FUNCTIONALIZED PEEK ANALOGUES FROM 2,4- AND 3,5-
DIFLUOROBENZOPHENONE 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 Hannah Fetters ENTITLED Functionalized PEEK Analogues from 2,4- and 3,5- Difluorobenzophenone Derivatives BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Fetters, Hannah. M.S. Department of Chemistry, Wright State University, 2019. Functionalized PEEK Analogues from 2,4- and 3,5- Difluorobenzophenone Derivatives

The synthesis of N-heterocycle functionalized benzophenone-type monomers and their incorporation into poly(arylene ether ketone)s were explored. Two benzophenone derivatives, 2,4-difluorobenzophenone and 3,5-difluorobenzophenone, were successfully functionalized with a carbazole group, via a copper-catalyzed C-N coupling reaction. Structural characterization was provided by NMR spectroscopy, GC/MS, and elemental analysis. The monomers were covalently incorporated, at various molar ratios, into poly(arylene ether) systems by copolymerization with 4,4’-difluorodiphenylsulfone (DPS) and 4,4’-dihydroxydiphenyl ether (DPE), as well as 4,4’-difluorotriphenylphosphine oxide (dFTPPO) and DPE, via nucleophilic aromatic substitution (NAS) chemistry. Most polymeric materials synthesized provided sufficient molecular weights to cast durable films, and also possessed good thermal stability with 5% weight loss temperatures (T\text{d-5\%}) all above 390 °C and glass transition temperatures, T\text{g}, values all above 170 °C. In general, TPPO and DPE copolymers provided higher T\text{g} and T\text{d-5\%} values. Photophysical analyses provided that all monomer and copolymer materials emitted in the blue-green region when excited at 365 nm.
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1. INTRODUCTION

1.1 Background about Lighting

As the need for greener and more efficient energy usage rises, the lighting industry has evolved to meet the demand. In recent years, light emitting diodes (LEDs) have become the most recommended lighting source for indoor usage due to the superior efficiency and lifetime compared to its more traditional counterparts (e.g. incandescent bulbs and fluorescent bulbs).

Incandescent bulbs are still commonly used in homes today. The bulbs are engineered to include a filament, traditionally tungsten, and the circuit will heat the filament until it burns white hot. As a result, 90% of the energy used by the bulb is lost as heat, and they have a relatively short life time of approximately 1,000 hours. A variation of the incandescent bulb is the halogen bulb. These bulbs encapsulate the filament with gas and are typically engineered with a heat-reflecting inner coating. This allows for improved efficacy and a longer lifetime ranging from 1,000 to 3,000 hours.

Fluorescent lighting for homes is typically in the form of compact fluorescent bulbs, and they consume approximately 75% less energy than incandescent bulbs. Their lifetimes range from 6,000 to 15,000 hours. These bulbs are designed as a coiled tube that contain mostly argon with small amounts of mercury gas. Upon driving a current
through the tube, the gases excite and emit energy as UV light. The UV light in turn excites the coating of fluorescent material housed on the inside of the tube, which then emit light in the visible range.\(^3\)

Currently, the most efficient lighting option is the LED. Similarly to compact fluorescent bulbs, LEDs consume at least 75% less energy than incandescent bulbs.\(^2\) LEDs are engineered with greater durability and lose little energy to heat. They have a projected lifespan of 15,000 to 25,000 hours. Their compact build also allows for versatility; along with indoor lighting, these bulbs are now used in various displays, such as TVs, computers, and smart phones.

1.2 LED

LEDs utilize semiconductors to generate photons from conducted electricity. The semiconductors typically found in LEDs are inorganic and designed with a p-n junction.\(^4\) The junction is created when the crystal structure of the semiconductor is interrupted by impurities, or dopants. A p-layer, or “positive” layer, can be made by adding a dopant that is relatively electron poor. Conversely, a n-layer, or “negative” layer, can be made by adding a dopant that is relatively electron rich. When these two layers exist within the same crystal, a p-n junction is created.\(^4\)

The p-n junction allows for a simple design that ensures electrons flow in only one direction through the semiconductor. This can be done by applying a voltage with forward bias. As a result, the electrons will flow from the n-type layer to the p-type layer. The holes, or a lack of electrons, will flow the opposite way. In this manner, holes
and electrons are directed to recombine at the p-n junction interface. When an electron recombines with a hole, the release of energy results in light emission of wavelength determined by the bandgap energy.\(^5\)

A generic device structure for LEDs (Figure 1) can be seen below. Most devices utilize a sapphire substrate on which the two inorganic layers are stacked. The cathode makes contact on the p-layer metal, while the anode makes contact on the n-layer metal. The semiconductor is mounted on a reflective cup in the LED housing, which redirects the emitted light through the top of the device.\(^5\)

![Figure 1. Basic structure of an LED device.](image)

LEDs provide a more efficient option for lighting and have been utilized in a wide variety of applications, however there are limitations on their potential. Due to the brittle nature of the metal layers, using LEDs for large-scale displays and flexible substrates becomes impractical or impossible.\(^6,7\) Additionally, materials used to prepare the semiconductor are frequently expensive and limited in supply. For example, InGaN semiconductors are commonly used to produce LEDs of blue to green emission while AlInGaP semiconductors are typically used to make yellow to red emitting LEDs.\(^5\) For
indoor usage, white LED bulbs are the most common, and they utilize a combination of red, blue, and green LEDs to produce white light. This compounds the demand for these more expensive materials.

1.3 OLED

Organic electroluminescence was first observed in the 1960s, and this led to an exploration into organic electroluminescent devices. However, these early devices required high driving voltages and gave low power-conversion efficiency. In 1987, Tang and VanSlyke published the first device that required less than 10 V to power emission. The success of this device was accredited to its novel design; it utilized two organic layers, rather than a single organic layer, sandwiched between the electrodes. This multi-organic layer design still inspires organic light emitting diode (OLED) designs today.

![Figure 2. Basic structure of an OLED device.](image)

A basic OLED device (Figure 2) has a minimum of two organic layers sandwiched between the cathode, usually a magnesium or aluminum alloy, and the anode, usually indium tin oxide (ITO). The organic layers are thin films of 100-200 nm
thickness that must facilitate the movement of holes or electrons. For efficiency, a hole transport layer (HTL) is paired with an electron transport layer (ETL). Frequently, additional organic layers are included in the stack to improve efficiency and lifetime of the device.\textsuperscript{9}

Similarly to traditional inorganic LEDs, a forward bias voltage is passed from the anode to the cathode. This allows electrons to be injected from the cathode into the ETL and holes to be injected from the anode into the HTL. The layer in which recombination occurs is called the emissive layer (EML). The EML may be the ETL, HTL, or a separate layer between the two. By using a glass or plastic substrate, the emitted light may pass through the substrate, unobstructed.\textsuperscript{10}

OLEDs are self-emitting; they emit light without the need for backlighting. This not only lowers energy usage, but it also allows for improved color contrast in displays. OLEDs may also be engineered with high-efficiency power conversion as the technology improves, making them a promising competitor for traditional LEDs. Additionally, due to their versatile nature, OLEDs may be used to produce flexible, durable, and large-area displays.
1.4 Small Molecule OLED

Small molecule OLEDs, or SMOLEDs, contain organic emissive layers comprised of non-polymeric compounds. These devices work similarly to traditional inorganic LEDs in that the organic layers may be considered as charge transporters; they are able to carry holes and electrons without changing state. Recombination in the organic layer interfaces results in the excitation of the emitting molecules from ground state to an excited state. Return to ground state releases energy in the form of light. This allows device efficiency to be calculated in relation to the spin statistics of the molecule.\textsuperscript{10}

Examples of fluorescent molecules utilized for OLED devices can be seen in Figure 3.\textsuperscript{11,12,13}

![Fluorescent molecules](image)

**Figure 3.** From left to right, red, green, and blue fluorescent emitting molecules for OLED devices.

The naphthylamine derivative in **Figure 3** (left) is an example of a red fluorescent emitter. This molecule gave efficient emission at 676 nm as a thin film.\textsuperscript{11} The diaminooanthracene derivative (center) gave green emission at 526 nm as a thin film.\textsuperscript{12} The diphenylaminofluorenylstyrene derivative (right) emitted deep blue at 465 nm as a thin film.\textsuperscript{13}

Phosphorescent molecules are commonly used in the emitting layers of OLED devices, as well. Efficient emission occurs due to the use of a metal complex. For
example, blue phosphorescent molecules commonly use iridium-based complexes. The compound shown in Figure 4 was added as a dopant into a host matrix of \(N,N'\)-dicarbazolyl-3,5-benzene (mCP) to produce a blue emissive layer with a reported high external quantum efficiency (EQE) of 7.5 ± 0.8\%\textsuperscript{14}.

![Figure 4](image)

**Figure 4.** A blue phosphorescent iridium-based compound.

A full RGB display may be accomplished using small molecule emitters. The variety of structures that may be synthesized is broad, and current SMOLED devices may improve as new combinations of molecules are discovered. However, small molecules have several downfalls that limit their potential in OLED devices. SMOLEDs tend to have short lifetimes due to low thermal stability. The efficacy of emission may be limited by the orientation and aggregation of the small molecules. Devices utilizing host/guest emissive layers may be difficult to achieve for some molecules, especially blue emitters, due to poor compatibility with host matrices. Further, device processing by vacuum deposition is expensive.\textsuperscript{10}
1.5 Emission Pathways

The emitting molecules of OLED devices are excited when charge transfer results in recombination in the organic layer interfaces. Quantum mechanics provides that of the electrons excited in a molecule, 25% will occupy the singlet (S) state while the other 75% will occupy the triplet (T) state. Relaxation to ground state releases energy in the form of light, and this may occur through various pathways.\textsuperscript{10}

![Diagram of emission pathways](image)

**Figure 5.** Types of emission and their internal quantum efficiencies (IQE).

Emission by fluorescence occurs when the singlet $S_1$ electrons relax to $S_0$. This relaxation is spontaneous and occurs very quickly. Depending on the molecule, the $S_1$ lifetime may range from picoseconds to several nanoseconds. The theoretical internal quantum efficiency (IQE) of the device is 25% because fluorescence only utilizes the $S_1$ electrons.\textsuperscript{15} This low IQE made phosphorescent molecules desirable for use in OLEDs.

