NOVEL SMALL MOLECULES FOR DETECTION OF SENSITIVE NUCLEAR MATERIALS

by

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ABSTRACT

Plastic scintillation is a simple detection process for sensitive nuclear materials such as uranium and plutonium isotopes. The material consists of a polymer matrix, a fluorescent primary dopant and a wavelength shifter and is directly connected to a photomultiplier tube. The matrix interacts with the incident radiation and transfers the absorbed energy to the primary dopant that then transfers some of the energy to the wavelength shifter. The cascade of energy transfers determines the efficiency of detection that currently is not on par with other radiation detectors e.g. crystal scintillators or gas-filled proportional counters in terms of energy resolution and neutron sensitivity. However, plastic scintillators are inexpensive, mass producible in different shapes and forms, and safe for transportation and field deployment. The efficient detection of sensitive nuclear materials that emit gamma and fast neutrons via plastic scintillator would provide an affordable and safe alternative to the existing state-of-the-art radiation detectors. To achieve a comparable level of detection, the understanding of the fundamental radiation detection process in plastic scintillator needs to be investigated further and more thoroughly.

In this thesis, two methods were explored to achieve enhanced radiation detection versus commercial products: 1. detection of mixed radiation fields (neutron and gamma) via over-doping of fluorescent aromatic small molecules and 2. detection of thermal neutrons via incorporation of boron containing aromatic small molecules. The over-doping method led us to explore several classes of fluorescent small molecules synthetically and computationally. These molecules were $p$-terphenyl (PTP), fluorene and 2,5-diphenyloxazole (PPO) derivatives. The solubility limit of para-alkylated and meta-alkylated PTP derivatives in polyvinyltoluene (PVT) were inversely correlated with the respective melting points of the derivatives. The para-alkylated PTP derivatives precipitated from the PVT matrix around 7 wt% despite showing promising radiation detection. On the other hand, meta-alkylated PTP had solubility limits up to 20 wt% in PVT with surprisingly poor mixed radiation discrimination. The reason for their poor performance was attributed due to the softening of the plastic matrix at higher dopants concentrations. This reason was confirmed by ground state geometry calculations that showed PTP derivatives as non-planar dopants prone to vibrationally dissipate triplet state energies. Experimentally, this was proved by the near identical discrimination of PPO and one of the meta-alkylated PTP mixed radiation discrimination in poly(methyl methacrylate).

Several fluorene derivatives were synthesized via simple chemistry with good to excellent yields. Half of the derivatives were planar and the other half were non-planar. The derivatives all had different optical and physical properties that determined their radiation detection performance. In these derivatives, material impurity (< 0.2%) drastically impacted their performance. Also, the isomeric effect on the detection efficiency was explored. Similar to PTP derivatives, the inverse correlation between melting point
of derivatives and their solubility limit in PVT were observed. One of the fluorene derivatives demonstrated the second best mixed radiation discrimination reported in literature. In addition, two of the fluorene derivatives showed superior mechanical hardness when overdoped compared to corresponding PPO concentrations. Encouraged by this result, high melting point PPO derivatives were synthesized, one of which showed superior mechanical hardness compared to PPO while demonstrating comparable radiation discrimination.

The detection of thermal neutrons was explored by both commercially available, and synthesized boron containing dopants. The synthesized boron dopants were produced via both microwave and conventional heating modified Miyaura borylation conditions from multi-halo functional benzene and pyrene starting materials. Non-symmetrical boron dopants showed high solubility and better overall thermal neutron detection. $^{10}$B enriched small molecule showed similar result as commercial scintillator but it needs to be explored more. Boron containing pyrene molecules developed a deep yellow color and demonstrated poor detection efficiency.
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DEDICATION

It's with a heavy heart that I dedicate my thesis to my late aunt Senekenesh Tilahun and best friend Muhudhin Mohammed whose sheer joy in life and deep curiosity for science helped me become the person I am today. RIP.
CHAPTER 1. LITERATURE REVIEW AND RESEARCH MOTIVATION

