8 (d), 7.0 (dd), 7.25 (d), 7.4 (s), 7.85 (d), 8.15 (d) $^{13}$C NMR (CDCl$_3$; δ): 31.0 (s), 42.5 (s), 109.1 (s), 111.7 (s), 117.0 (s), 117.5 (s), 118.5 (s), 119.5 (s), 120.0 (s), 122.8 (s), 127.7 (s), 128.2 (s), 129.8 (s), 132.7 (s), 135.5 (s), 143.5 (s), 147.0 (s), 149.6 (s), 153.9 (s), 154.1 (s), 157.8 (s), 162.0 (s), 162.1 (s).

Two additional polymers were synthesized, 11a (5% of 3), 0.435 grams (59.9%), and 11b (15% of 3), 0.407 grams (55.3%), using the same procedure with different ratios of reactants.

2.8 Polymerization of BoxBr with DPE and TPPO, 15a-c

For polymerizations using 3 with 4,4’-dihydroxydiphenyl ether, the procedure for 15c (25% of 3) is shown as an example. To a 10 mL round bottomed flask, equipped with a stir bar and a condenser with a nitrogen gas inlet, 4,4’-dihydroxydiphenyl ether (0.303 g, 1.50 mmol), 4,4’difluorotriphenylphosphate oxide (0.353 g, 1.13 mmol), K$_2$CO$_3$ (0.622 g, 4.50 mmol), and NMP (2.3 mL). Using a silicone oil bath and a thermostatted hotplate, the reaction was heated to 150°C. After 24 hours, 3 (0.116 g, 0.375 mmol) was added to
the flask and heated at 120°C for 24 hours. The reaction was precipitated from vigorously stirred water and the resulting solids were isolated using vacuum filtration. The solids were re-precipitated by dissolving in THF and added dropwise into isopropanol. The resulting off white, flaky solids were isolated using vacuum filtration and dried in a drying pistol to afford 0.458 grams (59.3%) of polymer. $^1$H NMR (CDCl$_3$; δ): 6.62 (s), 6.78 (d), 7.05 (s), 7.45 (m), 7.60 (m), 7.88 (s), 8.15 (d) $^{13}$C NMR (CDCl$_3$; δ): 108.1 (s), 111.7 (s), 116.1 (s), 116.3 (s), 119.9 (s), 120.0 (s), 120.4 (s), 120.9 (s), 121.8 (s), 123.0 (s), 125.2 (s), 126.8 (s), 127.9 (s), 128.4 (s), 128.7 (s), 132.0 (s), 132.1 (s), 132.9 (s), 133.5 (s), 134.0 (s), 134.1 (s), 143.5 (s), 149.4 (s), 151.9 (s), 154.0 (s), 158.1 (s), 161.2 (s), 162.1 (s).

Two additional polymers were synthesized, 15a (5% of 3), 0.432 grams (55.9%), and 15b (15% of 3), 0.461 grams (59.7%), using the same procedure with different ratios of reactants.

2.9 Polymerization of BoxCbz with BPA and 4,4'-Di-DPS, 16a-c

For polymerizations using 5a with bisphenol A, the procedure for 16c (25% of 5a) is shown as an example. To a 10 mL round bottomed flask, equipped with a stir bar and a condenser with a nitrogen gas inlet, were added 5a (0.069 g, 0.175 mmol), bisphenol A (0.159 g, 0.700 mmol), 4,4'-difluorophenylsulfone (0.133 g, 0.525 mmol), K$_2$CO$_3$ (0.290 g, 2.10 mmol), and NMP (1.09 mL). Using a silicone oil bath and a thermostatted hotplate, the reaction was heated to 150°C for 24 hours. The reaction was precipitated from vigorously stirred water and the resulting solids were isolated using vacuum filtration. The solids were re-precipitated by dissolving in THF and adding
dropwise into isopropanol. The resulting off white, flaky solids were isolated using vacuum filtration and dried in a drying pistol to afford 0.138 grams (38.2%) of polymer.

$^1$H NMR (CDCl$_3$; $\delta$): 1.7 (s), 6.7 (d), 6.8 (d), 7.0 (dd), 7.1 (s), 7.25 (d), 7.37 (s), 7.50 (dd), 7.75 (d), 7.87 (d), 7.94 (d), 8.17 (d), 8.25 (d)

$^{13}$C NMR (CDCl$_3$; $\delta$): 30.9 (s), 42.4 (s), 109.1 (s), 109.6 (s), 111.4 (s), 112.2 (s), 117.7 (s), 118.9 (s), 119.4 (s), 119.9 (s), 120.3 (s), 123.3 (s), 124.2 (s), 125.9 (s), 128.4 (s), 129.7 (s), 132.7 (s), 134.1 (s), 135.4 (s), 141.2 (s), 146.1 (s), 146.7 (s), 147.1 (s), 149.6 (s), 152.8 (s), 154.3 (s), 157.9 (s), 161.6 (s), 161.9 (s), 162.6 (s).

Two additional polymers were synthesized, 16a (5% of 5a), 0.071 grams (20.7%), and 16b (15% of 5a), 0.101 grams (39.8%), using the same procedure with different ratios of reactants.

2.10 Polymerization of BoxCbz with DPE and TPPO, 17a-c

For polymerizations using 5a with bisphenol-A, the procedure for 17c is shown as an example. To a 10 mL round bottomed flask, equipped with a stir bar and a condenser with a nitrogen gas inlet, were added 5a (0.069 g, 0.175 mmol), 4,4’-dihydroxydiphenyl ether (0.141 g, 0.700 mmol), 4,4’difluorotriphenylphosphine oxide (0.164 g, 0.525 mmol), K$_2$CO$_3$ (0.290 g, 2.10 mmol), and NMP (1.09 mL). Using a silicone oil bath and a thermostatted hotplate, the reaction was heated to 150°C for 24 hours. The reaction was precipitated from vigorously stirred water and the resulting solids were isolated using vacuum filtration. The solids were re-precipitated by dissolving in THF and adding dropwise into isopropanol. The resulting off white, flaky solids were isolated using vacuum filtration and dried in a drying pistol to afford 0.198 grams (52.9%) of polymer.
\(^1\)H NMR (CDCl\(_3\); \(\delta\)): 6.66 (d), 6.80 (d), 7.05 (s), 7.38 (s), 7.47 (d), 7.62 (m), 7.96 (s), 8.17 (d), 8.26 (d) \(^{13}\)C NMR (CDCl\(_3\); \(\delta\)): 108.1 (s), 109.5 (s), 111.7 (s), 117.1 (s), 117.3 (s), 118.9 (s), 119.8 (s), 119.9 (s), 120.1 (s), 121.0 (s), 121.7 (s), 123.3 (s), 124.2 (s), 125.3 (s), 125.9 (s), 126.7 (s), 128.4 (s), 128.6 (s), 131.9 (s), 132.0 (s), 132.8 (s), 133.5 (s), 133.9 (s), 134.1 (s), 141.2 (s), 143.2 (s), 149.5 (s), 150.8 (s), 154.0 (s), 158.2 (s), 161.3 (s), 162.1 (s) 162.5.