Phosphorescence occurs from the $T_1$ to $S_0$ transition, which is spin-forbidden. Using heavy metals, such as iridium, improves the efficiency of phosphorescence by inducing spin-orbit coupling. This allows for observable phosphorescence and conditions
that also favor intersystem crossing from $S_1$ to $T_1$.\textsuperscript{15} Theoretically, the IQE for phosphorescence is 75\% but may approach 100\% if intersystem crossing is efficient.\textsuperscript{16}

Additionally, improved IQEs were found through delayed fluorescence processes. The first, triplet-triplet annihilation (TTA), results from a collision between two $T_1$ molecules. The collision provides enough energy to upconvert one of the molecules to the $S_1$ state.\textsuperscript{15} Statistically, TTA may only occur to half of the $T_1$-state electrons, or 37.5\% of the total electrons of the emitting molecule. Added to the base 25\% of traditional fluorescence, this gives an IQE of 62.5\%.\textsuperscript{17}

The second commonly used delayed fluorescence type is thermally activated delayed fluorescence (TADF). This emission type relies on reverse intersystem crossing (rISC), or the transition of electrons from $T_1$ to $S_1$. For this to occur efficiently, the emitting molecule must have a small energy difference ($\Delta E_{st}$) between the $T_1$ and $S_1$ energy levels, as well as a longer $T_1$ state lifetime.\textsuperscript{15} If rISC is efficient, the $T_1$ state electrons may upconvert to the $S_1$ state and emit via fluorescence, allowing for an IQE approaching 100\%.\textsuperscript{18}
1.6 Bandgap and TADF Emitter Design

The bandgap of OLED emitters can be defined as the energy difference between the highest occupied molecular orbital, or HOMO, and the lowest unoccupied molecular orbital, or LUMO. The bandgap energy, $E_g$, is inversely proportional to the wavelength of light emitted. As a result, a red-emitting compound ($\sim 650$ nm) will have a smaller bandgap energy of 1.9 eV while a blue-emitting compound ($\sim 450$ nm) will have a larger bandgap of 2.8 eV. The large bandgap characteristic of blue emitters leads to problems with molecular stability, as well as poor compatibility with most host materials.\(^{19}\)

![Bandgap illustration for red, green, and blue emitters.](image)

**Figure 6.** Bandgap illustration for red, green, and blue emitters.

At the most basic description, TADF emitters are molecules that can be broken down into two different building blocks: donors and acceptors. Donors are electron rich groups and are associated with the HOMO. Conversely, the acceptors are electron poor groups and are associated with the LUMO. These groups are linked by $\pi$-bonds, thus the name donor-$\pi$-acceptor systems.
A variety of donors (Figure 7) and acceptors (Figure 8) exist such that a molecule may be tuned for TADF emission with a specific bandgap. Utilizing bulky substituents to twist the donor and acceptor out of planarity ensures that the HOMO and LUMO are sufficiently separated, which provides a small $\Delta E_{st}$, ideal for efficient TADF emission. The bandgap may be adjusted by using different combinations and connectivity of acceptors and donors.\(^{19}\)

In 2012, Adachi et al.\(^{18}\) reported their groundbreaking work of designing TADF emitters. The three molecules described in their communication utilized a sulfone system with varied carbazole derivatives (Figure 9). All three molecules emitted in the deep
blue region of 402-419 nm, with slight variation due to the incorporation of the \(t\)-butyl groups. The 3,6-di-tert-butylcarbazole donor unit (right) provided deep blue electroluminescent emission with an EQE of 9.9%. The results indicated that TADF molecules certainly outperform their traditional fluorescent counterparts and are competitive with phosphorescent emitters.

![Chemical Structure]

**Figure 9.** Blue emitting TADF molecules by the Adachi research group.

More recently, a 2016 paper by Lee and Lee\textsuperscript{20} reported the first TADF device with an EQE of approximately 20% and near pure-blue emission at 451 nm. The emitting molecule in this case was a design inspired by the Adachi group; the acceptor chosen was 9,9-dimethyl-9H-thioxanthene 10,10-dioxide and the donor chosen was acridine (**Figure 10**). The high efficiency of the emitter was due to its very slight overlap of HOMO and LUMO, which resulted in a calculated $\Delta E_{\text{st}}$ of 0 eV.
This emitter, dubbed DMTDAc, provided more insight into efficient blue emitter design. Unlike its predecessors, DMTDAc gave a narrower range of emission (61 nm wide at half peak height) that improved color purity compared to the compounds in Figure 9 (>65 nm wide at half peak height). The narrower emission range of DMTDAc was accredited to restricting molecular movement via bridging of the diphenyl sulfone acceptor moiety.\textsuperscript{20}

\textbf{1.7 Polymer OLED}

SMOLED devices have several disadvantages, but one of the larger setbacks is processing. Because TADF emitters readily crystallize, they are not easily processed by solution methods. Vacuum deposition is a commonly used, albeit expensive, processing technique to produce SMOLED devices, and this limits SMOLEDs to small-scale displays like smart phones and cameras.\textsuperscript{21}

Polymers are already known to be easily processable by inexpensive solution methods like spin-coating and inkjet printing. Utilizing a polymer emissive layer in an OLED device would allow for large-scale displays on flexible substrates.\textsuperscript{21} Despite this major advantage, research in polymer OLEDs, or POLEDs, is lacking.
Electroluminescence in polymers has been studied since the 1990s, starting with observed fluorescence in conjugated polymer poly(p-phenylenevinylene), or PPV.\textsuperscript{22} Today there exist both conjugated and non-conjugated polymers of various structures that utilize various kinds of emission pathways. Because TADF emission results in the largest IQE of near 100\%, it has become an appealing option for POLED researchers and will be the focus of this section.

TADF polymers must follow the same basic rule as TADF small molecules: the HOMO and LUMO must be sufficiently separated to create a small $\Delta E_{st}$ that allows for efficient rISC, and therefore enables 100\% electron harvesting. Achieving both efficient and strong luminescence can be difficult in conjugated systems, however.\textsuperscript{23}

Thus far, TADF polymer design can be sorted into four general strategies: alternating donor and acceptor groups in the backbone, alternating TADF units with backbone units, a backbone consisting of donor groups with acceptor groups grafted as side-chains, and backbone units with TADF units incorporated as pendant groups.

\textbf{Figure 12.} below was adapted from Xie and Li.\textsuperscript{23} The method that will be utilized in this project is the fourth, in which a TADF molecule is incorporated into the backbone as a pendant unit.
Figure 12. The four general TADF polymer designs.

An example of this last technique of incorporating TADF units as pendant units can be observed in Bryce and coworkers' first PTZ-DBTO2 copolymer. On a vinyl backbone, the benzene pendant unit and the TADF unit, which consisted of a phenothiazine donor group and a dibenzothiophene acceptor group, were originally synthesized in a 0.63:0.37 molar ratio. As a film, PTZ-DBTO2 copolymer 1 demonstrated emission at 540 nm.

In a follow up study, Bryce and coworkers prepared another set of PTZ-DBTO2 copolymers (Figure 13) that further elaborated on the styrene/phenothiazine system with iterations utilizing 0.80:0.20, 0.70:0.30, and 0.50:0.50 molar ratios. This study demonstrated the importance of the pendant benzene as a spacing agent, which was
shown to suppress internal conversion and triplet-triplet annihilation. Another observed trend was that as the styrene comonomer unit was increased in molar ratio, the $T_1$ state increased in energy while the $\Delta E_{st}$ values were kept small.

![Chemical structure](image)

**Figure 13.** Copolymer where TADF unit is incorporated as a pendant.

Devices utilizing PTZ-DBTO2 copolymers 2-4 were fabricated via spin-coating. The emitting layer was 45 nm thick and consisted of 10% polymer doped into 90% 1,3-bis(carbazol-9-yl)benzene (mCP). PTZ-DBTO2 copolymer 2-4 devices emitted in the green region, with copolymer 2 providing the strongest EQE of 20.1%.\(^{25}\)

### 1.8 PAE

Poly(arylene ether)s, PAE, are a class of engineering thermoplastics with a structure consisting of recurring aromatic rings connected by ether bonds. These polymers are favored for their excellent thermal and mechanical properties, which is attributed to their rigid structure and high electron density. Thermoplastics are easily
processed, and they may be molded and remolded without losing integrity in their physical properties. Examples of commercially available PAE can be seen in Figure 14.

**Figure 14.** Commercial PAE with associated $T_g$ and $T_m$ values.

Poly(arylene ether sulfones), PAES, are amorphous PAE thermoplastics that display excellent thermal stability. Due to their flexible structure, PAES allow for relatively easy processing via injection molding. Udel, introduced by Union Carbide in 1965, was the first commercially available PAES. It has a glass transition temperature ($T_g$) of 190 °C. In 1972, ICI made Victrex available for commercial use. With a $T_g$ of 230 °C, it displayed intermediate performance and processing. Radel was introduced by Union Carbide in the late 1970s, and it displayed superior performance in thermal properties and processing with a $T_g$ at 220 °C.26

Today, PAES are competitive with thermosetting plastics, and are replacing metals and ceramics, as well. They are commonly used in electrical components and
high-temperature appliances, such as ovens and lamp housings. The ability to cast PAES into film and foil, as well as their high operating temperatures and low flammability, have made them desirable for use in flexible circuitry.\textsuperscript{26}

Poly(ether ether ketone), PEEK, introduced by ICI in 1978, is a PAE thermoplastic that utilizes a ketone functional group in its backbone. PEEK is semicrystalline with a $T_g$ of 143 °C and a melting temperature ($T_m$) of 343 °C. Its impressive high temperature performance has made it suitable for various fabrication forms, including wire-coating, injection molding, and film casting. It also has excellent water resistance at 125 °C, preventing failure common in aromatic polyamides. PEEK is now commonly utilized in coating and insulation for high-performance wiring in aerospace and computer industries, oil wells, military equipment, and other applications.\textsuperscript{26}

\textbf{1.8.1 PAE as a Backbone}

TADF chromophores may be designed to resemble monomers for NAS polymerization (\textbf{Scheme 1}) and therefore may be easily incorporated into a PAE backbone. Small molecule TADF units are doped into another material to form a guest-host system in the emitting layer. As such, PAE backbones may be designed to act as a host matrix for the TADF unit, and thus eliminate the search for a compatible host material.

Because of their high thermal stability, excellent mechanical properties, and solution processability, PAE would make for excellent materials in a POLED device.
There is also the potential benefit of adding thermal stability to the TADF unit, which would prolong the device lifetime. It is also possible that incorporating the TADF unit into a PAE may prevent aggregation and self-quenching, and as a result, may improve the EQE of the device. Finally, as mentioned above, many PAE are solution processable, and would allow for large area devices to become more easily and inexpensively fabricated via methods like inkjet printing and spin coating.

Scheme 1. Nucleophilic Aromatic Substitution (NAS) general mechanism.

TADF units may be built with polymerization sites in the form of a halide leaving group, X. In this manner, the ipso carbon becomes an electrophile available for attack by a nucleophile. When the nucleophile attacks, aromaticity is broken to form a resonance-stabilized intermediate known as the Meisenheimer complex. Aromaticity is restored once the leaving group is eliminated from the ring\textsuperscript{27}.

Incorporation of the TADF unit into a backbone system may be performed via two different strategies: pre-functionalization and post-functionalization (Scheme 2). In a pre-functionalized method, the monomer (blue) has been functionalized with the donor group (FG) to be a TADF emitter prior to polymerization with either itself or with a backbone unit (yellow). In a post-functionalization method, a precursor functional group, such as a halide (X), survives the polymerization process. Once the precursor unit is
incorporated, X may be displaced with a donor group. Post-functionalization methods allow for variability of donor groups in one polymer.

**Scheme 2.** Pre- and Post-functionalization methods.

### 1.9 Previous Work

Group research in the incorporation of blue TADF emitters into PAE began with Picker’s work, which utilized iodinated 3,5-difluorodiphenylsulfone (3,5-DFDPS-I) previously synthesized by Tatli.29
Scheme 3. Synthesis of Picker’s 3,5-DFDPS-CBZ monomer and its incorporation into a PAES system.

Picker$^{28}$ attempted to post-functionalize the polymerized 3,5-DFDPS-I unit by substituting the iodide with carbazole and other donors in a copper catalyzed carbon-nitrogen coupling reaction. This post-functionalization route was unsuccessful and resulted in crosslinking at the iodo position. A pre-functionalization method was attempted instead and resulted in successful displacement of the iodide with carbazole (Scheme 3). Polymerization of the carbazole monomer with 4,4’-difluorodiphenylsulfone (DPS) and bisphenol A (BPA) was successful; various copolymers were produced in which thermal stability remained high and polymer films showed broad emission from 370-600 nm with peak emission occurring around 430 nm.

Kemboi$^{30}$ continued research in polymerizable TADF chromophores, however, his were based on benzoazole and benzothiazole acceptor groups functionalized with carbazole and indole donor groups (Figure 15). Monomers synthesized included
benzoxazole-carbazole (BOX-CBZ), benzoxazole-indole (BOX-IND), and benzothiazole-carbazole (BTZ-CBZ) units. In THF, these monomers were excited with wavelengths ranging from 250 to 340 nm, and each excitation wavelength resulted in broad emission centered around 460 nm with varying intensity.