1.1. Introduction

Radiation detection and measurement is an integral part of homeland security, power applications, medical treatment/diagnosis and academic discoveries with a few examples provided here. Homeland security mainly utilizes radiation detection for patrolling illegal trafficking of special nuclear materials (SNM) and monitoring environmental exposure. In medical applications, it’s widely used in the field of neutron therapy, x-ray imaging, and dosage and exposure management of radiation treatment for cancer patients. The applications of radiation detection in academia are vast and include the discovery of proton, elucidation of non-crystalline structures such as enzymes, colloids and polymers using small/wide-angle neutron scattering technique and gamma spectroscopy for isotopic analysis with high purity germanium (HPGe) detectors.

One of the methods to detect radiation uses scintillators. A scintillator may be defined as any material that emits fluorescence or phosphorescence light when it interacts with a high-energy particle or ionizing radiation. The light produced can often be analyzed to help identify the source and type of radiation. There are two different types of scintillators that are currently used based on the phase of their scintillator base - solid or liquid. Solid scintillators consist of inorganic or organic crystals such as sodium iodide (NaI), bismuth germanate (BGO), barium fluoride (BaF$_2$), anthracene and stilbene crystals. These crystals have high density, and efficient light collection and output. However, the difficulty to grow large area crystals, relatively high density (mass), brittleness and hygroscopic properties, together with expensive price tags makes them only useful in smaller scale applications or arrays. Solid scintillators that are affordable and easy to produce in large volumes are plastic scintillators such as poly(vinyltoluene) (PVT), polystyrene (PS), or poly(methylmethacrylate)-PMMA based scintillators doped with emissive molecules. These are mainly used as a first-line of detection to identify the existence of ionizing radiation. The second type of scintillator is liquid-based consisting of emissive dopants dissolved in organic solvents. Unlike plastic scintillators, liquid scintillators are often flammable, toxic, highly sensitive to oxidation leading to scintillation quenching, and prone to evaporation due to volatile solvents. As a result, they have to be thoroughly deoxygenated and then sealed well from ambient conditions; this is an additional cost to the manufacturing process.

Thus, plastic scintillators are a viable, inexpensive and safe alternative to crystals and liquid scintillators. Its detection mechanism generally relies on the fundamental interaction of radiation with matter; for example, photons or charged radiation interacting directly with electrons of a material and/or neutron radiation indirectly interacting via the nuclei of constituent atoms resulting in ionized electrons. The detection is reliant on non-radiative energy transfer from the polymer matrix to a primary fluorescent...
dopant and subsequent radiative energy transfer to a wavelength shifter.\textsuperscript{11-12} The emission of the wavelength shifter is matched to the most readily available photomultiplier tube (PMT) that commonly has a maximum photo-sensitivity between 400-450nm. The resulting scintillation pulse ionizes electrons at the cathode of the PMT that undergoes electron multiplication through dynodes and the output is registered as kilo-electron volt electron equivalent (KeV\textsubscript{ee}) (pulse height).\textsuperscript{13-14} It should be noted that there are other efficient PMTs based on silicon photodiodes but their utilization in plastic scintillators is currently less common.

The manufacturing of inexpensive, stable, efficient, and large scale radiation detectors is crucial to control nuclear threats at international borders, ports of entry and airports.\textsuperscript{15} In the literature, plastic scintillators as a first line of detection for gamma and neutron radiation is reported, but there is a lack of emphasis on novel synthetic efforts to minimize cost and improve current technologies. Few examples are listed below to give the reader an idea of the state of the art. Existing reviews on plastic scintillators could help the reader understand the subject matter better.\textsuperscript{16-17}