Two additional polymers were synthesized, 17a (5% of 5a), 0.067 grams (17.7%), and 17b (15% of 5a), 0.049 grams (18.8%), using the same procedure with different ratios of reactants.

2.11 “Post” Functionalization of 15c with Cbz, 17c’

To a 25 mL Schlenk flask, equipped with a stir bar and a nitrogen gas inlet, were added 15c (0.10 g, 0.052 mmol of bromo functionalized units), 5a (0.044 g, 0.263 mmol), CuI (1.01 mg, 0.00526 mmol), N,N-dimethylglycine (1.08 mg, 0.0105 mmol), and K\(_2\)CO\(_3\) (0.040 g, 0.289 mmol). The flask was then evacuated and backfilled with nitrogen and 0.62 mL of DMSO was added. Using a mineral oil bath and a thermostatted hotplate the reaction was heated to 90°C for 48 hours. The solution was diluted with NMP and added dropwise to a flask of vigorously stirred DI water and the resulting solids were isolated via filtration. The solids were re-precipitated by dissolving in THF and adding dropwise to water to remove excess NMP.
3. RESULTS AND DISCUSSION

3.1 Synthesis of BOX-Br, 3

The 2-(2,4-difluorophenyl)-6-bromo-benzoxazole (3) monomer was synthesized by reacting 2,4-difluorobenzoic acid with 2-amino-4-bromophenol in polyphosphoric acid (PPA) (Scheme 7). The reaction was started at 90°C to allow for the reactants to mix in the PPA. The temperature was increased to 130°C for 12 hours, heating the sides of the flask with a heat gun to melt any sublimed acid back into the reaction mixture. Once GC/MS analysis of an aliquot showed 99% conversion to the desired product, the reaction mixture was poured into a large excess of water and the resulting precipitate was isolated via filtration.

Scheme 7. Synthesis of BOX-Br, 3.

Compound 3 was recrystallized from ethanol/water and the resulting solids were isolated via vacuum filtration, followed by treatment with decolorizing carbon to afford a light pink solid in 57 % yield. The structure of 3 was confirmed via a combination of
GC/MS, elemental analysis and NMR spectroscopy. The $^1$H and $^{13}$C NMR spectra are shown in

**Figure 21** and **Figure 22**, respectively.

**Figure 21.** 300 MHz $^1$H (CDCl$_3$) spectrum of 3, * is residual CHCl$_3$.

The 300 MHz $^1$H spectrum of 3 shows 6 unique hydrogen peaks. Protons a and b appear at 7.0 ppm as a complex multiplet due to ortho coupling with two fluorines and meta and para coupling to protons b and c for proton a. Proton b has ortho and para coupling to two fluorines and ortho and meta coupling to protons a and c. Proton c appears as a multiplet at 8.2 ppm due to coupling with two meta fluorines and ortho coupling with b and para coupling with a. Protons e and f appear as doublets at 7.45 ppm due to ortho coupling with each other and para coupling to d for f and meta coupling with d for e. Proton d appears as a multiplet at 7.9 ppm due to para coupling with f and meta coupling to e.
Figure 22. 75.5 MHz $^{13}$C (CDCl$_3$) spectrum of 3.

The 75.5 MHz $^{13}$C (CDCl$_3$) spectrum of 3 shows 13 unique carbon peaks. The carbon assigned to a, 105.5 ppm, is a triplet due to the coupling of the two fluorine atoms ortho to a. The carbon signals assigned to c, d, and e, 112.25, 132, and 111.6 ppm, appear as a doublet of doublets due to the coupling of the fluorines; ortho and para for c and e, and meta for d. The carbon signals assigned to b and f are doublets of doublets with a very large coupling constant (~ 250 Hz) for the ipso-fluorine and a smaller coupling constant for the fluorine in the meta position. The carbon signal assigned to g, 159.75 ppm, appears as a doublet of doublets due to coupling with a meta fluorine and weak coupling with a para fluorine. The carbon signals assigned to l, k, i, j, m, and h appear as singlets at 111.85, 117.5, 123.2, 128.5, 143.2, and 149.3 ppm.

3.2 Synthesis of BOX-CBz and BOX-PTz, 5a-b (“Pre” method)

The polymerizable carbazole-based chromophore, 2-(2,4-difluorophenyl)-6-(9H-carbazole)-benzoxazole (5a), was synthesized by reacting 3 with 4a, in the presence of
CuI as a catalyst, in DMSO at 90 °C (Scheme 8). The ligand used in this reaction was \(N,N\)-dimethylglycine. Ascorbic acid was added to the reaction to help the CuI remain at the appropriate oxidation state, Cu\(^+\).

\[
\begin{array}{c}
\text{F} & \text{F} \\
\text{Br} & \text{O} \\
& \text{R} \\
\end{array}
\quad + \quad
\begin{array}{c}
\text{F} \\
\text{O} \\
& \text{N} \\
\end{array}
\rightleftharpoons
\begin{array}{c}
\text{F} \\
\text{O} \\
& \text{R} \\
\end{array}
\]

Scheme 8. Synthesis of BOX-CBz and BOX-PTz, 5a-b.

GC/MS analysis showed 87% conversion to the desired product 5a, a small amount of debrominated 3, a small amount of unreacted 3 and excess 4a. The reaction mixture was precipitated from water to isolate the product and remove inorganic impurities. The resulting solids were dissolved in a 50:50 ethanol:chloroform mixture and house vacuum was utilized to remove chloroform so 5a could be separated from 4a, which has better solubility in ethanol. The resulting solids were recrystallized using ethanol and chloroform to remove any unreacted 3, affording 0.320 grams of 5a as a tan solid (50.1%).

The structure of 5a was confirmed via a combination of GC/MS, elemental analysis and NMR spectroscopy. The \(^1\)H and \(^{13}\)C (CDCl\(_3\)) NMR spectra are shown in Figure 23 and Figure 24, respectively.
Figure 23. 300 MHz $^1$H (CDCl$_3$) spectrum of 5a, * is residual CHCl$_3$.

The 300 MHz $^1$H spectrum of 5a shows 10 unique hydrogen peaks. Protons a, b, and c appear as a multiplets at 7.10 ppm and 8.31 ppm as observed in 3 due to coupling with fluorines. Proton e appears as a doublet of doublets at 7.60 ppm due to ortho coupling with f and meta coupling with d. Protons f and d appear as a doublet, 7.85 ppm and 8.05 ppm, due to coupling para to each other and ortho coupling with e for proton f and meta coupling with e for proton d. New peaks, g, h, i, and j, from carbazole have been introduced into the spectrum. Protons g and h appear as a complex multiplet, 7.45 ppm, due to coupling with each other and protons i and j. Proton i appears as a multiplet, 7.35 ppm, due to coupling with two ortho protons (h, j) and a meta proton (g). Proton j appears as a doublet at 8.2 ppm.
The 75.5 MHz $^{13}$C (CDCl$_3$) spectrum of 5a shows 19 unique carbon peaks. There are 6 new carbons introduced to the structure, n, o, p, q, r, and s. The carbon atom assigned to a, 105.5 ppm, is a triplet due to the coupling of the two fluorine atoms as in compound 3. The carbon atoms assigned to c, d, e, and g, appearing at 112.25, 132, 111.7, and 159.75 ppm, respectively, appear as a doublet of doublets as observed in compound 3. The carbon atoms assigned to b and f are doublets of doublets with a very large coupling constant (~ 250 Hz). The remaining carbon atoms appear as singlets at 109.6, 111.6, 119.2, 120.1, 120.4, 123.4, 124.9, 126.1, 134.6, 141.2, 142.9, and 149.4 ppm as assigned in Figure 24.