![Chemical structures](image)

**Figure 15.** Kemboi’s TADF monomers.

Polymerization of these monomers was performed in NAS polycondensation reactions with 4,4’-difluorotriphenylphosphine oxide (dFTPPO) and 4,4’-biphenol (Scheme 4). Thermal analyses indicated that each copolymer had sufficiently high backbone rigidity for OLED use with $T_g$ values ranging from 210 °C to 243 °C. Films were successfully cast from each, with the benzoxazole copolymers emitting around 430 nm, and the benzothiazole-carbazole copolymer resulting in true-blue emission peaking at 451 nm.$^{30}$
Scheme 4. Synthesis of Kemboi’s polymers.

Slaybaugh\textsuperscript{31} elaborated on the benzoxazole system and successfully synthesized a 2,4-difluoro derivative and functionalized it with carbazole (Scheme 5). The 2,4-difluoro BOX-CBZ in THF, excited at 340 nm, showed peak emission occurring at 430 nm. This was 30 nm blue-shifted compared to the 3,5-difluoro derivative.

Scheme 5. Functionalization of Slaybaugh’s 2,4-difluoro benzoxazole derivative.

Pre-functionalized polymers using the carbazole monomer were successful with two different backbone systems: DPS/BPA and dFTPPO/4,4’-dihydroxydiphenyl ether (DPE). An example of the former system can be seen in Scheme 6. Thermal analyses of the DPS/BPA system and the dFTPPO/DPE system indicated sufficient thermal properties with T\textsubscript{g} values ranging from 182 °C to 206 °C.\textsuperscript{31}

Films cast from the copolymers showed highly efficient emission at deep blue wavelengths centered around 416 nm. The improved emission efficiency was accredited to its unsymmetrical system, which allowed for weak charge transfer from the chromophore to the polymer host matrix.\textsuperscript{31}

Other teams outside of the Fossum research group have begun looking into fluorescent PAE-based polymers in which TADF units are incorporated as pendant units. In 2018, Wang and coworkers\textsuperscript{32} reported a red-emitting polymer using 2-(N-(4-octyloxyphenyl)diphenylamino)-4’-anthraquinone, or ROC8, as the TADF emitter. The poly(fluorene-co-3,3’-dimethyl diphenyl ether), or PFDMPE, backbone unit has a high triplet energy compatible with the ROC8 TADF unit, which allows it to act as a host matrix for the TADF unit.
PFDMPE-ROC copolymers displayed high thermal stability, but quite low $T_g$ values ranging from 86 °C to 88 °C. As for emission, the ROC8 TADF monomer displayed peak emission at 593 nm in toluene. Incorporation into the PFDMPE backbone in various ratios resulted in a trend of red-shifted emissions as the ratio of TADF unit ($x$) increased. At $x = 0.01$, peak emission occurred at 579 nm, while at $x = 0.10$, peak emission occurred at 602 nm. When incorporated into devices, the polymers gave red emission averaging around 606 nm with an EQE of 5.6%.

### 1.10 Current Research

The primary objective of this project was to synthesize a true blue (450 nm) TADF emitter using a donor-$\pi$-acceptor system. With structural tailoring, the wavelength of the chromophores may be tuned, and the $\Delta E_{st}$ value may be adjusted to allow for efficient TADF-type emission. The chromophores constructed for this project were two benzophenone derivatives, 2,4-difluorobenzophenone and 3,5-difluorobenzophenone, functionalized with a carbazole donor on the pendant phenyl ring (Scheme 7). With the donor group attached, the system will act as a “push-pull” compound where charge...
transfer is possible. Photophysical properties of the monomers will be determined via UV/Vis and fluorescence.

![Scheme 7. Chromophore synthesis utilizing benzophenone derivatives.](image)

Designing chromophores with polymerization sites, i.e. fluorine atoms, allows for convenient incorporation of the TADF chromophore or its precursor into a PAE backbone via NAS reactions. Post-functionalization, or polymerization of the precursor monomer, allows for variability of donor groups in the same polymer. However, this synthesis route could result in cross-linking of the backbone to what was previously the halide-carbon bond. Pre-functionalized copolymers were the strategy choice for this project.

A secondary project goal was to incorporate the benzophenone-carbazole chromophores into a PAE backbone. By using PAE systems DPS/DPE and TPPO/DPE,
high thermal stability and higher Tg values were expected. It was also expected to improve device efficiency and lifetime, as well as allow for cheaper solution-phase processing, imperative for large-scale OLED devices. Finally, by incorporating the TADF unit as a pendant group, it is expected that the backbone will act as a host material, making it possible for a single emission layer.
2. EXPERIMENTAL

2.1 Instrumentation

A Bruker AVANCE 300 MHz Nuclear Magnetic Resonance (NMR) spectrometer was used to acquire $^1$H and $^{13}$C spectra, operating at 300 MHz and 75.5 MHz, respectively. All compounds were dissolved in CDCl$_3$ at a concentration ca. 30 mg/0.6 mL. A Hewlett-Packard (HP) 6890 Series GC, coupled with a HP 5973 Mass Selective Detector/Quadrupole was used to perform GC/MS analyses. Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed on TA Instruments TGA Q500 and DSC Q200 (under nitrogen), respectively, at a heating rate of 10 °C/min. Size Exclusion Chromatography (SEC) was performed using a system consisting of a Viscotek Model VE3580 Refractive Index Detector (IR) 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 an eluent solution of THF/5% (v/v) acetic acid and a GPC max VE-2001 with pump operating at 1.0 mL/min. The RI signal, calibrated using polystyrene standards from Scientific Polymer Product, INC, was used to determine number average, $M_n$, and dispersity values. UV/Vis and Fluorescence spectra were obtained on an Agilent Cary 60 UV/Vis Spectrometer and an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer, respectively. Melting points were determined using a MEL-TEMP instrument and are uncorrected. Elemental analyses were acquired from Midwest Micro Labs, Inc., Indianapolis, IN.
2.2 Materials

The compounds \(N,N\)-dimethylglycine, carbazole, copper (I) iodide (CuI), potassium carbonate, aluminum chloride, hydrochloric acid (HCl), bromobenzene, chloroform-\(d\) (CDCl\(_3\)), \(N\)-methylpyrrolidinone (NMP), \(m\)-cresol, and dimethyl sulfoxide (DMSO) were purchased from Sigma Aldrich. \(N,N\)-dimethylglycine, carbazole, aluminum chloride, HCl, bromobenzene, \(m\)-cresol, and CDCl\(_3\) were used as received. CuI was activated in a Soxhlet extractor using tetrahydrofuran (THF) using the procedure described by Kohnen and coworkers. DMSO and NMP were distilled from calcium hydride under nitrogen. Potassium carbonate was dried in an oven at 130°C. The compounds 2,4-difluorobenzoyl chloride, 3,5-difluorobenzoyl chloride, and bis-(4-fluorophenyl) sulfone (DPS) were purchased from Oakwood Chemicals and were used as received. The compounds L-ascorbic acid, sodium bicarbonate, THF, toluene, ethyl acetate, and magnesium sulfate were purchased from Fisher Chemical and were used as received. The compound 4,4’-dihydroxydiphenyl ether (DPE) was purchased from TCI and was recrystallized from toluene and dried prior to use. 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 EMD Millipore Corp and was used as received. The compound bis-(4-fluorophenyl)phenylphosphine oxide (dFTPPO) was purchased from Daychem Laboratories and was used as received.
2.3 Synthesis of 2,4-DFK-Br, 3

To a 50 mL round-bottomed flask (RBF), equipped with an addition funnel, condenser, and a gas inlet, was added aluminum chloride (5.41 g, 40.6 mmol), weighed under a nitrogen pocket. To the addition funnel were added 2,4-difluorobenzoyl chloride (7.12 g, 40.3 mmol) and bromobenzene (6.34 g, 40.4 mmol). The resulting solution was added dropwise to the AlCl₃, with stirring. During addition, the reaction mixture was kept below 10 °C and was allowed to warm to 25 °C over several hours. The reaction was allowed to stir for 24 hours to afford a thick, dark colored paste. The reaction mixture was diluted with an addition of bromobenzene (25.4 g, 149 mmol) to make the final ratio of 2,4-difluorobenzoyl chloride to bromobenzene of 1:5. Following this addition, the reaction was allowed to stir for 5 days. GC/MS analysis of a small worked up sample showed that the reaction was roughly 98% complete with minor production of ortho, meta, and debrominated derivatives.

The reaction mixture was quenched and precipitated with a dilute HCl solution and extracted with toluene. The organic layer was washed with a saturated sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to afford a reddish-orange oil. The oil was diluted in ethanol and recrystallized to afford 7.7 g (65%) of an off-white crystalline material. The melting point was determined to be 87-88 °C.

Elemental Analysis: Calculated: C - 52.56%, H - 2.37%. Found: C - 52.65%, H – 2.36%.

1H NMR (CDCl₃; δ): 6.93 (dt, 1H), 7.03 (dt, 1H), 7.65 (m, 5H). 13C NMR (CDCl₃; δ):
104.8 (t), 112.1 (dd), 122.9 (dd), 128.7 (s), 131.1 (s), 131.9 (s), 132.6 (dd), 136.2 (s), 160.9 (dd), 165.1 (dd), 191.1 (s).
**2,4 Synthesis of 2,4-DFK-CBZ, 5**

To a 15 mL RBF, equipped with a nitrogen gas inlet, were added 3 (1.161 g, 3.91 mmol), carbazole (0.719 g, 4.30 mmol), activated CuI (0.150 g, 0.787 mmol), \(N,N\)-dimethylglycine (0.161 g, 1.56 mmol), \(K_2CO_3\) (0.919 g, 6.65 mmol), and 3.91 mL of distilled DMSO. The flask was heated in an oil bath at 90°C, with stirring and under nitrogen for approximately 24 hours. After cooling, a sample was collected and filtered for GC/MS analysis, which indicated 98.5% conversion to desired product.

The reaction mixture was added dropwise to approximately 800 mL of DI water with vigorous stirring and was left to stir overnight. The resulting solid was isolated via vacuum filtration and the product was left to dry over the vacuum for a few hours. A pre-work up weight was determined to be approximately 1.42 g. The precipitate was dissolved in toluene and washed with a 5% HCl solution, a 5% bisulfite solution, and finally with water. The aqueous layers were extracted with ethyl acetate, and then combined with the toluene layer, followed by drying over MgSO4. The solvents were then removed via rotary evaporation to afford a reddish-orange oil. The flask was then placed under vacuum to remove excess toluene from the flask, yielding a bright yellow solid.

Chloroform was added dropwise until all of the compound was dissolved, and then ethanol was added dropwise until the solution became turbid. Chloroform was added dropwise to take the solution back to clear and the solvents were allowed to evaporate slowly for recrystallization.

The resulting crystals were isolated via vacuum filtration to afford 1.16 g (77.3%) of bright yellow crystals. The melting point was determined to be 134 – 137 °C. Elemental
Analysis: Calculated: C – 78.32%, H -3.94%. Found: C - 78.34%, H - 3.76%. $^1$H NMR (CDCl$_3$; $\delta$): 6.99 (m), 7.09 (m), 7.35 (m), 7.46 (m), 7.55 (d), 7.73 (m), 8.09 (d), 8.17 (d). $^{13}$C NMR (CDCl$_3$; $\delta$): 104.8 (t), 109.9 (s), 112.1 (dd), 120.5 (s), 120.7 (s), 123.2 (dd), 124.0 (s), 126.2 (s) 126.3 (s), 131.5 (s), 132.6 (dd), 135.6 (s), 140.1 (s), 142.6 (s), 161.0 (dd), 165.0 (dd), 191.1 (s).

**2.5 Synthesis of 3,5-DFK-Br, 7**

To a 50 mL RBF, equipped with an addition funnel, condenser, and a gas inlet, was added bromobenzene (6.340 g, 40.4 mmol). Aluminum chloride (5.924 g, 44.4 mmol) was weighed under a nitrogen pocket and slowly added to the bromobenzene with stirring. To the addition funnel was added 3,5-difluorobenzoyl chloride (7.129 g, 40.4 mmol). The 3,5-difluorobenzoyl chloride was added dropwise to the RBF while the flask was immersed in an ice bath. After the addition, the reaction mixture was allowed to warm to 25 °C over several hours. After 48 hours, an aliquot was removed for GC/MS analysis, which indicated that the reaction had reached approximately 97% conversion to the desired product.