1.2. Commonly Used Polymer Matrices and Fluorescent Dopants

Plastic scintillators utilize inexpensive, readily available and easily fabricated polymers for initial moderation and absorption of radiation. The optical transparency of plastic scintillators is crucial to reduce reabsorption of emitted light and increase the collection of light. Figure 1.1 provides chemical structures for commonly used polymer scintillation matrices. Note that relative to other matrices, PMMA lacks an aromatic chromophore in its polymer backbone but has the lowest refractive index aiding its light transmission properties. As a result, plastic scintillators made out of PMMA require incorporation of UV absorbing additives such as naphthalene. This usually leads to less efficient scintillating properties that are susceptible to radiation damage and environmental exposure.\textsuperscript{16} Poly(dimethylsiloxane-co-diphenylsiloxane) derivatives, commonly known as silicone rubber, are the most robust plastic matrices capable of withstanding high radiation exposure. Despite this characteristic, silicone rubber is rarely used as a plastic base because 1) it is an elastomer allowing additives to migrate and aggregate which eventually leads to quenching of emitted light, 2) its elasticity inhibits manufacturing of different sizes, shapes and forms of plastic scintillators.\textsuperscript{18-19} On the other hand, polycarbonate is a hard thermoplastic that easily degrades in UV light causing it to yellow and compromise its scintillation efficiency. The most commonly used matrices are PS and PVT due to their relative ease of fabrication, compatibility range with dopants and high scintillating efficiencies relative to other inexpensive matrices.\textsuperscript{20}
Figure 1.1 Common polymer matrices used in plastic scintillators.

There has been only a few literature reports targeting better performing polymer matrices. Few exceptions are the synthesis of poly(pentafluorostyrene) as a high density thermoplastic for fast neutron detection \(^{21}\), polyimide derivative thin films targeting improved hardness and radiation resistance \(^{22-23}\) and poly(benzylMMA-co-MMA) to reduce quenching of light by excimer trapping.\(^{24}\) It’s important to note that a $1/g plastic scintillator is the targeted price set by Department of Defense and the modification of current polymer matrices or discovery of new matrices should consider this constraint. There is a good review on conjugated polymers used for radiation detection, but the cost of these materials will unlikely meet the constraints listed above.\(^ {25}\)

1.2.1. The Making of Plastic Scintillators

Commercially, plastic scintillators are fabricated via bulk thermal polymerization, injection molding or extrusion. For small scale set ups, cell casting is preferred because of simplicity and affordability of materials. It’s highly recommended to avoid the use of azobisisobutyronitrile (AIBN) or benzoyl peroxide as radical initiators as they may result in yellowing of final scintillator due to unquenched radicals interacting with ambient oxygen.\(^ {26}\) This has been reported in the case of both PS and PVT based scintillators. A uniquely different approach to prepare plastic scintillators is photopolymerization that uses UV or even visible light to initiate polymerization.\(^ {27}\) The usual recipe consists of a photosensitizer that breaks down into a radical upon UV/visible light exposure, then the radical initiates a photoinitiator that later initiates the monomer. Thereafter, the initiated monomer carries on the propagation. In some cases, an
organic base and a cross-linker may be used to fully cure the initiated monomer. Photopolymerization has the advantage of curing a small-scale plastic within hours as demonstrated for scintillation application.

1.2.2. Commonly Used Fluorescent Dopants

The most commonly used primary fluorescent dopants in plastic scintillators are 2,5-diphenyloxazole (PPO), \( p \)-terphenyl (PTP) and naphthene (Figure 1.2). PPO is superior compared to the other dopants due to its high photoluminescence quantum efficiency (PLQE), high solubility in common polymer matrices, short emissive lifetime (<10 ns) and optical overlap with PVT/PS (emission of PVT/PS overlaps with absorption of PPO). The wavelength shifters (Figure 1.3) are mainly selected based on their high PLQE, short emissive lifetime, absorption overlap with the emission of primary dopants to ensure maximum radiative energy transfer (Figure 1.4) and emission within the photosensitivity of blue PMT.