The polymerizable phenothiazole-based chromophore, 2-(2,4-difluorophenyl)-6-(10H-phenothiazine)-benzoxazole (5b), was attempted to be synthesized by reacting 3 with 4b, in the presence of Pd$_2$(dba)$_3$ as a catalyst, in anhydrous toluene at 110 °C (Scheme 8). The ligand used in this reaction was triphenylphosphine and the base used was cesium carbonate. The reaction progress was monitored via GC/MS. The traces
showed possible conversion to 5b but the progress appeared to be slow. The temperature was increased to 100°C for 24 hours after little progress had been made at 90°C for 24 hours. The expected molecular ion peak for 5b is 428 amu, but the observed peak in the GC/MS is 396 amu signifying that a sulfur atom might be lost first in the column. GC/MS analysis of an aliquot showed two peaks with the MW of 396 amu. The peaks had the same molecular weight as a PTz-PTz dimer as well as the observable peak for 5b. The temperature was increased to 110°C for 24 hours with no progress observed and the reaction was stopped.

3.3 “Post” Method, Model Reaction, 2-(2,4-di-m-cresol)-6-bromo-benzoxazole, 7

A model reaction, using m-cresol as the nucleophile, was carried out to determine if the bromo group would survive typical NAS conditions, thus providing a pathway for post polymerization modification reactions. In addition, the product of the model reaction would provide a platform to determine the optimal conditions for C-N coupling reactions to be performed on the corresponding polymers. The reaction of BOX-Br and m-cresol, 6, in the presence of K₂CO₃ (Scheme 9) was performed in NMP at 120 °C for 24 hours. The reaction progress was monitored via GC/MS analysis of aliquots removed from the reaction mixture showing a small amount of debrominated 7 (~2%) and > 98 % conversion to the desired product 7.
Scheme 9. Model Reaction, 7, of compounds 3 with 6.

The reaction mixture was precipitated from water and the organic materials were extracted into chloroform. The chloroform layer was washed with a 1M KOH solution and dried over magnesium sulfate to afford a light red solid (77% yield).

The structure of 7 was confirmed based off GC/MS analysis and the following $^1$H and $^{13}$C (CDCl$_3$) NMR spectra, which can be found in Figure 25 and Figure 26, respectively.

![Figure 25. 300 MHz $^1$H (CDCl$_3$) spectrum of 7.](image)
The 300 MHz $^1$H spectrum of 7 shows 9 unique hydrogen peaks. Proton a appears as a doublet at 6.7 ppm due to coupling with proton b and weakly with proton c. Proton b appears as a doublet of doublets at 6.81 ppm due to meta coupling with a and ortho coupling with c. Proton c at 8.2 ppm appears as a doublet due to ortho coupling with b. Proton d is a doublet of doublets at 7.9 ppm due to para coupling with f and meta coupling with e. Proton f appears as a doublet of doublets due to para coupling with d and ortho coupling with e. Protons h and m appear as a multiplet at 7.26 ppm. Protons g, i, k, l, n, and p appear at 6.95 ppm as a multiplet. Protons j and o appear most upfield at 2.36 ppm. The integration of proton c relative to protons j and o can also be used to show successful fluorine displacement and m-cresol substitution by observing a 1 to 6 ratio of protons. When comparing c relative to j and o, the integration shows the expected ratio for substitution of m-cresol.

Figure 26. 75.5 MHz $^{13}$C (CDCl$_3$) spectrum of 7.
The 75.5 MHz $^{13}$C spectrum of 7 shows 27 unique carbon peaks. When compared to the spectrum of 3, there are 14 new carbons introduced to the structure, n, o, p, q, r, s, t, u, v, w, x, y, z, and aa. The fluorines in 3 have been replaced by m-cresol producing only singlets in the spectrum. The carbon atom a was previously a triplet due to fluorine coupling in the meta positions has now become a singlet at 109.1 ppm due to the displacement of the fluorines by the m-cresol groups. The carbon atoms assigned to c, d, and e appeared as a doublet of doublets due to the coupling of the fluorines; ortho and para for c and e, and meta for d have now become singlets due to the displacement of the fluorines by the m-cresol groups. The singlets now appear at 124.8 ppm (e), 125.4 ppm (c), and 132.6 ppm (d). The carbon atoms assigned to b and f previously were doublet of doublets the ipso-fluorine have now become singlets at 157.8 and 161.8 ppm, respectively. The carbon atom assigned to g, 162.4 ppm, previously appeared as a doublet of doublets due to coupling with a meta fluorine and weak coupling with a para fluorine now appears as a singlet due to the displacement of the fluorines. The remaining singlets appear at 21.3, 21.4, 111.7, 112.5, 116.8, 117.0, 119.9, 120.5, 122.8, 127.6, 129.6, 129.7, 140.1, 140.2, 143.5, 149.6, 155.3, and 156.3 ppm.

3.4 “Post” Functionalization Method Model Reaction, 8

In order to explore “post” functionalization of the aryl bromide containing polymers, the product of the model reaction, 7, was reacted with a 5 times excess of 4a in the presence of CuI as a catalyst, in DMSO at 90°C for 48 hours. The ligand used in this reaction was N,N-dimethylglycine (Scheme 10). Reaction progress was monitored via GC/MS. The final product was too large to be detected in the GC/MS but the
disappearance of starting material was monitored relative to the carbazole peak, simulating pseudo first order conditions. The reaction was stopped when GC/MS showed ~2% of 7 remaining.

Scheme 10. Model reaction for post functionalization process.

The reaction was precipitated from water and extracted with chloroform. In order to attempt to remove the excess carbazole, the reaction was recrystallized using ethanol and chloroform. NMR data were attempted to be obtained but due to the large excess of carbazole used, and similarities in solubility between 8 and 4a, a clean NMR of just 8 could not be obtained. Recrystallization was attempted multiple times with varying ratios of ethanol and chloroform with no success.

3.5 General Polymerization Conditions

Two different approaches were used to synthesize polymers. The first types of polymers that were synthesized were “Post” polymers using monomer 3 and various comonomers to achieve different thermal properties as shown in Scheme 11 and Scheme 12. The “Post” polymers were used to alter the functional groups after polymerization had occurred. The second types of polymers that were synthesized were the “Pre” polymers using monomer 5a and the same comonomers as the “Post” polymers. The
desired functional group is attached to the monomer before polymerization.

Polycondensation reactions were performed under typical NAS conditions for both the “Pre” and “Post” methods. Varying ratios of functionalized and non-functionalized monomers were employed as depicted in Scheme 13 and Scheme 14. NMP was utilized as the solvent with \( \text{K}_2\text{CO}_3 \) used as the base to generate the necessary phenoxide nucleophiles.