The reaction mixture was quenched by slowly pouring it into dilute HCl solution and then the organic material was extracted with toluene. The organic layer was washed with a 5 % sodium bicarbonate solution and water, followed by drying over magnesium sulfate. The organic layer was removed via rotary evaporation to afford an off-white solid. The solid was dissolved in ethanol and recrystallized to afford 3.77 g (31.4%) off-white crystals. A melting point of 89 – 91 °C was determined. $^1$H NMR (CDCl$_3$; $\delta$): 6.98
(s, 1H), 7.21 (m, 2H), 7.59 (s, 4H). $^1$H NMR (CDCl$_3$; $\delta$): 108.0 (t), 112.8 (dd), 128.4 (s), 131.4 (s), 132.0 (s), 135.1 (s), 140.1 (t), 162.8 (dd), 192.8 (t).

2.6 Synthesis of 3,5-DFK-CBZ, 8

To a 10 mL RBF, equipped with a nitrogen gas inlet, were added 7 (1.161 g, 3.91 mmol), carbazole (0.719 g, 4.30 mmol), activated CuI (0.150 g, 0.790 mmol), N,N-dimethylglycine (0.161 g, 1.56 mmol), K$_2$CO$_3$ (0.919 g, 6.65 mmol), and 3.91 mL of distilled DMSO. The flask was heated in an oil bath at 90°C, with stirring and under nitrogen for approximately 24 hours. After cooling, a sample was collected and filtered for GC/MS analysis, which indicated 98.5% conversion to desired product.

The reaction mixture was added dropwise to approximately 800 mL of DI water with vigorous stirring. The pH of the solution was adjusted from 9-10 down to 5-6 using concentrated HCl and was left to stir overnight. The resulting solid was isolated via vacuum filtration and the product was left to dry over the vacuum for a few hours. A pre-workup weight was determined to be approximately 1.38 g. The precipitate was dissolved in toluene and washed with a 5% HCl solution, a 5% bisulfite solution, and finally with water. The aqueous layers were extracted with ethyl acetate, and then combined with the toluene layer, followed by drying over MgSO$_4$. The solvents were then removed via rotary evaporation to afford a bright yellow solid.

Chloroform was added dropwise until all of the compound dissolved, and this resulted in a cloudy solution. Ethanol was added, and then the solution was heated to a boil for hot filtration. Hot filtration cleared the appearance of the solution. The volume
was reduced by lightly heating the solution and removing vapors with a vacuum hose connected to the house vacuum. Crystal formation occurred as the solution cooled.

The resulting crystals were isolated via vacuum filtration to afford light yellow platelets. GC/MS analysis of a small sample determined >99% purity of compound. A final yield was determined to be 1.33 g (88.5%). Melting point analysis determined a melting point of 174 – 176 °C. Elemental analysis: Calculated: C – 78.32%, H – 3.94%; Found: C – 78.21%, H – 3.88%. 

$^1$H NMR (CDCl$_3$; $\delta$): 7.10 (m), 7.35 (m), 7.44 (m), 7.55 (d), 7.73 (m), 8.07 (d), 8.17 (d). $^{13}$C NMR (CDCl$_3$; $\delta$): 108.0 (t), 109.8 (s), 112.9 (dd), 120.5 (s), 120.8 (s), 124.0 (s), 126.3 (s) 126.4 (s), 131.8 (s), 134.6 (s), 140.1 (s), 140.4 (t), 142.4 (s), 162.8 (dd), 192.8 (t).

2.7 General Procedure for 2,4-DFK-CBZ Copolymers with DPS and DPE, 11a-c

The procedure for polymer 11c is provided as an example.

To a 5 mL RBF, equipped with a condenser column and a nitrogen inlet, were added 5 (0.0960 g, 0.251 mmol), bis-(4-fluorophenyl) sulfone (DPS) (0.191 g, 0.750 mmol), 4,4’-dihydroxydiphenyl ether (DPE) (0.202 g, 0.999 mmol), K$_2$CO$_3$ (0.415 g, 3.00 mmol), and 1.56 mL of distilled NMP. The reaction was heated at 150 °C for 32 hours. The reaction material was then diluted with ~2 mL of THF and precipitated from vigorously stirred water, and the resulting solids were isolated via vacuum filtration. The solids were dissolved in THF (0.5 mL), re-precipitated from methanol (MeOH), and dried to afford 0.302 g (67.4 %) of the desired polymer.
Two additional copolymers were synthesized, \textbf{11a} (10\% of \textbf{5}), 0.325 g (74.5\%) and \textbf{11b} (15\% of \textbf{5}), 0.342 g (79.5\%).

\textbf{2.8 General Procedure for 3,5-DFK-CBZ Copolymers with DPS and DPE, 12a-b}

The procedure for polymer \textbf{12b} is provided as an example.

To a 5 mL RBF, equipped with a condenser column and a nitrogen inlet, were added \textbf{8} (0.0716 g, 0.187 mmol), DPS (0.143 g, 0.562 mmol), DPE (0.152 g, 0.749 mmol), \textbf{K}_{2}\text{CO}_3 (0.311 g, 2.25 mmol), and 1.2 mL of distilled NMP. The reaction was heated at 185 °C for 24 hours. The reaction material was then diluted with ~2 mL of THF and precipitated from vigorously stirred water. The resulting solids were isolated via vacuum filtration and dissolved in THF (0.5 mL), re-precipitated from MeOH, and dried to afford 0.221 g (65.6 \%) of the desired polymer.

$^1$H NMR (CDCl$_3$; $\delta$): 6.75 (d), 7.01 (m), 7.18, (s), 7.32 (m), 7.46 (m), 7.73 (d), 7.88 (d), 8.09 (m).  $^{13}$C NMR (CDCl$_3$; $\delta$): 109.8 (s), 111.3 (s), 113.2 (m), 117.3 (m), 120.3 (m), 120.5 (s), 120.7 (s), 121.9 (s), 123.9 (s), 126.2 (m), 129.8 (s), 131.9 (s), 132.5 (s), 135.2 (s), 135.5 (m), 140.0 (s), 141.1 (s), 142.6 (s), 150.4 (m), 154.2 (s), 159.4 (s), 162.2 (s), 194.1 (s).

An additional copolymer was synthesized, \textbf{12a} (15\% of \textbf{8}), 0.365 g (83.8\%).
2.9 General Procedure for 2,4-DFK-CBZ Copolymers with TPPO and DPE, 14a-c

The procedure for polymer 14c is provided as an example.

To a 5 mL RBF, equipped with a condenser column and a nitrogen gas inlet, were added 5 (0.0815 g, 0.213 mmol), *bis*-4-fluorophenyl)phenylphosphine oxide (dFTPPO) (0.172 g, 0.850 mmol), DPE (0.200 g, 0.637 mmol), K₂CO₃ (0.352 g, 2.55 mmol), and 1.3 mL of distilled NMP. The reaction was heated at 150 °C for 60 hours. The reaction material was then diluted with ~2 mL of THF and precipitated from vigorously stirred water. The resulting solids were isolated via vacuum filtration. The solids were dissolved in THF (0.5 mL), re-precipitated from isopropanol (IPA), and dried to afford 0.282 g (67.1 %) of the desired polymer.

¹H NMR (CDCl₃; δ): 6.67 (d), 6.80 (d), 7.04 (m), 7.32 (m), 7.48 (m), 7.64 (m), 8.07 (d), 8.14 (d). ¹³C NMR (CDCl₃; δ): 107.6 (s), 109.7 (s), 111.8 (s), 117.2 (m), 120.2 (m), 120.5 (s), 120.6 (s), 121.7 (s), 123.8 (s), 124.5 (s), 125.3 (m), 126.1 (d), 126.8 (m), 128.4 (m), 131.3 (s), 132.0 (m), 132.5 (s), 133.5 (s), 134.1 (m), 134.5 (s), 136.7 (s), 140.2 (s), 141.8 (s), 150.9 (m), 154.0 (m), 157.2 (s), 161.4 (s), 162.2 (s), 193.7 (s).

Two additional copolymers were synthesized, 14a (10% of 5), 0.306 g (74.4%) and 14b (15% of 5), 0.324 g (78.4%).

2.10 Synthesis of 3,5-DFK-CBZ Copolymer with TPPO and DPE, 15

To a 5 mL RBF, equipped with a condenser column and a nitrogen gas inlet, were added 8 (0.144 g, 0.375 mmol), DPE (0.303 g, 1.50 mmol), K₂CO₃ (0.623 g, 4.51 mmol), and 0.64 mL of distilled NMP. The reaction was heated at 185 °C for 24 hours, at which
point the flask was removed from heat and cooled to room temperature for an addition of
dFTPPO (0.353 g, 1.12 mmol) and 0.50 mL NMP. The reaction was heated for an
additional 60 hours, for a total of 84 hours. The reaction material was diluted with ~2
mL of THF, and then precipitated from vigorously stirred water. The resulting solids
were dissolved in THF (2 mL) and re-precipitated from 400 mL of IPA to afford 0.367 g
(49.5%) of grey-brown powdery solid.

$^1$H NMR (CDCl$_3$; δ): 6.90 (d), 7.04 (m), 7.17 (s), 7.32 (m), 7.48 (m), 7.64 (m), 8.07 (d),
8.14 (d). $^{13}$C NMR (CDCl$_3$; δ): 109.7 (s), 111.3 (s), 113.2 (m), 117.4 (m), 120.2 (m),
120.5 (s), 120.7 (s), 121.7 (s), 123.8 (s), 125.6 (d), 126.3 (s), 128.5 (m), 130.0 (s), 132.0
(m), 132.8 (d), 134.1 (m), 135.2 (s), 140.0 (s), 140.1 (s), 142.0 (s), 151.3 (m), 153.9 (m),
159.4 (s), 161.3 (m), 194.2 (s).

2.11 Copolymer Film Casting

Approximately 75 mg of copolymer was weighed and transferred to a 10 mL vial
and dissolved in approximately 1 mL of solvent. THF was used for copolymers 11a-c
and 12a-b, and 5% (v/v) acetic acid THF solution was used for copolymers 14a-c and 15.
The resulting viscous solution was allowed one hour to equilibrate. Using a Pasteur
pipet, the solution was applied to a glass slide and then loosely covered with a watch
glass to allow for slow evaporation of the solvent overnight. The resulting film was
gently lifted at the corner with a razor blade and peeled from the glass slide with forceps.
3. RESULTS AND DISCUSSION

3.1 Synthesis of 2,4-DFK-Br, 3

The chromophore precursor, 2,4-DFK-Br, 3, was synthesized by reacting 2,4-difluorobenzoyl chloride (1) and bromobenzene (2) in a Friedel-Crafts acylation (Scheme 8).

![Scheme 8. Synthesis of 2,4-DFK-Br, 3.](image)

Compounds 1 and 2 were combined in equimolar amounts, and the solution was added dropwise over the AlCl₃ at 0 °C. Once the addition was complete, the ice bath was removed and the reaction was allowed to return to room temperature to stir for 24 hours, at which point the solution was further diluted with four equivalents of compound 1 and was left to stir over several days.
GC/MS analysis determined this method provided 98% conversion to product with minor conversion to ortho, meta, and debrominated derivatives. Following work up of the remaining reaction mixture, approximately 7.74 g of a white solid were recovered for a 64.6% yield. A melting point of 87 – 88 °C was determined following drying of the sample. The structure of compound 3 was confirmed with GC/MS, elemental analysis, and NMR spectroscopy.