![Napathalene](image1)

![2,5-diphenyloxazole](image2)

Napathalene

\( p \)-terphenyl

2,5-diphenyloxazole

Figure 1.2 Typical primary dopants used in plastic scintillators.

![POPOP](image3)

![Trans-4,4'-diphenylstilbene](image4)

POPOP

Trans-4,4'-diphenylstilbene

Figure 1.3 Typical wavelength shifters used in plastic scintillators.
1.3. Synthetic Efforts to Maximize Output of Plastic Scintillators

As described earlier, there have been very few examples of newly developed dopants for plastic scintillators. The dopants in Figure 2&3 have been used since 1950’s and there seems to be little to no reports in literature geared towards the synthesis of alternative dopants for higher efficiency plastic scintillators. One promising example was reported by Park and coworkers. They synthesized a quantum dot (Q-dot) to replace the commonly used wavelength shifters, tested its optical overlap with PPO and compatibility in PS. The Q-dot had an outer shell of ZnS and inner core of CdSe. The fluorescence of the Q-dot was hypothesized to be dependent on the size of the dots which can be useful to shift the emission peak to a suitable PMT (not just blue sensitive PMTs). However, due to poor optical overlap between PPO and the Q-dot and unmatched Q-dot emission well outside of blue PMT, the final scintillation properties were very low and there were two final luminescence peaks (PPO and Q-dot) indicative of incomplete radiative energy transfer. The PLQE of the Q-dot was not reported and different sizes of Q-dots were not prepared in order to validate their hypothesis. Another example was the use of an iridium (III) complex doped in biocompatible polymer dots for x-ray detection. The detection mechanism is similar to plastic scintillators and utilizing a high-Z atom (Ir) enhances the probability of x-ray interaction with the detector. This will be thoroughly discussed in section 1.3.1.

Aminabhavi et al. have done a study on the efficiency of energy transfer processes between a primary (Exalite 416) and a wavelength shifter (Coumarin 515) in PS solutions. In the study, the concentration of Exalite 416 was kept constant and the amount of Coumarin 515 was varied. They have shown that by exciting the mixture at the excitation wavelength of Exalite 416, the combined fluorescence appeared to look more like a pure Coumarin 515 fluorescence as its concentration increased. This was
attributed to complete dipole-dipole resonance energy transfer from Exalite 416 to Coumarin 515. This is a good example of how a primary dopant is matched to a wavelength shifter for efficient radiative energy transfer. Similar studies have come to the same conclusion. These early studies show the importance of concentration and energy transfer from host (primary) to dopant (wavelength shifter) in related systems. The overlap of primary dopant photoemission and photoabsorption of wavelength shifter is crucial for complete radiative energy transfer.

A more recent study focused on copolymerizing 1,8-naphthalimide derivatives with vinyltoluene, styrene and methacrylate. It was proposed that incorporating a fluorescent dopant into the backbone of polymer matrices could increase the non-radiative energy transfer from the matrix to the dopant since the energy transfer is highly dependent on the distance between the matrix and the dopant (Equation 1.1). Despite the proposed increase in non-radiative energy transfer, the study didn’t report the effect of copolymerization of dopants has to the final light output and hardness of the plastic scintillators. In addition, the study reported that 1.0% of the synthesized monomers did not show pulse shape discrimination which was to be expected due to insufficient delayed energy (see section 1.3.3). Similar studies with more emphasis on immobilization of PPO derivatives in polystyrene matrix were conducted. The studies showed that incorporation of fluorescent dopants led to superior mechanical strength but the shortcomings were decreased light output and lower solubility.

\[
\text{Efficiency of FRET transfer} = \frac{1}{\tau_d \left( \frac{R_0}{R} \right)^6}
\]  

(1.1)

Equation 1.1 Dependence of non-radiative energy transfer on distance and lifetime of donor. \( \tau_d \) is the lifetime of donor (PVT), \( R_0 \) is the critical transfer distance where radiative deactivation and non-radiative transfer occur equally. \( R \) is the distance between the donor and acceptor (primary dopant). FRET stands for Förster Resonance Energy Transfer which is the non-radiative energy transfer from the matrix to the primary dopant.