3.5.1 “Post” BoxBr with BPA Polymerization, 11a-c

Polymerizations for “Post” monomer 3 with 4,4’-diphenylsulfone (DPS), 9, and bisphenol-A (BPA), 10, (Scheme 11) were performed at 120°C to avoid potential debromination of 3.

![Scheme 11. Synthesis of polymers 11a-c.](image)

Based off the model reaction, after 24 hours the reaction mixture was added dropwise to vigorously stirred DI water and the resulting solids were isolated via vacuum filtration. The solids were then re-precipitated by dissolving in THF and added dropwise to excess isopropanol.

Synthesis of the desired polymers was confirmed based off the \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra, which can be found in Figure 27 and Figure 28, respectively.
Figure 27. 300 MHz $^1$H (CDCl$_3$) NMR of 11a-c.

The 300 MHz $^1$H spectra of 11a-c show the incorporation of 3 into a polymer containing DPS and BPA. The increasing concentration of 3 can be observed by an increase in intensity of the signals assigned to protons c, e, f, b, and a when comparing 11a, 11b, and 11c. The incorporation of the copolymer units can be observed in protons g, h, i, j, and k. The integration of proton c relative to proton k demonstrates the ratios of 3 to 10 in the polymer backbone. When observing 11c, the ratio of c relative to k is 0.242:6 which represents successful incorporation of 3 into the polymer backbone. The desired amount of 3 for 11c was 25% and 24.2% was achieved when compared to BPA. Polymer 11b has an integration ratio of 0.161:6 when integrating c relative to k which confirms the desired ratio of 3 has been incorporated into the polymer. The desired amount of 3 for 11b was 15% and 16.6% was achieved when compared to BPA. Polymer 11a has an integration ratio of 0.066:6 when integrating c relative to k. The desired amount of 3 for 11a was 5% and 6.6% was achieved when compared to BPA. Based off
the integrations, 3 was successfully incorporated into the polymer backbone in the
desired amounts (11a: 5%, 11b: 15%, 11c: 25%) for the set of polymers.

**Figure 28.** 75.5 MHz $^{13}$C (CDCl$_3$) NMR of 11a-c.

The 75.5 MHz $^{13}$C spectra of polymers 11a-c show the incorporation of 3 into a
polymer backbone containing BPA and DPS. The carbon atoms assigned to 3 can be
observed to have increasing concentrations when comparing 11a, 11b, and 11c. The
incorporation of the DPS monomer can be observed by a slight decrease in
concentrations from 11a to 11c due to the increasing amounts of 3 present.

3.5.2 “Post” BoxBr with DPE and TPPO Polymerization, 15a-c

Polymerizations to prepare the materials necessary for the “Post” methodology,
with different comonomers, 4,4’difluorotriphenylphosphine oxide (dFTPPO), 12, and
4,4’-diphenol ether (DPE), 13, were carried out in two steps (Scheme 12). These
monomers were chosen with the goal of incorporating chromophore material into a
polymer backbone containing a potential host material. The TPPO material contains a
high triplet energy level which makes it an ideal host material for OLED emitting layers. By incorporating the chromophore into a host containing backbone a one component system for the emitting layer may be achieved. Oligomers of the 4,4’-diphenol ether (DPE) and dFTPPO monomers were synthesized first at a higher temperature (150°C) to allow the dFTPPO to react, then monomer 3 was added to the reaction mixture at a lower temperature (120°C) to avoid debromination of the BoxBr. In addition, by synthesizing dFTPPO and DPE first as oligomers and then introducing 3 into the system, even spacing in the polymeric backbone is possible.


After 24 hours, the reaction mixture was added dropwise to vigorously stirred DI water and the resulting solids were isolated via vacuum filtration. The solids were then re-precipitated by dissolving in THF and adding dropwise to a large excess of isopropanol.

The synthesis of the desired polymers was confirmed via their $^1$H and $^{13}$C NMR spectra, which can be found in Figure 29 and Figure 30, respectively.
Figure 29. 300 MHz $^1$H (CDCl$_3$) NMR of 15a-c, * is residual CHCl$_3$.

The 300 MHz $^1$H spectra of 15a-c show the incorporation of 3 into a polymer containing DPE and TPPO. The increasing concentration of 3 can be observed by an increase in intensity of the signals assigned to protons c, e, f, b, and a when comparing 15a, 15b, and 15c. The incorporation of the copolymer units can be observed in protons g, h, i, j, k, l, and m. The integration of proton c to protons l and m demonstrates the ratios of 3 relative to 13 in the polymer backbone. When observing 15c, the ratio of c relative to l and m is 0.148:8 this shows that not all of 3 was incorporated into the polymer backbone. The desired amount of 3 for 15c was 25% but only 14.8% was actually achieved when compared to DPE. Polymer 15b has an integration ratio of 0.096:8 when integrating c relative to l and m, this also shows that the desired amount of 3 has not been incorporated into the polymer. The desired amount of 3 for 15b was 15% but only 9.6% was actually achieved when compared to DPE. Polymer 15a has an integration ratio of 0.037:8 when integrating c relative to l and m. The desired amount of 3 for 15a was 5% but only 3.7% was actually achieved when compared to DPE. The
integration of 15a is closer to the desired ratio for this set of polymers. Based off the integrations, 3 was incorporated into the polymer backbone but not in the desired amounts (15a: 5%, 15b: 15%, 15c: 25%) leading to the conclusion that the reaction might need longer reaction times or higher reaction temperatures. Another possibility for the low incorporation of 3 could be due to cyclization of the TPPO oligomers, which would essentially remove reactive phenol species from the mixture.

The 75.5 MHz $^{13}$C spectra of polymers 15a-c show the incorporation of 3 into a polymer backbone containing DPE and TPPO. The carbon atoms assigned to 3 can be observed to have increasing concentrations when comparing 15a, 15b, and 15c. The incorporation of the TPPO monomer can be observed by a slight decrease in concentrations from 15a to 15c due to the increasing amounts of 3 present.

The initial characterization data (composition, molecular weight and dispersity) data for the polymers containing 3 can be found in Table 3.