![NMR spectrum](image)

**Figure 17.** 300 MHz $^1$H (CDCl$_3$) NMR of 3. * indicates residual chloroform.

The 300 MHz $^1$H (CDCl$_3$) NMR spectrum of 3 shows three multiplet signals. Both the proton positioned between the fluorine atoms, a, as well as the proton labeled b, appear as doublets of triplets at 6.93 and 7.03 ppm, respectively. The splitting pattern for a is the result of coupling with two ortho fluorine atoms and the meta proton, b. Proton b has ortho coupling to a fluorine atom and proton c, as well as meta coupling to a and
para coupling to a fluorine atom. Protons c, d, and e (5H) appear as overlapping multiplets at 7.65 ppm, which integrates to 4.75 relative to a and b (2H).

The 75.5 MHz $^{13}$C (CDCl$_3$) NMR spectrum for 3 (Figure 19) shows 12 unique carbon atom signals. The carbon atom assigned b appears as a triplet at 104.8 ppm due to coupling to the two fluorine atoms ortho to b. Carbon atoms a and c are aromatic C-F, and they appear as doublets of doublets at 160.9 and 165.1 ppm, respectively. Carbon atom d appears as a doublet of doublets at 112.1 ppm due to coupling with the ortho fluorine. Carbon atoms e, meta to the two C-F groups, appear as a doublet of doublets at 132.6 ppm. Quaternary carbon f is ortho and para to the C-F groups and appears as a doublet of doublets at 122.9 ppm. Carbonyl g appears as a singlet at 191.1 ppm. Carbon atoms h, j, and k on the brominated ring appear as singlets at 136.2, 131.1, 131.9, and 128.7 ppm, respectively, while i appears at 131.1 ppm as a doublet due to through-space coupling to the 2-fluorine atom.

3.2 Synthesis of 2,4-DFK-CBZ, 5

![Scheme 9. Synthesis of 2,4-DFK-CBZ, 5.](image)
Optimization of 2,4-DFK-CBZ chromophore, 5, synthesis involved various combinations of catalysts, ligands, solvents, and temperatures. The best results were obtained using the following conditions: compounds 3 and carbazole, 4, were reacted in the presence of CuI catalyst, using N,N-dimethylglycine as the ligand, in DMSO at 90 °C (Scheme 9).

After 24 hours, GC/MS analysis indicated 98% conversion to the desired product. The remaining impurities were due to unreacted 3 and 4 and disubstituted derivatives of the product. The reaction material was precipitated from water to remove DMSO, catalyst, and other inorganic impurities. The resulting solids were isolated via vacuum filtration, and then dissolved in toluene and washed with various water-based solutions (5% HCl, 5% sodium bisulfite, and water). Recrystallization was performed using a mixture of chloroform and ethanol (~1:5). Due to the better solubility of 4 in ethanol, this recrystallization method removed excess 4 from the chloroform layer, and crystal formation excluded unreacted starting material and disubstituted product derivatives.

Recrystallization and drying afforded 1.16 g (77.3%) of a bright yellow solid with a melting point of 134 – 137 °C. The structure of compound 5 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 18** and **Figure 19**, respectively.
Figure 18. 300 MHz $^1$H (CDCl$_3$) NMR of 5. * indicates residual chloroform.

The 300 MHz $^1$H (CDCl$_3$) NMR spectrum for 5 shows 9 unique signals and supports successful incorporation of carbazole via substitution of the bromo group. As in 3, protons a and b appear as doublets of triplets at 7.00 and 7.10 ppm. Previously on 3, protons (4H) d and e appeared as overlapping multiplets with proton c. Substitution of the carbazole group resulted in a greater separation of proton d from e and c. Proton d (2H) appears at 8.09 ppm as a doublet of doublets due to ortho coupling to e, as well as through-space coupling of the 2-fluorine atom of the upper ring. Protons e and c overlap as a multiplet centered around 7.72 ppm and integrate to three protons.

The eight protons of the carbazole group can also be clearly distinguished. Proton f appears as an asymmetrical doublet at 7.55 ppm. Proton g appears at 7.46 ppm as a
doublet of doublets due to ortho coupling to protons f and h and meta coupling to proton i. Similarly, proton h appears at 7.35 ppm as a doublet of doublets due to its ortho coupling to protons g and i and meta coupling to proton f.

The 75.5 MHz $^{13}$C (CDCl$_3$) NMR spectrum (Figure 19) of 5 shows 17 unique carbon atom signals, with 6 new signals introduced from the substitution of the carbazole group. These new carbons were labeled as l, m, n, o, p, and q. As was observed in 3, b appears as a triplet at 104.8 ppm, a and c appear as a doublets of doublets at 160.9 and 165.1 ppm, respectively, d appears as a doublet of doublets at 112.2 ppm, e appears as a doublet of doublets at 132.6 ppm, and g appears as a singlet at 191.1 ppm.

With the addition of the carbazole group, carbon atoms f, h, i, j, and k shifted from what was observed in 3. Previously in 3, f appeared at 122.9 ppm, h appeared at 136.2 ppm, i appeared at 131.1 ppm, j appeared at 131.9, and k appeared at 128.7 ppm. In 5, f, h, i, j, and k appear at 123.2, 135.7, 131.5, 126.3, 142.6 ppm, respectively. New signals from the carbazole group, j, k, l, m, n, and o, appear as singlets at 140.2, 109.8, 126.3, 120.5, 120.8, and 123.9 ppm, respectively.
Figure 19. 75.5 MHz $^{13}$C (CDCl$_3$) overlay of 3 and 5.
3.3 Synthesis of 3,5-DFK-Br, 7


The synthesis for 7 followed Stuck’s method with minor variation. While Stuck reacted bromobenzene, 1, and 3,5-difluorobenzoyl chloride, 6, by adding both dropwise over AlCl₃, an attempt at adding the acid halide dropwise over bromobenzene and AlCl₃ was made. Stuck reported her reaction to take 4 hours to go to completion, while this attempt took 70 hours to react to completion. It is speculated the AlCl₃ may not have been as reactive. Stuck also observed her reaction material thickened to a dark paste, while this reaction attempt remained as a dark-colored liquid solution. A small sample of the resulting solution was worked up and analyzed using GC/MS, which suggested approximately 97% conversion to the desired product with the remaining 3% consisting of ortho and meta substituted derivatives. Following work up and recrystallization of the remaining reaction mixture, approximately 3.77 g of product were obtained for a 31.42% yield.

Following drying under a vacuum pump, the melting point was measured to be 89 – 91 ℃, which closely agrees with Stuck’s observed melting point of 87 – 89 ℃. The
structure was confirmed via GC/MS and NMR spectroscopy. The $^1$H and $^{13}$C NMR spectra are shown in Figure 20 and Figure 22, respectively.

**Figure 20.** 300 MHz $^1$H (CDCl$_3$) NMR spectrum of 7.

The $^1$H NMR spectrum shows three distinct signals. The protons positioned between the fluorine atoms, a, appears as a triplet of triplets at 6.98 ppm. The two hydrogen atoms of the fluorinated ring labeled b appear as a multiplet at 7.20 ppm. The aromatic protons *ortho* (d) and *meta* (c) to the bromine atom appear as a singlet at 7.58 ppm, and the peak area integrates to 4 atoms to confirm this.

The 75.5 MHz $^{13}$C (CDCl$_3$) NMR spectrum (Figure 22) shows 9 unique carbon atom signals. The carbon atom assigned a appears as a triplet at 108.0 ppm due to coupling to the two fluorine atoms *ortho* to a. Carbon atom b is an aromatic C-F, and it
appears as a doublet of doublets at 162.9 ppm. For carbon atom \textbf{c}, the doublet of
doublets signal at 112.8 ppm is inverted in shape. Carbon atoms \textbf{d} \textit{meta} to the C-F and
carbonyl \textbf{e} both appear as triplets at 140.1 and 192.8 ppm, respectively. Carbon atoms \textbf{f},
\textbf{g}, \textbf{h}, and \textbf{i} on the brominated ring all appear as singlets at 135.1, 131.4, 132.0, and 128.4
ppm, respectively.

3.4 Synthesis of 3,5-DFK-CBZ, 8

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=0.4\textwidth]{reaction.png}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 11.} Synthesis of 3,5-DFK-CBZ, 8.

The 3,5-DFK-CBZ chromophore, 8, was synthesized by reacting 7 with 4, in the
presence of CuI catalyst and \textit{N},\textit{N}-dimethylglycine ligand, in DMSO at 90 °C. Conditions
were based on the optimal conditions determined for 5. GC/MS analysis indicated >99%
conversion to product with undetectable amounts of 7 and disubstituted derivatives of
product. Any impurities were due to debrominated derivatives of 7 and excess 4.

The reaction material was precipitated into water, and to ensure a clean
separation, the pH of the solution was adjusted from 9 – 10 down to 5 – 6 using
concentrated HCl. The resulting compound was isolated easily from the solution via
vacuum filtration and recrystallized from a chloroform/ethanol solution to afford 1.34 g (89.3%) of colorless platelets.

The structure was confirmed via 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$_3$) NMR of 8.](image)

The $^1$H NMR spectrum (Figure 21) confirms the successful incorporation of carbazole via substitution of the bromo group. Previously on compound 7, protons (4H) c and d appeared as a broad singlet at 7.58 ppm. With the substitution of the carbazole group, the protons now appear as multiplets with c at 8.07 ppm and d at 7.77 ppm. The protons (8H) of the carbazole group can also be observed with e appearing as an asymmetrical doublet at 7.55 ppm, g appearing as a doublet of triplets at 7.36 ppm, and h appearing as a doublet at 8.17 ppm. Protons f and b appear as overlapping multiplets at 7.45 ppm.
The 75.5 MHz $^{13}$C (CDCl$_3$) NMR spectrum (Figure 22) shows 15 unique carbon atom signals, with 6 new signals introduced from the substitution of the carbazole group. These new carbons were labeled as j, k, l, m, n, and o. As was observed in 7, a appears as a triplet at 108.0 ppm, b appears as a doublet of doublets at 162.8 ppm, c appears as a doublet of doublets at 112.9 ppm, d appears as a triplet at 140.4 ppm, and e appears as a triplet at 192.8 ppm, and g appears as a singlet at 131.8 ppm.

With the addition of the carbazole group, carbon atoms f, h, and i shifted from what was observed in 7. Previously in 7, f appeared at 135.1 ppm, h appeared at 132.0 ppm, and i appeared at 128.4 ppm. In 8, f, h, and i appear at 134.6, 126.5, and 142.5 ppm, respectively. New signals from the carbazole group, j, k, l, m, n, and o, appear as singlets at 140.15, 109.8, 126.4, 120.5, 120.8, and 124.0 ppm, respectively.

Figure 22. 75.5 MHz $^{13}$C (CDCl$_3$) overlay of 7 (top) and 8 (bottom).
3.5 Photophysical Analyses of Monomers

Figure 23. Absorbance and emission of 3, 5, 7, and 8 in toluene (a) and (b), respectively) and THF (c) and (d), respectively). All solution concentrations were 20 μM. Excitation wavelength used for (b) and (d) was 340 nm.

Photophysical analyses of chromophores 5 and 8 and their precursor compounds, 3 and 7, were performed via UV/Vis spectrophotometry and fluorimetry (fluorescence spectroscopy). Solutions of each compound were prepared to similar concentrations of roughly 20 μM to minimize variation of results due to concentration differences.

Analyses were also performed in two solvents, toluene and THF, to illustrate the effects of solvent polarity on emission behavior.

The absorption spectra of chromophores 5 and 8 were very similar despite structural differences. Absorption occurred in a major peak centered around 290 nm (not shown)
due to phenyl groups, and a broad range of wavelengths of 310 to 390 nm, with peak absorption occurring at 340 nm due to the donor-π-acceptor system. This was true in both toluene (Figure 23a) and THF (Figure 23c), illustrating that solvent effects have very little impact on absorption. Precursors 3 and 7 showed little to no absorbance in this region.