1.3.1. Detection of Gamma Radiation by Plastic Scintillators

Any radiation that is capable of directly ionizing an electron while interacting with a material is simply known as ionizing radiation. Some examples of ionizing radiation are alpha particles, protons and gamma radiation. The scope of this section will be limited to gamma radiation. Gamma radiation originates from radionuclide decay of unstable isotopes such as \(^{232}\text{Th}, {^{137}\text{Cs}}\) and \(^{60}\text{Co}\). Depending on the energy of the gamma radiation and electron density of a material, the result of a gamma ray interaction with the material could vary. If the material doesn’t have high Z atoms, the gamma radiation will scatter at various angles off electrons losing small fractions of energy along the way. This interaction is called Compton scattering. In the presence of high Z atoms, a gamma ray could lose all its energy while ejecting an electron.
(photoelectric absorption), giving rise to a characteristic photopeak equal to the energy of the incident gamma. In the case of a gamma ray with energy higher than 1.023MeV, it can produce an electron-positron pair as a result of pair production.  

Plastic scintillators commonly detect gamma radiation via Compton scattering. The reason for this is the lack of high Z atoms in plastic scintillators that are mainly composed of carbon and hydrogen (effective nuclear charge, \(Z_{\text{eff}}<10\)). Increasing the \(Z_{\text{eff}}\) increases the probability of interaction with gamma radiation and induces a photopeak as a result of photoelectric absorption. A high-density material also enhances the stopping power of the medium in which the radiation is traveling. Stopping power of a particle in a medium is a function of its charge and mass as well as the electron density of the medium. For instance, the stopping powder of gamma radiation is higher in concrete than plastic due to the electron density difference between the two materials.

Recently, a Lawrence Livermore National Lab group reported a commercially available organobismuth compound loaded into plastic scintillators. For instance, triphenylbismuth (BiPh\(_3\)) was shown to be compatible with poly(vinylcarbazole) and 9,10-diphenylanthracene (DPA) as the wavelength shifter. The relative gamma light yield was very low due to static fluorescence quenching and unoptimized light emission. In addition, due to BiPh\(_3\), the final plastic had a deep yellow color that explains the low efficiency with a blue sensitive PMT. Up to 40% BiPh\(_3\) by weight was mixed in PVK, increasing the \(Z_{\text{eff}}\) of the plastic by nearly six-fold. It’s doubtful that inclusion of 40% dopant in a polymer matrix will lead to ‘excellent’ mechanical strength and optical clarity. A complete characterization of BiPh\(_3\) doped plastic scintillators over a wide range of gamma energies was described by Boatner and coworkers. The authors noted that the use of Ir-complex increased the light output compared to the use of traditional wavelength shifter DPA. However, DPA has the advantage of nearly 90-fold shorter emission lifetime that makes it more practical for border patrolling applications.

A similar system with standard plastic formulation (PS as a matrix) incorporating tricarboxylate and triaryl bismuth compounds was reported by Hammel and coworkers with maximum loadings up to 17% Bi by weight. This study only focused on low-energy gamma radiation. A complete characterization over a wide range of gamma energies might be useful due to radiation dose dependence of polystyrene discoloration.

The most recent Bi-loaded plastic scintillator utilizes bismuth tripivalate (contains 40.8% Bi). The standard PVT as a matrix, 2% PPO as a primary dopant and 0.1% DPA as a wavelength shifter were used. Up to 70% Bi-tripivalate was incorporated into the plastic. The mechanical strength of such high dopant loaded plastic is expected to be soft due to incomplete termination of propagating radicals. Varying the concentration of bismuth in the plastic didn’t alter the optical transparency of the samples, however; as the concentration increased, the samples became noticeably colored. Despite the optical clarity of the samples,
the light yield decreased significantly as the amount of Bi-tripivalate was increased. This quenching was attributed to increased triplet excitons that are not being exploited in this system. It’s not clear why a triplet harvesting metal complex was not used in this study to compare it to the previous system. In all of these studies, the aging effect of high Bi loaded plastics after irradiation of samples is not reported. This would be an important parameter to predict its longevity.