Figure 30. 75.5 MHz $^{13}$C (CDCl$_3$) NMR of 15a-c.
Table 3. Monomer ratios, %yield, molecular weight, and dispersity for 11a-c and 15a-c.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ratio of 3:(1-x)</th>
<th>%Yield</th>
<th>Mn (Da)</th>
<th>Đ</th>
</tr>
</thead>
<tbody>
<tr>
<td>11a</td>
<td>0.05:0.95</td>
<td>59.9</td>
<td>33,047</td>
<td>2.5</td>
</tr>
<tr>
<td>11b</td>
<td>0.15:0.85</td>
<td>55.3</td>
<td>23,259</td>
<td>1.7</td>
</tr>
<tr>
<td>11c</td>
<td>0.25:0.75</td>
<td>34.3</td>
<td>12,016</td>
<td>1.9</td>
</tr>
<tr>
<td>15a</td>
<td>0.05:0.95</td>
<td>55.9</td>
<td>9,939</td>
<td>2.9</td>
</tr>
<tr>
<td>15b</td>
<td>0.15:0.85</td>
<td>59.7</td>
<td>20,595</td>
<td>6.6</td>
</tr>
<tr>
<td>15c</td>
<td>0.25:0.75</td>
<td>59.3</td>
<td>14,302</td>
<td>5.8</td>
</tr>
</tbody>
</table>

The percent yields for the polymers are all consistent with the exception of 11c and were determined after the re-precipitation process. The molecular weights were determined using size exclusion chromatography (SEC) in a THF/5% acetic acid solution. For polymers 15a-c they were synthesized as oligomers first then polymerized by adding 3 to the reaction mixture. The lower molecular weights for 15a could be due to incomplete conversion from oligomer to polymer. The dispersities for 15a-c were also higher than 11a-c polymers which could also be due to incomplete conversion from oligomers to polymers. The SEC traces for each set of 3 containing polymers can be found in Figure 31.

Figure 31. SEC traces for a) 11a-c, b) 15a-c.
When observing the traces for 11a-c, 11a and 11c exhibit secondary peaks in the trace which could be attributed to cyclic species formed during the polymerization process. These cyclic species could have contributed to lower $M_n$ values for 11c and a slightly higher dispersity value than desired for 11a. When observing the traces for 15a-c, all three polymers in the set exhibit a secondary peak in their traces leading to the conclusion of cyclic species being present in the polymer. All three polymers have higher than desired dispersities which could be caused by the cyclic species. When observing the traces for 15a-c, the primary peak for each polymer is broad which could indicate various length polymer chains are present. These observations along with the lower than expected integration ratios could give rise to the trends observed in $M_n$ and dispersities for 15a-c.

3.5.3 “Pre” BoxCbz Polymer with BPA, 16a-c

Polymerizations for “Pre” were carried out using monomer 5a with 9 and 10 (Scheme 13) at 150°C.

Scheme 13. Synthesis of Polymer 16a-c.
After 24 hours, the reaction mixture was added dropwise to vigorously stirred DI water and the resulting solids were isolated via vacuum filtration. The solids were then re-precipitated by dissolving in THF and adding dropwise to a large excess of isopropanol.

The synthesis was confirmed based off the $^1$H and $^{13}$C NMR spectra, which can be found in Figure 32 and Figure 33, respectively.

![Figure 32](image-url). 300 MHz $^1$H (CDCl$_3$) NMR of 16a-c, * is residual CHCl$_3$.

The 300 MHz $^1$H spectra of 16a-c show the incorporation of 5a into a polymer containing DPS and BPA. The increasing concentration of 5a can be observed by an increase in intensity of the signals assigned to protons c, j, d, g, h, i, e, f, b, and a when comparing 16a, 16b, and 16c. The incorporation of the copolymer units can be observed in protons k, l, m, n, and o. The integration of proton c relative to proton k demonstrates the ratios of 5a to 10 in the polymer backbone. When observing 16c, the ratio of c relative to k is 0.263:6 which represents successful incorporation of 5a into the polymer backbone. The desired amount of 5a for 16c was 25% and 26.3% was achieved when compared to BPA. Polymer 16b has an integration ratio of 0.124:6 when integrating c.
relative to 0 which confirms the desired ratio of 5a has been incorporated into the polymer. The desired amount of 5a for 16b was 15% and 12.4% was achieved when compared to BPA. Integration was unable to be performed on 16a due to broad peaks. Based off the integrations, 5a was successfully incorporated into the polymer backbone in the desired amounts (16b: 15% and 16c: 25%) for the set of polymers.

**Figure 33.** 75.5 MHz $^{13}$C (CDCl$_3$) NMR of 16a-c.

The 75.5 MHz $^{13}$C spectra of polymers 16a-c show the incorporation of 5a into a polymer backbone containing BPA and DPS. The carbon atoms assigned to 5a can be observed to have increasing concentrations when comparing 16a, 16b, and 16c. The incorporation of the DPS monomer can be observed by a slight decrease in concentrations from 16a to 16c due to the increasing amounts of 5a present.

**3.5.4 “Pre” BoxChz Polymer with DPE, 17a-c**

Polymerizations for a second series of “Pre” functionalized materials were carried out using monomer 5 with dFTPPO and DPE (Scheme 14) at 150°C. These polymers did
not have to be synthesized in two steps because the bromine atom had already been
replaced with a carbazole group.

![Scheme 14](image)

**Scheme 14.** Synthesis of Polymer 17a-c.

After 24 hours, the reaction mixture was added dropwise to vigorously stirred DI
water and the resulting solids were isolated via vacuum filtration. The solids were then
re-precipitated by dissolving in THF and adding dropwise to a large excess of isopropanol.

The synthesis was confirmed based off the following $^1$H and $^{13}$C NMR spectra,
which can be found in **Figure 34** and **Figure 35**, respectively.

![Figure 34](image)

**Figure 34.** 300 MHz $^1$H (CDCl$_3$) NMR of 17a-c, * is residual CHCl$_3$. 
The 300 MHz $^1$H spectra of $17\text{a-c}$ show the incorporation of $5\text{a}$ into a polymer containing DPE and TPPO. The increasing concentration of $5\text{a}$ can be observed by an increase in intensity of the signals assigned to protons c, j, d, e, f, g, h, i, b, and a when comparing $17\text{a}$, $17\text{b}$, and $17\text{c}$. The incorporation of the copolymer units can be observed in protons k, l, m, n, o, p, and q. The integration of proton c relative to protons p and q demonstrates the ratios of $5\text{a}$ relative to 13 in the polymer backbone. Polymer $17\text{c}$ has an integration ratio of 0.217:8 when integrating proton c relative to protons p and q. The desired amount of $5\text{a}$ for $17\text{c}$ was 25% and 21.7% was incorporated into the polymer backbone. When observing $17\text{b}$, the ratio of c relative to p and q is 0.0925:8 this shows that not all of $5\text{a}$ was incorporated into the polymer backbone that was desired to be. The desired amount of $5\text{a}$ for $17\text{b}$ was 15% but only 8.75% was actually achieved when compared to DPE. Polymer $17\text{a}$ has an integration ratio of 0.0654:8 when integrating c relative to p and q, this shows that the desired amount of $5\text{a}$ has been incorporated into the polymer. The desired amount of $5\text{a}$ for $17\text{a}$ was 5% and 6.5% was achieved when compared to DPE. The integration of $17\text{a}$ is closer to the desired ratio for this set of polymers. Based off the integrations, $5\text{a}$ was incorporated into the polymer backbone but not in the desired amounts ($17\text{a}$: 5%, $17\text{b}$: 15%, $17\text{c}$: 25%) leading to the conclusion that longer reaction times or higher reaction temperatures were required. Another possibility for the low incorporation of $5\text{a}$ could be due to cyclization of the polymer chains.
Figure 35. 75.5 MHz $^{13}$C (CDCl$_3$) NMR of 17a-c.