**Table 1.** Chromophore peak emission wavelength (\(\lambda\)) and width at half intensity of 5 and 8 in toluene and THF.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>Toluene Peak emission (\lambda) (nm), Width (nm)</th>
<th>Toluene</th>
<th>THF Peak emission (\lambda) (nm), Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>430 70</td>
<td></td>
<td>463 70</td>
</tr>
<tr>
<td>8</td>
<td>445 85</td>
<td></td>
<td>481 85</td>
</tr>
</tbody>
</table>

Fluorimetry was performed using 340 nm as the excitation wavelength. Interestingly, precursor 7 displayed low intensity emission around 400 nm in toluene, while precursor 5 gave a similar spectrum to the solvent blank. In THF, the reverse occurred; 5 gave low intensity emission ranging from 400 to 460 nm and 7 mirrored the solvent blank closely.

Emission of chromophores 5 and 8 behave very similarly in toluene (Figure 23b), however, emission intensity is relatively low compared to emission in THF (Figure 23d). Structural effects appear very subtly in toluene: 5 shows slightly blue-shifted emission centered around 430 nm compared to 8, which shows emission centered around 445 nm. In THF, the structural differences between 5 and 8 appear much more dramatically. Despite having similar concentrations, the emission intensity of 8 is roughly double that of 5, suggesting that THF is positively affecting emission efficiency of the 3,5-difluoro system of 8.
Consistent with emission in toluene, 5 is more blue-shifted (463 nm) compared to 8 (481 nm). These wavelengths are red-shifted compared to those in toluene due to the polar nature of THF. This is more clearly illustrated with an overlay of the emission results of 5 in both solvents, normalized to 1 (Figure 24). In THF, 5 experiences a red shift of about 30 nm.

Figure 24. Solvent effects on emission of 5 in toluene and THF, excited at 340 nm.
3.6 Synthesis of 2,4-DFK-CBZ DPS/DPE copolymers, 11a-c

Scheme 12. Synthesis of 2,4-DFK-CBZ DPS/DPE copolymers, 11a-c.

Polymerizations of 5 with 4,4’-difluorodiphenylsulfone (DPS, 9) and 4,4’-
dihydroxydiphenyl ether (DPE, 10) were performed in NMP at 150 °C via nucleophilic
aromatic substitution, NAS, polycondensation reactions. After 24 hours, the reaction
material was precipitated from vigorously stirred water, and the resulting solids were
isolated via vacuum filtration. The material was re-precipitated by dissolving in THF and
adding dropwise to an excess of methanol.

By varying the ratio of 5 (x) to 9 (1-x), three copolymers were produced where x =
0.10, 0.15, and 0.25 for copolymers 11a, 11b, and 11c, respectively. Synthesis of these
copolymers was confirmed via ¹H and ¹³C NMR analyses, Figure 25 and Figure 26,
respectively.
Figure 25. 300 MHz $^1$H (CDCl$_3$) NMR of 11a-c. * indicates residual CHCl$_3$.

The 300 MHz $^1$H spectra of 11a-c show the successful incorporation of 5 into a polymer backbone consisting of DPS and DPE. The increasing concentration of 5 in copolymers 11a-c is reflected by the increasing intensities of proton signals labeled a, b, c, d, e, f, g, h, and i. Protons j and k result from the DPS unit and appear at 7.88 ppm, and the decrease of these signals from 11a-c reflects the 1-x ratio to 5. DPE protons, l and m, appear around 7.03 ppm.

The ratios of 5 to 10 can be confirmed via comparison of the integrations of proton signals i and d to l and m. Calibrating the l, m signal to 8 protons to represent one unit of 10 results in a calculated i, d integration of 0.92 for 11c. Because i and d combined account for 4 protons of 5, 0.92 can be divided by 4 and results in 0.23, which is
representative of the ratio of 5 compared to 10. The desired amount of 5 in 11c was 25%, and integration indicates that 23% incorporation was achieved. An integration ratio 0.51:8 is observed for 11b, providing 13% incorporation was achieved. The desired amount of 5 in 11b was 15%. The integration ratio observed in 11a was 0.35:8. The desired amount of 5 in 11a was 10%, and 8.8% was achieved.

Figure 26. 75.5 MHz $^{13}$C (CDCl$_3$) NMR of 11a-c.

The 75.5 MHz $^{13}$C (CDCl$_3$) NMR spectrum (Figure 26) further supports the incorporation of 5 into a DPS DPE backbone system. Signals that were previously split by fluorine atoms in the 5 monomer, carbons a-f, now appear as singlets due to the successful substitution of the fluorine atoms with oxygen atoms. Carbon signals corresponding to 5 can be observed to slightly increase in intensity from 11a to 11c, and carbon signals corresponding to the DPS comonomer can be observed to slightly decrease from 11a to 11c.
Table 2. Monomer ratios, % yield, molecular weight, and dispersity for 11a-c.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ratio of x:(1-x)</th>
<th>% Yield</th>
<th>M_n (Da)</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>11a</td>
<td>0.10:0.90</td>
<td>79.5</td>
<td>7,300</td>
<td>3.5</td>
</tr>
<tr>
<td>11b</td>
<td>0.15:0.85</td>
<td>74.5</td>
<td>5,200</td>
<td>2.9</td>
</tr>
<tr>
<td>11c</td>
<td>0.25:0.75</td>
<td>67.4</td>
<td>11,900</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Characterization results of 11a-c are summarized in Table 2. The percent yields were consistent through the set. Size exclusion chromatography (SEC) was used to determine the molecular weights and dispersity of the copolymers. The mobile phase used was 5% (v/v) acetic acid THF solution. The SEC traces for 11a-c are overlaid in Figure 27.

The determined M_n values for polymers 11a-c varied slightly between iterations, with 11c providing the largest M_n at 11,900 Da with a relatively lower dispersity of 2.9, 11a providing intermediate M_n value of 7,300 Da and a slightly larger dispersity of 3.5, and 11b providing lower M_n of 5,200 Da and similar dispersity to 11c. These M_n values are relatively low but exceed the critical chain entanglement length necessary for viable film formation.
**Figure 27.** SEC traces for 11a-c. * indicates syringe filter contaminant.

A secondary peak is visible in each trace in **Figure 27**. This is attributed to contaminants solubilized from the filtration procedure, which uses a syringe filter within a plastic housing. The contaminant overlaps slightly with the lower molecular weights of the peak, which decreases the average molecular weights and slightly increases dispersity. Meyer$^{35}$ determined the contaminant may be removed with several washes through the syringe filter housing prior to filtering the sample for analysis.
3.7 Synthesis of 3,5-DFK-CBZ DPS/DPE copolymers, 12a-b


Polymerizations of 8 with 9 and 10 were performed in NMP at 185 °C via nucleophilic aromatic substitution, NAS, polycondensation reactions. A higher temperature was required for the polymerization of 8 due to its lower reactivity at the polymerization sites. Compared to 5, which is electronically active through both inductive and resonance effects, 8 is electronically active through inductive effects only.

After 24 hours, the reaction material was precipitated from vigorously stirred water, and the resulting solids were isolated via vacuum filtration. The material was re-precipitated by dissolving in THF and adding dropwise to an excess of methanol.

By varying the ratio of 8 (x) to 9 (1-x), two copolymers were produced where x = 0.15 and 0.25 for copolymers 12a and 12b, respectively. Synthesis of these copolymers was confirmed via 1H and 13C NMR analyses, Figure 28 and Figure 29, respectively.
Figure 28. 300 MHz $^1$H (CDCl$_3$) NMR of 12a-b. * indicates residual CHCl$_3$.

The 300 MHz $^1$H spectra of 12a-b show the successful incorporation of 8 into a polymer backbone consisting of DPS and DPE. The increasing concentration of 8 in copolymers 12a-b is reflected by the increasing intensities of proton signals labeled a, b, c, d, e, f, g, and h. Protons i and j resulting from the DPS unit can be observed to decrease in intensity from 12a-b, which reflects the l-x ratio to 8. DPE protons, k and l, appear around 7.03 ppm.

The ratios of 8 to 10 can be confirmed via comparison of the integrations of proton signals h and c to k and l. Calibrating the l, m signal to 8 protons results in an 8:10 ratio of 0.79:8 in 12b. The desired amount of 8 in 12b was 25%, and integration indicates that approximately 20% incorporation was achieved. An integration ratio 0.46:8 is observed.
for 12a, determining that approximately 12% incorporation was achieved. The desired amount of 8 in 12a was 15%.

Figure 29. 75.5 MHz $^{13}$C (CDCl$_3$) overlay of 12a-b.

The 75.5 MHz $^{13}$C (CDCl$_3$) NMR spectrum (Figure 29) further supports the incorporation of 8 into a DPS DPE backbone system. Signals that were previously split by fluorine atoms in the 8 monomer, carbons a-e, now appear as singlets due to the successful displacement of the fluorine atoms by oxygen atoms. Carbon signals corresponding to 8 can be observed to slightly increase in intensity from 12a to 12b, and carbon signals corresponding to the DPS comonomer can be observed to slightly decrease from 12a to 12b.
Table 3. Monomer ratios, % yield, molecular weight, and dispersity for 12a-b.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ratio of x:(1-x)</th>
<th>% Yield</th>
<th>M_n (Da)</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>12a</td>
<td>0.15:0.85</td>
<td>83.8</td>
<td>8,100</td>
<td>3.7</td>
</tr>
<tr>
<td>12b</td>
<td>0.25:0.75</td>
<td>65.8</td>
<td>5,400</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Characterization results of 12a-b are summarized in Table 3. The percent yields of 12a and 12b differed slightly, with 12b showing a more successful yield. The lower % yield for 12b may be due to an increased likelihood of cyclization. Reprecipitation from methanol would have removed any low molecular weight material, such as cyclic species, and therefore resulted in a lower yield. It is also possible that 24 hours was insufficient for reaction completion in this case.

Size exclusion chromatography (SEC) was used to determine the molecular weights and dispersity of the copolymers. The mobile phase used was 5% (v/v) acetic acid THF solution. The SEC traces for 12a-b are overlaid in Figure 30. The same secondary peak resulting from the plasticizer in the filter housing is visible in each trace in Figure 30 as in Figure 27. Copolymer 12a showed a better M_n value of 8,100 Da compared to 12b (5,400 Da). Dispersity was also lower in 12a than in 12b, most likely for similar reasons affecting the % yield.
Figure 30. SEC traces for 12a-b. * indicates syringe filter contaminant.

3.8 Synthesis of 2,4-DFK-CBZ TPPO/DPE copolymers, 14a-c

Scheme 14. Synthesis of 2,4-DFK-CBZ TPPO/DPE copolymers, 14a-c.

Polymerizations of 5 with 4,4’-difluorotriphenylphosphine oxide (dFTPPO, 13) and DPE, 10, were performed in NMP at 150 °C via nucleophilic aromatic substitution, NAS, polycondensation reactions. After 60 hours, the reaction material was precipitated from vigorously stirred water, and the resulting solids were isolated via vacuum filtration. The
material was re-precipitated by dissolving in THF and adding dropwise to an excess of isopropanol.

By varying the ratio of 5 (x) to 13 (1-x), three copolymers were produced where x = 0.10, 0.15, and 0.25 for copolymers 14a, 14b, and 14c, respectively. Synthesis of these copolymers was confirmed via $^1$H and $^{13}$C NMR analyses, Figure 31 and Figure 32, respectively.

The 300 MHz $^1$H spectra (Figure 31) of 14a-c show the successful incorporation of 5 into a polymer backbone consisting of triphenylphosphine oxide (TPPO) and DPE. DPE protons, o and p, appear around 7.03 ppm. The increasing concentration of 5 in copolymers 14a-c should theoretically result in an increase of intensities of proton signals labeled a, b, c, d, e, f, g, h, and i. Protons j, k, l, m, and n resulting from the TPPO unit overlap in a multiplet centered around 7.55 ppm and should theoretically decrease in intensity, reflecting the 1-x ratio to 5. Due to the broader peaks of 14b, it is difficult to see these trends progress. The difference in intensity is more obvious when comparing 14a to 14c.
Figure 31. 300 MHz $^1$H (CDCl$_3$) NMR of 14a-c. * indicates residual CHCl$_3$.