Lead is another high Z metal that is commercially available up to 5% loadings in plastic scintillators with Eljen Technologies (EJ-256) and Saint Gobain Crystals (BC-452). Recently, there has been very few Pb dopants reported for detection of ionizing radiation. Lead methacrylate was recently reported as a dopant used for low dose x-ray detection in plastic scintillators.46

In addition to bismuth and lead, high Z containing additives are not frequently reported in the literature for gamma spectroscopy. This is due to fluorescence quenching and optical clouding of scintillators leading to significant light output decrease. To get around this problem, gadolinium was incorporated in a nanocrystal capped by non-polar groups for dispersion in PVT by Pei and coworkers.47 They went further by attaching a copolymerizable substituent on the nanocrystals that enabled loading up to 40% gadolinium oxide nanocrystals in PVT. The incorporation of a high-density nanocrystal in PVT increases the stopping power of the medium, and the presence of a high Z atom increases interaction with gamma radiation. One of the composites (31% nanocrystal) had excellent optical and mechanical properties and demonstrated a photoelectric peak with 11.4% energy resolution. It would have been interesting if they had tested the response of their composites to thermal neutrons. The reason for this suggestion will become clear after section 1.3.2. As the low cost of scintillators is a huge incentive, it also would have been useful to compare the cost of preparing such a hybrid plastic scintillator to a commercially available crystal or plastic scintillator used for gamma spectroscopy.

It's noteworthy that the high-Z dopants reported in the literature are commercially available. The lack of synthetic modification of these dopants to decrease static quenching, increase solubility and improve mechanical properties is apparent. In recent years, multiple examples on the synthesis of bismuth aryl compounds have been reported,48 however their utilization in practice is non-existent to our knowledge.

1.3.2. Neutron Radiation Detection by Plastic Scintillators

Neutron radiation is produced from very specific sources. It is encountered in nuclear reactors, small scale or national laboratory neutron sources, medical physics and nuclear weapons (SNM). Despite its widespread use, detecting neutron radiation is more difficult than photons and charged ionizing radiation. Its lack of charge and weak magnetic dipole moment enables it to go through materials without interacting via Coulombic forces. As a result, a neutron transfers its energy via scattering off the nucleus in which the recoiled nucleus behaves like a high-energy charged particle and loses its energy to the material via Coulombic interaction. Because a neutron has similar mass to a hydrogen nucleus, it could elastically
bounce off small Z atoms such as hydrogen or helium nuclei while losing a significant portion of its energy. This is the main mechanism used to slow down a high-energy neutron (slowed down neutrons are commonly referred as ‘thermalized neutrons’). A thermal neutron could also induce a fission reaction when it interacts with a fissile nuclide such as $^{233/235/239}$U, $^{233}$Th and $^{239/241}$Pu. This reaction is mainly used for nuclear power and weapons production. Lastly, absorption of a thermal neutron by a material may lead to a release of gamma rays (radiative capture) and a release of positively charged particles such as protons or alpha particles. This is the main mechanism by which thermal neutrons are detected.