The 75.5 MHz $^{13}$C spectra of polymers 17a-c show the incorporation of 5a into a polymer backbone containing DPE and TPPO. The carbon atoms assigned to 5a can be observed to have increasing concentrations when comparing 17a and 17c. The incorporation of the TPPO monomer can be observed by a slight decrease in concentrations from 17a to 17c due to the increasing amounts of 5a present.

The initial characterization data (composition, molecular weight and dispersity) data for the polymers containing 5a can be found in Table 4.

Table 4. Monomer ratios, %yield, molecular weight, and dispersity for 16a-c and 17a-c.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ratio of 5a:(1-x)</th>
<th>%Yield</th>
<th>Mn (g/mol)</th>
<th>$\bar{D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16a</td>
<td>0.05:0.95</td>
<td>20.7</td>
<td>12,975</td>
<td>1.8</td>
</tr>
<tr>
<td>16b</td>
<td>0.15:0.85</td>
<td>39.8</td>
<td>13,874</td>
<td>2.3</td>
</tr>
<tr>
<td>16c</td>
<td>0.25:0.75</td>
<td>38.3</td>
<td>15,130</td>
<td>2.4</td>
</tr>
<tr>
<td>17a</td>
<td>0.05:0.95</td>
<td>17.7</td>
<td>9,341</td>
<td>2.8</td>
</tr>
<tr>
<td>17b</td>
<td>0.15:0.85</td>
<td>18.8</td>
<td>6,225</td>
<td>2.7</td>
</tr>
<tr>
<td>17c</td>
<td>0.25:0.75</td>
<td>52.9</td>
<td>6,445</td>
<td>1.9</td>
</tr>
</tbody>
</table>
The percent yields for the polymers were determined after the re-precipitation process. The molecular weights were determined using size exclusion chromatography (SEC) in a THF/5% acetic acid solution. Polymers 16a-c showed a decent molecular weight with low dispersities. Polymers 17a-c showed low molecular weights with reasonable dispersities. The low molecular weights could be due to reaction times needing to be longer. The SEC traces for each set of 5a containing polymers can be found in Figure 36.

![SEC traces for 16a-c and 17a-c](image)

**Figure 36.** SEC traces for a) 16a-c, b) 17a-c.

When observing the traces for 16a-c, small secondary peaks in the trace are present which could be attributed to cyclic species formed during the polymerization process. When observing the traces for 17a-c, all three polymers in the set exhibit a secondary peak in their traces leading to the conclusion of cyclic species being present in the polymer.

### 3.5.5 Functionalization of 15c with 4a, 17c’

Using the same procedure as for the model reaction, 8, polymer 15c was used to post-functionalize a polymer. The polymer was reacted with a 5 times excess of 4a in the
presence of CuI as a catalyst, in DMSO at 90°C for 48 hours (Scheme 15). The ligand used in this reaction was \(N,N\)-dimethylglycine.

Scheme 15. Post functionalization of polymer 15c.

The resulting polymer was diluted with NMP due to lack of solubility in DMSO and precipitated from water. The resulting solids were isolated via vacuum filtration. The solids were dissolved in THF and reprecipitated from water to remove any remaining NMP.

The polymer had a change in solubility after the reaction; the polymer was no longer soluble in chloroform. This suggested the polymer was altered in the reaction. In order to obtain a spectrum a combination of THF/DMSO-\(d_6\) was used. Unfortunately, the \(^{13}\)C NMR spectrum indicated that the post functionalization was unsuccessful (Figure 37).
Figure 37. 75.5 MHz $^{13}$C NMR of Homopolymer (CDCl$_3$), 15c (CDCl$_3$), 17c’ (THF/DMSO-$d_6$), and 17c (CDCl$_3$).

In the above spectra, the DPE and TPPO homopolymer is compared to the bromo-containing polymer that was attempted to be post functionalized, a sample of the reaction after attempting post functionalization, and the pre version of the polymer attempted to be synthesized. The circled area in the above spectra show peaks at 107.3 ppm and 111.1 ppm that are associated with excess carbazole (17c’), peaks at 107.7 ppm and 111.4 ppm are associated with 3 (15c and 17c), and a peak at 109.5 ppm for carbazole attached to 3 (17c). The peak at 109.5 ppm does not appear in 17c’ which can be used to conclude that the reaction did not successfully incorporated carbazole into the polymer.

3.6 Thermal Analysis

All of the polymers were analyzed via Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). TGA analysis was performed in nitrogen and air to determine 5% weight loss temperatures ($T_{d,5\%}$) for polymers 11a-c, 15a-c, 16a-c,
and 17a-c. The homopolymer of DPE and dFTPPO had been previously prepared in our research group and was used as a basis for comparison of the thermal properties. The TGA traces of polymers 11a-c and 15a-c under N₂ and air can be found in Figure 38.

![TGA traces of polymers](image)

**Figure 38.** TGA traces of polymers a) 11a-c in N₂, b) 15a-c and Homopolymer in N₂, c) 11a-c in air, d) 15a-c and Homopolymer in air.

In the above traces, polymers 11a-c and 15a-c all exhibited relatively similar decomposition temperatures showing good thermal stability with varying amounts of 3 present in the polymer chains (Table 5). It was observed that the decomposition temperature decreased in general with increasing amounts of 3. For example, in N₂, 11a has a T_d-5% of 470°C while
11c has a T$_{d,5\%}$ of 464°C. The systems containing DPE and TPPO units exhibited higher thermal stability when compared to the BPA and DPS systems, for example the Homopolymer has a T$_{d,5\%}$ of 523°C in N$_2$ and when 3 is added to the backbone the T$_{d,5\%}$ decreases. For example, 15a has a T$_{d,5\%}$ of 513°C and 15c has a T$_{d,5\%}$ of 468°C in N$_2$. The air traces showed that there is a decrease in decomposition temperature for both sets when compared to N$_2$. Also observed was a secondary step varying from approximately 500°C to approximately 600°C in the air trace that could be the bromine or the TPPO decomposing which was not observed in the N$_2$ traces. When comparing 11a (T$_{d,5\%}$ of 443°C) to 11b (T$_{d,5\%}$ of 440°C) the trend of decreasing with increasing amounts of 3 is observed however 11c has an increased T$_{d,5\%}$ (453°C) value with an increase in the amount of 3. The Homopolymer has a T$_{d,5\%}$ of 493°C in air and when 3 is added to the backbone the T$_{d,5\%}$ decreases. For example, 15a has a T$_{d,5\%}$ of 491°C and 15c has a T$_{d,5\%}$ of 421°C in air.

Differential scanning calorimetry (DSC) was used to determine the glass transition temperatures (T$_g$) of the new materials. The traces for polymers 11a-c, 15a-c, and Homopolymer can be found in Figure 39.
The polymers all exhibited relatively similar glass transition temperatures, ranging from 181 up to 200 °C, with varying amounts of 3 and backbone units present in the polymer chains. It was observed that the T\textsubscript{g} decreased with increasing amounts of 3 for 11a-c. For example, 11a has a T\textsubscript{g} of 190°C and 11c and a T\textsubscript{g} of 181°C. The decrease in T\textsubscript{g} is attributed to the polymer backbone having increasing flexibility due to the increasing amount of 3 added to the backbone. The T\textsubscript{g} for polymers 15a-c and the Homopolymer have the opposite trends that were observed in 11a-c. The Homopolymer exhibited the lowest T\textsubscript{g} (187°C) of the set with the values increasing with increasing amounts of 3. Polymer 15a has a T\textsubscript{g} of 190°C and 15c has a T\textsubscript{g} of 200°C suggesting that the incorporation of 3 decreases the backbone flexibility of the polymer. A summary of the thermal data can be found in Table 5.