The ratios of 5 to 10 can be confirmed via comparison of the integrations of proton signals i and d to o and p. Calibrating the o, p signal to 8 protons results in a 5:10 ratio of 0.84:8 in 14c. The desired amount of 5 in 14c was 25%, and integration indicates that 21% incorporation was achieved. An integration ratio 0.45:8 is observed for 14b, providing 11% incorporation was achieved. The desired amount of 5 in 14b was 15%. The integration ratio observed in 14a was 0.34:8. The desired amount of 5 in 14a was 10%, and 8% was achieved.
The 75.5 MHz $^{13}$C (CDCl$_3$) NMR spectrum (Figure 32) further supports the incorporation of 5 into a TPPO DPE backbone system. Signals that were previously split by fluorine atoms in the 5 monomer, carbons a-f, now appear as singlets due to the successful substitution of the fluorine atoms with oxygen atoms. Carbon signals corresponding to 5 are observed to slightly increase in intensity from 14a to 14c, and carbon signals corresponding to the TPPO comonomer are observed to slightly decrease from 14a to 14c.
Table 4. Monomer ratios, % yield, molecular weight, and dispersity for 14a-c.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ratio of x:(1-x)</th>
<th>% Yield</th>
<th>$M_n$ (Da)</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>14a</td>
<td>0.10:0.90</td>
<td>74.4</td>
<td>5,600</td>
<td>4.0</td>
</tr>
<tr>
<td>14b</td>
<td>0.15:0.85</td>
<td>78.4</td>
<td>8,400</td>
<td>14.2</td>
</tr>
<tr>
<td>14c</td>
<td>0.25:0.75</td>
<td>67.1</td>
<td>4,500</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Characterization results of 14a-c are summarized in Table 4. The percent yields of 14a-c remained consistent. Size exclusion chromatography (SEC) was used to determine the molecular weights and dispersity of the copolymers. The mobile phase used was 5% (v/v) acetic acid THF solution. The SEC traces for 14a-c are overlaid in Figure 33. The same secondary peak is visible in each trace in Figure 30 as in the SEC traces above (Figure 27).

The $M_n$ values for this set of copolymers are variable despite nearly identical reaction conditions. While 14a and 14c are very similar in both $M_n$ values and dispersity, 14b shows a broad range of high molecular weights that increases the $M_n$ value to nearly double that of 14a and 14c but provides an undesirably high dispersity value of 14.2. This high dispersity of molecular weights may be cause for the broad signals in the $^1$H NMR of 14b above (Figure 31). The cause is unknown, as 14a and 14b were synthesized in parallel within the same oil bath.
**Figure 33.** SEC traces of 14a-c. * indicates syringe filter contaminant.

### 3.9 Synthesis of 3,5-DFK-CBZ TPPO/DPE copolymer, 15

![Synthesis diagram](image)

**Scheme 15.** Synthesis of 3,5-DFK-CBZ TPPO/DPE copolymer, 15.
Polymerizations of 8 with 13 and 10 were performed via nucleophilic aromatic substitution, NAS, polycondensation reactions. Previous attempts at polymerizing TPPO at 185 °C resulted in gelling.\textsuperscript{35} To prevent this, a stepwise addition consisting of two steps was utilized (Scheme 15). The first step included reacting 8 with 10 in NMP at 185 °C. After 24 hours, the reaction was cooled to room temperature and comonomer 13 was added for the second step. The reaction was heated to 150 °C for 60 hours. The reaction material was precipitated from vigorously stirred water, and the resulting solids were isolated via vacuum filtration. The material was re-precipitated by dissolving in THF and adding dropwise to an excess of isopropanol.

Due to the difficulties of polymerizing 13 to completion, only one ratio of 8 (x) to 13 (1-x) was used to produce copolymer 15, where x = 0.25. Synthesis of this copolymer was confirmed via \textsuperscript{1}H and \textsuperscript{13}C NMR analyses, Figure 34 and Figure 35, respectively.
The 300 MHz $^1$H spectra of 15 shows the successful incorporation of 8 into a polymer backbone consisting of TPPO and DPE. As monomer 8, proton a appeared as a triplet of triplets due to coupling to the two ortho fluorine atoms. Polymerized, a shows as a broad doublet, split by the meta protons b. TPPO protons i-m appear as a broad multiplet centered around 7.6 ppm and are overlapped with chromophore 8 protons, d, f, g, and h. DPE protons (8H) n and o appear at 7.03 ppm.

The ratio of 8 to 10 can be confirmed via comparison of the integrations of proton signals h and c to n and o. Calibrating the n, o signal to 8 protons results in a 8:10 ratio of 0.99:8 in 15. The desired amount of 8 in 15 was 25%, and integration indicates that approximately 25% incorporation was achieved.
Figure 35. 75.5 MHz $^{13}$C (CDCl$_3$) NMR of 15.

The 75.5 MHz $^{13}$C (CDCl$_3$) NMR spectrum (Figure 35) further supports the incorporation of 8 into a TPPO DPE backbone system. Signals that were previously split by fluorine atoms in the 8 monomer, carbons a-e, now appear as singlets due to the successful displacement of the fluorine atoms by oxygen atoms. The overlapping doublets at 117.6 ppm (q) suggest fluorine end groups are still present in TPPO units. These doublets are consistent with the monosubstituted derivatives of TPPO with DPE in a homopolymer study of the TPPO/DPE backbone system performed by Meyer.$^{35}$

Table 5. Monomer ratios, % yield, molecular weight, and dispersity for 15.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ratio of x:(1-x)</th>
<th>% Yield</th>
<th>$M_n$ (Da)</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.25:0.75</td>
<td>49.5</td>
<td>2,100</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Characterization results of 15 are summarized in Table 5. The percent yield of 15 was relatively low compared to 14a-c. However, this low yield is comparable to 12b. Size exclusion chromatography (SEC) was used to determine the molecular weights and dispersity of the copolymer. The mobile phase used was 5% (v/v) acetic acid THF solution. The SEC trace for 15 is shown in Figure 36. Copolymer 15 shows a later elution than previously discussed copolymers. Also visible is the same secondary peak as in the SEC traces above (Figure 27).

The determined $M_n$ value for 15 was very low at only 2,100 Da, further supporting incomplete incorporation of TPPO. Another possible reason for the low molecular weights is the formation of cyclic species during the first step of the polymerization.

![Figure 36. SEC trace of 15. * indicates syringe filter contaminant.](image)
3.10 Thermal Analyses

The thermal properties of all copolymers were evaluated via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

The TGA thermograms for all DPS/DPE copolymers, 11a-c and 12a-b, and TPPO/DPE copolymers, 14a-c and 15, are depicted in Figure 37a and Figure 37b, respectively. The thermal stability of a polymer is often defined as a 5 % weight loss temperature or $T_{d-5\%}$. $T_{d-5\%}$ values were determined for all of the polymeric materials and are summarized in Table 6. Both the DPS/DPE copolymers and the TPPO/DPE copolymers showed excellent thermal stability with all $T_{d-5\%}$ values higher than 390 ℃, a temperature well above the operating temperature of an OLED device.

Table 6. Thermal data for all copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ratio of x:(1-x)</th>
<th>$T_{d-5%}$ (℃)</th>
<th>$T_k$ (℃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11a</td>
<td>0.10:0.90</td>
<td>411</td>
<td>183</td>
</tr>
<tr>
<td>11b</td>
<td>0.15:0.85</td>
<td>408</td>
<td>181</td>
</tr>
<tr>
<td>11c</td>
<td>0.25:0.75</td>
<td>448</td>
<td>180</td>
</tr>
<tr>
<td>12a</td>
<td>0.15:0.85</td>
<td>396</td>
<td>184</td>
</tr>
<tr>
<td>12b</td>
<td>0.25:0.75</td>
<td>436</td>
<td>178</td>
</tr>
<tr>
<td>14a</td>
<td>0.10:0.90</td>
<td>459</td>
<td>186</td>
</tr>
<tr>
<td>14b</td>
<td>0.15:0.85</td>
<td>434</td>
<td>190</td>
</tr>
<tr>
<td>14c</td>
<td>0.25:0.75</td>
<td>427</td>
<td>181</td>
</tr>
<tr>
<td>15</td>
<td>0.25:0.75</td>
<td>429</td>
<td>173</td>
</tr>
</tbody>
</table>
The DPS/DPE copolymers 11a and 11b provide similar T\textsubscript{d-5}\% of 411 and 408 °C, respectively, while 11c shows a higher T\textsubscript{d-5}\% of 448 °C. Copolymers 12a-b show an increase of T\textsubscript{d-5}\% as incorporation of 8 is increased; 12a gives a lower T\textsubscript{d-5}\% of 396 °C, while 12b gives a higher T\textsubscript{d-5}\% of 436 °C, suggesting the chromophores 5 and 8 are more thermally stable than the polymer backbone. In addition, copolymers 12a-b resulted in lower T\textsubscript{d-5}\% values when compared to 11a-c, suggesting the 2,4- polymerization sites may provide slightly better thermal stability for the DPS/DPE backbone system.

![Figure 37. TGA traces of a) 11a-c and 12a-b and b) 14a-c and 15.](image)

The TPPO/DPE copolymer system shows the opposite trend: increasing the percentage of chromophore results in progressively lower thermal stability. The TPPO/DPE homopolymer shows excellent thermal stability with a T\textsubscript{d-5}\% of 524 °C.\textsuperscript{35} Copolymer 14a provides the highest T\textsubscript{d-5}\% of the set at a value of 459°C. 14b has an intermediate value of 434 °C, and 14c has the lowest value at 427 °C. Copolymer 15 has a T\textsubscript{d-5}\% value similar to 14c, suggesting a similar trend may exist for 3,5- derivatives of the TPPO/DPE system. Overall, the TPPO/DPE system displayed superior thermal stability and less variability when compared to the DPS/DPE system.
Figure 38. DSC traces of a) 11a-c and 12a-b and b) 14a-c and 15.

DSC traces, up to 250 °C, indicated the presence of completely amorphous materials, with only glass transition temperatures, \( T_g \), present. This temperature indicates the transition of amorphous material from a glassy state to rubbery state due to the ability for bonds to “freely” rotate to relieve an applied stress. Standard practice defines the midpoint of the change in the baseline, or inflection point, of the heat flow trace (exotherm up) as the \( T_g \) value (Figure 38).

The DPS/DPE copolymers show very little variation in \( T_g \) values. \( T_g \) of the homopolymer is currently unknown. Copolymers 11a-c were determined to have \( T_g \) values of 183, 181, and 180 °C, respectively, and 12a-b were determined to have \( T_g \) values of 184 and 178 °C, respectively.

The TPPO/DPE copolymers displayed slightly higher \( T_g \) values compared to the DPS/DPE system. Meyer\(^3\) determined the TPPO/DPE homopolymer to have a \( T_g \) of 187 °C. Copolymers 14a-c were determined to have \( T_g \) values of 186, 190, and 181 °C, and 15 gave a \( T_g \) value of 173 °C.
3.11 Photophysical Analyses of Copolymers

Photophysical analyses were performed on both solution phase and films of each copolymer. The DPS/DPE copolymer (11a-c and 12a-b) solutions were made to 20 μM concentrations in THF. The TPPO/DPE copolymers (14a-c and 15) displayed poor solubility in THF, and so a 5% (v/v) acetic acid THF solution was utilized to make 20 μM copolymer solutions for analysis.