Materials capable of detecting neutrons should have two characteristics in order to be ideal for use as neutron detectors. They must contain a lighter element to slow down fast neutrons and an isotope with a high neutron absorption cross section to capture the thermalized neutrons. State of the art thermal neutron detectors use $^3$He gas because it has a high neutron cross-section value of 5333 Barns (1 Barn is equivalent to 100fm$^2$). When the $^3$He filled detectors (termed proportional counters) are exposed to thermal neutrons they release protons and triton charged particles (Table 3). Because this reaction is exothermic (a positive Q-energy value), the released charged particles can ionize atoms in a gas causing the release of electrons that can be collected by applying an external voltage. The collected electrons are ‘counted’ and the equivalent electron energy (in units of kilo-electronVolt electron equivalent-keV$_{ee}$) is reported that is proportional to the incident neutron energy. However, $^3$He (0.000137% of natural helium) is scarce and has become prohibitively expensive so not a good candidate going forward to meet the growing demands due to concerns of proliferation of nuclear materials. As a result, there is a widespread effort in academia and industry to replace $^3$He gas towards lower cost and high neutron cross-section elements such as those shown in Table 3. The main goal here is to find high neutron cross-section materials that can be formulated into stable plastic scintillators.

One such element is lithium, of which the $^6$Li isotope (7.6% natural abundance) has a relatively high neutron cross-section value of 940 Barns. Lithium dopants are based on hydrophilic organic salts that are difficult to blend into hydrophobic plastic scintillator formulations. This undesirable property typically leads to clouding of plastic scintillators due to water absorption, and subsequent decline of scintillation output. However, there have been few examples of lithium dopants successfully incorporated in basic plastic formulations (Table 1). Lithium pivalate and methacrylate, for example have shown compatibility with PVT and PS at loadings up to 0.14 and 0.63% $^6$Li respectively. Although Breukers et al have managed to put the most $^6$Li (0.63%) in a plastic scintillator by copolymerizing lithium methacrylate with styrene, they didn’t test their product with a neutron source. It’s possible that they have run these experiments but have chosen not to disclose their results, which seems to be a common practice in this field. $^6$Li enriched salicylate offered a better potential material as a thermal neutron capture dopant in poly(2-vinylnaphthalene) composite films, but the composite had minimal transparency that quenched the light
yield as well as thermal neutron capture signal. The best thermal neutron capture was shown by $^6\text{Li}$ pivalate doped in PVT with a neutron capture peak at 400keVee. The decline of scintillation overtime (aging effects) is not reported.

Table 1.1 Commonly used isotopes for thermal neutron detection and their properties.

<table>
<thead>
<tr>
<th>Isotopes used for neutron capture</th>
<th>Isotopic Abundance (%)</th>
<th>Cross section (Barns)</th>
<th>Absorption product(s)</th>
<th>Examples of use</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\text{He}$</td>
<td>0.000137</td>
<td>5333</td>
<td>$^3\text{H} + p + Q$ $Q=0.764$ MeV</td>
<td>Proportional gas chamber</td>
</tr>
<tr>
<td>$^6\text{Li}$</td>
<td>7.59</td>
<td>940</td>
<td>$^3\text{H} + \alpha + Q$ $Q=4.78$ MeV</td>
<td>Li(OCOCH$_3$) Li-3-PSA Li(OCCCH$_2$CH$_3$)</td>
</tr>
<tr>
<td>$^{10}\text{B}$</td>
<td>19.9</td>
<td>3835</td>
<td>$^7\text{Li} + \alpha + \gamma$(0.48MeV) + Q $Q=5.10$ MeV</td>
<td>BF$_3$, B(OCH$_3$)$_3$ m-Carborane</td>
</tr>
<tr>
<td>$^{155}\text{Gd}$</td>
<td>14.80</td>
<td>61100</td>
<td>$^{156}\text{Gd}^{*}$$\rightarrow^{158}\text{Gd} + \gamma + \text{CE} + Q$ $Q=8.54$ MeV</td>
<td>GdOOCCH$_2$COPh Gd(I-OPr)$_3$ Gd(NO$_3$)$_3$(TBP)$_3$</td>
</tr>
<tr>
<td>$^{157}\text{Gd}$</td>
<td>15.65</td>
<td>259000</td>
<td>$^{158}\text{Gd}^{*}$$\rightarrow^{158}\text{Gd} + \gamma + \text{CE} + Q$ $Q=7.94$ MeV</td>
<td>GdOOC(CH$_2$)$_2$Ph</td>
</tr>
</tbody>
</table>