Figure 39. DSC Analysis of Bromo-polymers, 11a-c, 15a-c, and Homopolymer.
Table 5. Thermal Data for Polymers 11a-c, 15a-c, and Homopolymer.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ratio of 3:(1-x)</th>
<th>$T_d$-$5%$ in $N_2$ (°C)</th>
<th>$T_d$-$5%$ in Air (°C)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11a</td>
<td>0.05:0.95</td>
<td>470</td>
<td>443</td>
<td>190</td>
</tr>
<tr>
<td>11b</td>
<td>0.15:0.85</td>
<td>460</td>
<td>440</td>
<td>186</td>
</tr>
<tr>
<td>11c</td>
<td>0.25:0.75</td>
<td>464</td>
<td>453</td>
<td>181</td>
</tr>
<tr>
<td>15a</td>
<td>0.05:0.95</td>
<td>513</td>
<td>491</td>
<td>190</td>
</tr>
<tr>
<td>15b</td>
<td>0.15:0.85</td>
<td>497</td>
<td>476</td>
<td>193</td>
</tr>
<tr>
<td>15c</td>
<td>0.25:0.75</td>
<td>468</td>
<td>421</td>
<td>200</td>
</tr>
<tr>
<td>Homopolymer</td>
<td>-</td>
<td>535</td>
<td>493</td>
<td>187</td>
</tr>
</tbody>
</table>

The TGA traces of polymers 16a-c and 17a-c under $N_2$ and air can be found in Figure 40.

Figure 40. TGA traces of polymers a) 16a-c in $N_2$, b) 17a-c and Homopolymer in $N_2$, c) 16a-c in air, d) 17a-c and Homopolymer in air.
In the above traces, polymers 16a-c and 17a-c all exhibited relatively similar decomposition temperatures showing good thermal stability with varying amounts of 5a present in the polymer chains.

Table 6). The decomposition temperatures exhibited a general trend of decreasing with increasing amounts of 5a for polymers 17a-c. For example, 17a had a $T_{d-5\%}$ of 501°C and 17c had a $T_{d-5\%}$ of 425°C. When comparing the Homopolymer ($T_{d-5\%}$ of 535°C in nitrogen) to 17a ($T_{d-5\%}$ of 501°C in nitrogen), $T_{d-5\%}$ values decreased with the introduction of 5a into the backbone. Polymers 16a-c had $T_{d-5\%}$ values above 400°C and generally increased with increasing amounts of 5a but a consistent trend was not observed. Polymers 16a-c had higher $T_{d-5\%}$ values in air than in nitrogen and decreased with increasing amounts of 5a added to the backbone. For example, 16a had a $T_{d-5\%}$ of 433°C and 16c had a $T_{d-5\%}$ of 416°C. In air, 17a-c had lower $T_{d-5\%}$ values than in nitrogen. Similar to what was observed with 11a-c and 15a-c, the DPE and TPPO systems exhibited higher thermal stability when compared to the BPA and DPS systems.

Differential scanning calorimetry (DSC) was used to determine the glass transition temperatures ($T_g$) of the new materials. The traces for polymers 16a-c and 17a-c can be found in Figure 41.
The polymers all exhibited relatively similar glass transition temperatures, ranging from 182 up to 206 °C, with varying amounts of 5a present in the polymer chains. No trend was observed for 16a-c with 16b having the highest $T_g$ (190°C) and 16a with the lowest $T_g$ (182°C). Polymer 16b has really large secondary peak in the SEC trace, which could be causing the $T_g$ value to be out of line when compared to 16a and 16c. Polymers 17a-c had increasing $T_g$ values with increasing amounts of 5a. Polymer 17a has a $T_g$ of 184°C and 15c has a $T_g$ of 206°C suggesting that the incorporation of 5a decreases the backbone flexibility of the polymer. A summary of the thermal data can be found in

**Figure 41.** DSC Analysis of Carbazole-polymers, 16a-c, 17a-c, and Homopolymer.
Table 6.

Table 6. Thermal Data for Polymers 16a-c and 17a-c.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ratio of 5:(1-x)</th>
<th>T_{d-5%} in N_2 (°C)</th>
<th>T_{d-5%} in Air (°C)</th>
<th>T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16a</td>
<td>0.05:0.95</td>
<td>412</td>
<td>433</td>
<td>182</td>
</tr>
<tr>
<td>16b</td>
<td>0.15:0.85</td>
<td>419</td>
<td>431</td>
<td>190</td>
</tr>
<tr>
<td>16c</td>
<td>0.25:0.75</td>
<td>414</td>
<td>416</td>
<td>185</td>
</tr>
<tr>
<td>17a</td>
<td>0.05:0.95</td>
<td>501</td>
<td>479</td>
<td>184</td>
</tr>
<tr>
<td>17b</td>
<td>0.15:0.85</td>
<td>436</td>
<td>421</td>
<td>201</td>
</tr>
<tr>
<td>17c</td>
<td>0.25:0.75</td>
<td>425</td>
<td>428</td>
<td>206</td>
</tr>
<tr>
<td>Homopolymer</td>
<td>-</td>
<td>535</td>
<td>493</td>
<td>187</td>
</tr>
</tbody>
</table>

3.7 Analysis of photophysical behavior

Monomer absorption and emission spectra were obtained in THF at a 20 micromolar concentration for 5a. Compound 5a showed broad absorption wavelengths between 300 and 400 nm with discernible absorption maxima present at 325 and 340 nm (Figure 42).
**Figure 42.** Absorbance spectra (a) of 5a and emission spectrum (b) of 5a excited at 340 nm.

When excited at 340 nm, compound 5a displayed a wavelength emission of 430 nm. When compared to Kemboi’s 3,5 version of compound 5a there is a blue shift in wavelength emission. Kemboi’s 3,5 system had a maximum wavelength emission at 460 nm. By changing the orientation of the fluorines from 3,5 to 2,4 there is a 30 nm blue shift in wavelength. The goal wavelength emission is 452 nm in order to achieve a “true blue” color. While the 2,4 system has more of a blue shift in wavelength the 3,5 system has a wavelength closer to the desired wavelength even though it has a slight red shift in wavelength.

The absorption spectra of polymers 16a-c and 17a-c were acquired in THF at a concentration of 10 µM (Figure 43). Polymers 16a-c and 17a-c show broad absorption wavelengths between 300 to 400 nm with the absorption maxima present at 337 nm for polymers 16b-c and 17b-c and 340 nm for 16a and 17a.
Figure 43. Solution phase absorbance spectra of 16a-c and 17a-c.

Solution phase emission spectra of 16a-c and 17a-c were acquired in THF at a concentration of 0.5 µM (Figure 44). The instrument was set to have a slit width of 5
microns and the photomultiplier tube detector voltage was set to 600 volts.