All copolymer solutions showed both strong and weak absorptions in the absorbance spectra (Figure 39a and Figure 40a). The strongest absorption occurred at 264 nm for the DPS/DPE copolymers, 11a-c and 12a-b, due to phenyl groups within the compounds. Similarly, the TPPO/DPE copolymers, 14a-c and 15, showed strong absorption at 250 nm. The distinct shoulders centered at 340 are consistent among all copolymers, indicating the absorption due to the chromophore units. Copolymers 11a-c and 14a-c show increasing absorption as the percent of incorporated 5 increases. This trend is not observed in 12a-b.

Fluorimetry for all solutions was performed with the following parameters on a Cary Eclipse fluorescence spectrophotometer: The slit width was set for 5 microns and the photomultiplier tube was set to “high voltage” at 800 V. Excitation was performed at 340 nm and 365 nm. Emission spectra for the DPS/DPE copolymer solutions and the TPPO/DPE copolymer solutions are given in Figure 39b-c and Figure 40b-c, respectively.
Figure 39. Absorption spectra (a) and emission spectra for DPS/DPE copolymer (11a-c and 12a-b) solutions in THF, 20 μM. THF 11a 11b 11c 12a 12b. Excitation wavelengths used were 340 nm (b) and 365 nm (c).

Emission behaviors varied depending on the excitation energy. With higher energy excitation, 340 nm, emission in the UV region was observed to be very strong for the 2,4- derivatives of the DPS/DPE system, 11a-c, while the 3,5- derivatives, 12a-b, showed weaker emission in the UV region and stronger emission in the visible region (Figure 39b). When excited at 365 nm, the emission in the UV range is very minor, with the most intense emission occurring in the blue region, ranging from 400 to 630 nm (Figure 39c). It is speculated that excitation energies higher than 365 nm resulted in emission from the DPE comonomer in the backbone, which may be the high-intensity emission observed in the UV region. Copolymers 11b-c were determined to have peak emission at 460 nm, while copolymer 11a showed peak intensity at 430 nm. Of the iterations of 11, 11a provided the weakest emission, and 11c showed emission intensities similar to 11b. This suggests that there is a cap in emission efficiency, possibly due to self-quenching. Copolymers 12a-b showed similar peaks and intensities centered at 475
nm. Copolymers 11b-c and 12a-b had measurable width at half height and are summarized in Table 7.

As seen in chromophores 5 and 8, emission intensities of the 3,5- derivatives (12a-b) are much more intense than the 2,4- derivatives (11a-c). As monomers, 8 showed intensity double that of 5 when excited in THF solution. Polymerized, however, the 3,5- system is more intense by more than ten-fold, and so it is difficult to say how much of the intensity difference is due to solvent effects. It is possible that polymerization of the 2,4- system resulted in its loss of planarity, and thus reduces the ability for efficient TADF emission.

**Figure 40.** Absorption spectra (a) and emission spectra for TPPO/DPE copolymer (14a-c, and 15) solutions in 5% Acetic Acid THF solution, 20 μM. Included is also the homopolymer. 5% Acetic Acid THF  TPPO/DPE homopolymer  14a  14b  14c  15. Excitation wavelengths used were 340 nm (b) and 365 nm (c).
As a baseline for the TPPO/DPE backbone system, photophysical analyses were performed on the TPPO/DPE homopolymer previously prepared by Meyer, and were included in the overlays of Figure 40. The homopolymer was observed to emit most intensely at deep-blue wavelengths 400 – 425 nm when excited at 340 nm and 365 nm. The copolymers, 14a-c and 15, provided very different emission behaviors when compared to the homopolymer. When excited at 340 nm, copolymers 14a-c were determined to have the most intense emission in the UV region around 365 nm, and they also displayed a secondary emission band over a broad range of wavelengths of 405 – 620 nm (Figure 40b). When excited at 365 nm, these copolymers gave a single emission peak centered around 455 nm and ranging from 390 – 620 nm (Figure 40c). Of the iterations of 14, 14a and 14c displayed similar emission intensities, with 14b showing the lowest intensity. Copolymer 15 displayed similar emission behaviors when excited at 340 nm and 365 nm. When excited at 340 nm, 15 showed minor emission in the UV region centered around 365 nm. When excited at 365 nm, emission in the UV region is very weak. In both cases, 15 showed an intense emission peak centered at 465 nm.

These results are very similar to the peak emission wavelengths observed for the DPS/DPE system. Stronger emission intensity is again observable for 15, the 3,5-derivative compared to 14a-c. Copolymers 14a-c and 15 had measurable width at half height and are summarized in Table 7. Overall, excitation at 365 nm provided cleaner emission in the visible region but reduced the emission intensity. Sharp signals at 340 nm in Figure 39b and Figure 40b, as well as at 365 nm in Figure 39c and Figure 40c, are due to the detector observing the excitation wavelength, 340 nm and 365 nm, respectively.
Fluorimetry for all films was performed with the same parameters as for the solutions. Films were positioned at a 45° angle to the detector within a cuvette, and excitation was performed at 365 nm. Emission spectra for the DPS/DPE copolymer films and the TPPO/DPE copolymer films are shown in Figure 41 and Figure 42, respectively. Emission intensity of the films is difficult to compare directly due to variable thickness and opacity of each one. To make comparisons easier, the spectral results (Figure 41a and Figure 42a) were approximately normalized to 1 to produce Figure 41b and Figure 42b.

![Fluorescence spectra](image)

**Figure 41.** a) Emission and b) normalized emission spectra for DPS/DPE copolymer films, 11a-c and 12a-b. Excitation wavelength was 365 nm.

Copolymers 11a-c displayed variable emission between films, with peak emission occurring at 455, 490, and 465 nm, respectively. While 11b showed the most intense emission (Figure 41a) it is more red shifted compared to 11a and 11b (Figure 41b). 11b also had a long tail of green wavelengths emitting at relatively high intensities. 12a-b showed similar peak emissions, but 12b showed more intense emission in the UV region.
Figure 42. a) Emission and b) normalized emission spectra for TPPO/DPE copolymer films. Excitation wavelength was 365 nm.

Copolymers 14a-c displayed variable emission between films, as well, with peak emission occurring at 495, 480, and 465 nm, respectively. This may suggest that increasing the concentration of 5 results in a blue shift in emission. 14c showed the most intense emission of the set (Figure 42a). Copolymer 15 gave very weak emission, possibly due to the difficulty to position the film in the cuvette. Because of the very low molecular weights, 15 was unable to hold a film and broke very easily. In order to obtain emission analysis on 15, pieces of the film were placed at the bottom of the cuvette, which was not seated all the way down in the sample holder. Normalizing the results enhanced the emission spectrum for 15, and a clear peak is visible with peak emission occurring at 445 nm.

Copolymer solution and film peak emission values and their width at half height (where measurable) were recorded in Table 7.
Table 7. Peak emission wavelength and the width at half intensity for all copolymers as solutions and films, excited at 365 nm.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Ratio  x:(1-x)</th>
<th>Solution Peak emission (nm)</th>
<th>Width (nm)</th>
<th>Film Peak emission (nm)</th>
<th>Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11a</td>
<td>0.10:0.90</td>
<td>430</td>
<td>N/A</td>
<td>455</td>
<td>101</td>
</tr>
<tr>
<td>11b</td>
<td>0.15:0.85</td>
<td>460</td>
<td>127</td>
<td>490</td>
<td>133</td>
</tr>
<tr>
<td>11c</td>
<td>0.25:0.75</td>
<td>460</td>
<td>115</td>
<td>465</td>
<td>92</td>
</tr>
<tr>
<td>12a</td>
<td>0.15:0.85</td>
<td>470</td>
<td>89</td>
<td>475</td>
<td>86</td>
</tr>
<tr>
<td>12b</td>
<td>0.25:0.75</td>
<td>475</td>
<td>92</td>
<td>475</td>
<td>103</td>
</tr>
<tr>
<td>14a</td>
<td>0.10:0.90</td>
<td>455</td>
<td>130</td>
<td>495</td>
<td>130</td>
</tr>
<tr>
<td>14b</td>
<td>0.15:0.85</td>
<td>455</td>
<td>101</td>
<td>480</td>
<td>122</td>
</tr>
<tr>
<td>14c</td>
<td>0.25:0.75</td>
<td>455</td>
<td>97</td>
<td>465</td>
<td>108</td>
</tr>
<tr>
<td>15</td>
<td>0.25:0.75</td>
<td>465</td>
<td>90</td>
<td>445</td>
<td>96</td>
</tr>
</tbody>
</table>

Additionally, photos were taken of each film while excited at 365 nm by a TLC lamp and can be seen in Figure 43. All copolymers, except for 15 and 14c, were able to hold a viable and flexible film. Copolymer 15 could not be handled with forceps without breaking, and so a photo could not be taken. To the naked eye, 14a-c appear more green than blue under the TLC lamp.
Figure 43. Films under TLC lamp, excited at 365 nm.
4. CONCLUSION

The syntheses of (4-9H-carbazolylphenyl)(2,4-difluorophenyl)methanone, 5, and its 3,5-difluoro geometric isomer, 8, were achieved with excellent yield and purity. The structures of the compounds were confirmed via GC/MS analysis, NMR spectroscopy, and elemental analysis. Photophysical analyses determined 5 and 8 have similar absorption patterns, with optimal emission occurring when excited at 340 nm. Chromophore 5 displayed blue-shifted emission (450 nm) when compared to 8 (470 nm) in THF solution, while 8 displayed enhanced intensity in THF solution.

Both chromophores were successfully incorporated into polymers via NAS polycondensation reactions with two different backbone systems: 4,4’-diphenylsulfone (DPS) and 4,4’-dihydroxydiphenyl ether (DPE), and 4,4’-difluorotriphenylphosphine oxide (dFTPPO) and DPE. A total of nine copolymers were prepared in this project by varying the percentages of 5 and 8, seven of which could be cast into viable films. Copolymers 14c and 15 resulted in fragile copolymers that fragmented easily under applied stress. All copolymers displayed good thermal properties with 5% weight loss temperatures, $T_{d-5\%}$, occurring above 385 °C and most occurring above 400 °C. Glass transition temperatures, $T_g$, were all above 170 °C, with most observed above 180 °C.

Photophysical analyses of copolymers in solution determined common absorption ranging from 310 to 390 nm, indicating absorption from the chromophore units. When excited at 365 nm, broad emission peaks were observed centered at 430 nm for 11a, 460
nm for 11b-c, 470 nm for 12a, 475 nm for 12b, 455 nm for 14a-c, and 465 nm for 15. In general, copolymers with 5 showed blue-shifted emission compared to copolymers with 8, and this trend is consistent with monomer emission behavior for 5 and 8. Copolymers using the DPS/DPE backbone system, 11a-c and 12a-b, displayed blue-shifted emission when compared to TPPO/DPE copolymers, 14a-c and 15. In THF, copolymers using 8 showed enhanced emission intensities when compared to copolymers using 5, potentially due to solvent effects and/or structural effects due to increased steric demands after the polymerization.
5. FUTURE WORK

Current research has determined the difluorobenzophenone derivatives can be used as a sufficient acceptor group for blue-emitting thermally activated delayed fluorescence (TADF) chromophores. Incorporation of the 2,4- and 3,5- derivatives into poly(arylene ether) (PAE) backbone systems were successfully performed using 4,4’-diphenylsulfone (DPS) and 4,4’-dihydroxydiphenyl ether (DPE), as well as 4,4’-difluorotriphenylphosphine oxide (dFTPPO) and DPE. Polymerization into the TPPO/DPE backbone system should be optimized for 8, as the molecular weights were very low when compared to the 2,4- derivatives, 14a-c, possibly due to the separate addition of TPPO into the reaction flask. Exploration into incorporating precursor units 3 and 7 would provide a “post”-functionalization route to allow for various donor groups to be easily incorporated, theoretically.

Photophysical analyses of copolymers containing 5 and 8 resulted in interesting behavioral differences. Further study into the structural effects of geometric isomerism and the resulting steric constraints should be performed with the 2,6- derivative, model compounds of all isomers, as well as with additional polymeric materials.
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