**Figure 44.** Solution phase emission spectra of 16a-c and 17a-c; 16b-c, 17b-c excited at 337nm, 16a and 17a excited at 340nm.

When excited at 340 nm polymers 16a and 17a exhibited a maximum wavelength emission at ~420 nm. When excited at 337 nm polymers 16b and 17c exhibited a maximum wavelength emission at ~422 nm and 16c and 17b exhibited a maximum wavelength emission at ~420 nm. Polymers containing DPE and TPPO showed less intense emission spectra when compared to the systems containing BPA and DPS.

The incorporation of 5a into a polymer backbone with varying backbone units has caused a blue shift in wavelength emission when compared to 5a. The absorbance intensity for the polymers was much greater than that of the monomer. The polymer concentration had to be decreased significantly when compared to the monomer in order to not reach the maximum emission limit.
The emission spectra of polymers 16a-c and 17a-b were also acquired as polymer films (Figure 45). When the films were attempted to be acquired using the instrument conditions used for solution phase fluorescence, the instrument reached maximum intensity. In order to obtain emission spectra for the films, the settings for the instrument had to be adjusted. The slit width remained the same as what was used for the solution phase, but the photomultiplier tube detector voltage was lowered to 450 volts for all the polymers with the exception of 17b.

![Figure 45. Emission spectra for 16a-c and 17a-b as films.](image)

Polymer 17c was cast into a film but became very brittle after being removed from the block and continued to dry. When fluorescence analysis was attempted the film tore and could not be analyzed. The polymers all exhibited lower maximum wavelength emissions. Polymer 16a has a maximum wavelength emission at 413 nm, 16b has a maximum wavelength emission at 415 nm and 16c has a maximum wavelength emission
at 416 nm. Polymer 17a has a maximum wavelength emission at 407 nm and 17b has a maximum wavelength emission at 416 nm. The intensity of each film is difficult to compare due to the films being made with varying concentrations in order to obtain a uniform film that could survive the removal process from the Teflon block. In order to remove the film from the block, a razor blade was used to loosen the edges of the film until it could be peeled off. The films were excited under a TLC lamp at 365 nm to observe the following blue emitting films (Figure 46) in order to demonstrate their emitting capabilities and compare film thickness.

Figure 46. Polymer films under TLC lamp.

In the above films, it can be observed that the thinnest films are 17b-c which corresponds to the weakest emitting film in Figure 45. Films 16a and 17a appear to be the most uniform in terms of thickness and 16b appears to be the thickest film.
4. CONCLUSION

The syntheses of 2-(2,4-difluorophenyl)-6-bromo-benzoxazole (3) monomer and 2-(2,4-difluorophenyl)-6-(9H-carbazole)-benzoxazole (5a) chromophore were successfully carried out. The structures of the compounds were confirmed using NMR spectroscopy and elemental analysis. The compounds were successfully incorporated into polymeric backbones using 4’-diphenylsulfone (DPS), 9, and bisphenol-A (BPA), 10, as well as by using 4,4’difluorotriphenylphophine oxide (dFTPPO), 12, and 4,4’-diphenol ether (DPE), 13, via NAS chemistry. The structures of the polymers were confirmed by NMR spectroscopy and their properties were characterized by TGA, DSC, and SEC analyses.

Polymers 11a-c (with 3, 9, and 10 units) and 15a-c (with 3, 12, and 13 units) showed good thermal stability with 5% weight loss temperatures 460°C and above in nitrogen and 420°C and above in air. Polymers 15a-c (with TTPO units) showed generally higher 5% weight loss temperatures when compared to polymers 11a-c (with DPS units). Glass transition temperatures for DPS systems decreased with the increasing amounts of 3 added to the backbone and were all above 180°C. The decrease in glass transition temperature suggests that increasing amounts of 3 increased the flexibility of the polymeric backbone. Glass transition temperatures for 15a-c increased with increasing amounts of 3 added to the backbone and were all above 190°C. The increased glass transition temperatures suggest that when the amounts of 3 are increased the flexibility of the polymer decreases.
Polymer **15c** was modified via a post polymerization process using **4a**. A change in solubility was observed after the post modification process suggesting that the polymer had been altered during the reaction. A mixture of solvents had to be used in order to obtain NMR data, which disproved the conversion.

Polymers **16a-c** and **17a-c**, which incorporated the donor moiety with the monomer, showed good thermal stability with 5% weight loss temperatures 412°C and above in nitrogen and 420°C and above in air. Polymers **17a-c**, with the TPPO comonomer, showed generally higher 5% weight loss temperatures than **16a-c**. Polymers **16a-c** showed higher 5% weight loss percent temperatures in air than in nitrogen. The glass transition temperatures for both sets were above 180°C and increased with increasing amounts of **5a** suggesting a decrease in backbone flexibility.

Compound **5a** showed broad absorption wavelengths between 300 and 400 nm with discernable absorption maxima at 325 and 340 nm in THF. When excited at 340 nm, compound **5a** displayed an emission with a peak wavelength centered at 430 nm in THF. Polymers **16a-c** and **17a-c** showed broad absorption spectra between 300 to 400 nm with absorption maxima at 337 nm for polymers **16b** and **17b** and 340 nm for **16a** and **17a** in THF. When excited at 340 nm, polymers **16a** and **17a** exhibited a maximum wavelength emission at ~420 nm in THF. When excited at 337 nm polymers **16b** and **17b** exhibited a maximum wavelength emission at ~424 nm in THF.

Overall, the systems containing BPA and DPS showed higher Mₙ values when compared to the TPPO and DPE systems. However the TPPO and DPE systems generally had higher thermal properties. The photophysical data show that the orientation of the 2,4 system in a polymer matrix affects the intensity of fluorescence emission. The
concentrations of the systems had to be diluted significantly when compared to the monomer in order to get a trace that did not reach the maximum limits of the instrument showing how efficient the polymers are at emitting. The intensity of emission increased with the increasing amounts of 5a added to the system. The structure of the 2,4 system plays a significant role in the emission properties observed. By having an unsymmetric system it allows for a weak charge transfer from the chromophore to the host material in the polymeric backbone due to the electron deficient DPS or TPPO. This weaker charge transfer allowed for the strong emission and stability of the polymeric systems.
5. PROPOSED WORK

The reaction conditions for 5b need to be optimized in order to successfully synthesize the desired product. The conditions determined for 5b were unsuccessful, however with optimization could be successful. Alternative catalysts and ligands may be needed for the reaction to proceed. With successful synthesis of 5b, photophysical analysis can be performed as well as polymerizations using various comonomers to achieve PAEs with good thermal properties.

In order to obtain a “true blue” color using 3, various donor groups should be tested to determine the optimal donor-acceptor pairing to obtain the desired wavelength. Other colors could also be obtained using various donor groups with 3. Conditions for “post” functionalization using Pd catalysts could be determined for potentially easier functionalization. Once the fluorines are no longer a part of the system, reaction conditions could be more aggressive in order to displace the temporary functional group with the desired donor group to achieve various colors.
6. REFERENCES


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