*Represents excited nuclei. CE is conversion electrons, which are monoenergetic electrons. Li(OCOCH=CH$_2$) is lithium methacrylate. Li-3-PSA is Li-salt of 3-phenylsalicylic acid. Li(OCOC(CH$_3$)$_3$) is lithium pivalate. B(OCH$_3$)$_3$ is trimethoxyborate. B$_2$Pin$_2$ is bis(pinacolato) diboron, 124TrBB is 1,2,4-triborylated benzene. GdOOCCH$_2$COPh is gadolinium benzyol acetate, Gd(OiPr)$_3$ is gadolinium(III) isopropoxide, Gd(NO$_3$)$_3$(TBP)$_3$ is gadolinium trinitrate tributylphosphate, GdOOC(CH$_2$)$_2$Ph is gadolinium phenylpropionate.

$^{10}\text{B}$ has a higher neutron absorption cross-section (3835 Barns) and natural abundance (19.9%) than lithium and is more compatible with plastic scintillator formulations. The boron dopant most reported in literature and commercially sold is m-carborane, icosahedral clusters of boron (~75%), carbon and hydrogen (Figure 1.5). Simulation results from Zaitseva’s group (Lawrence Livermore National Lab) has shown that 0.74% $^{10}\text{B}$ (equivalent to 3.7% natural boron) in a 1cm thick plastic scintillator can capture 84% of thermal neutrons. However, increasing the amount of boron in plastics compromises the light output, mechanical strength and lifetime of the final product. Furthermore, m-carborane is very expensive (1g/$84 Alfa-Aesar). We have shown that synthesizing small molecules via slightly modified Miyuara borylation conditions could substitute the expensive m-carborane. Please refer to chapter 5 for detailed synthesis and discussion of these boron containing small molecules that includes enriched $^{10}\text{B}$ molecule.
Gadolinium isotopes have the highest neutron absorption cross-section (Table 1.1). Despite its higher natural abundances, Gd containing additives for plastic scintillations are rare. Figure 1.6 shows three Gd additives and their light output decline over an increase in concentration. Therefore, it’s evident that Gd additives drastically change the light output of plastic scintillators. It is also reported in the literature that increasing the concentration of thermal neutron sensitive additives decreases the optical clarity and efficiency of plastic scintillators. Thus, there is a need for better design and synthesis of Gd ligands that inhibit aggregation and minimize fluorescence quenching. Other studies have explored different ligands demonstrating promising results.\textsuperscript{53,54} Note that there is a lack of standard amount of primary and wavelength shifters in literature reports when thermal neutron additives are used. As a result, the reader should be careful in directly comparing Gd loaded plastic scintillators in Figure 1.6.
1.3.3. Identifying Mixed Radiation by Pulse Shape Discrimination

The types of radiation encountered in the field is a mix of different types of radiation, for example, neutron and gamma radiation. The difference in ionizing energies of neutron and gamma radiation leads to different concentrations of singlet and triplet excited states in plastic scintillators. The de-excitation of single states exponentially decays via prompt fluorescence on the order of nanoseconds, whereas direct de-excitation of triplet states is practically quenched via non-exponential radiationless processes. In the case of liquid and crystal scintillators, triplet excitons migrate and collide with other triplet excitons to give rise to triplet-triplet annihilation. This produces a de-excited singlet state and a ground singlet state. The de-excited single state is quenched via delayed fluorescence (Q\text{tail}) with the same spectral shape as the prompt fluorescence but at a longer decay time on the order of microseconds. Because neutron radiation has higher ionizing energy than gamma, the relative intensity of delayed fluorescence compared to total light collected (Q\text{total}) is higher compared to gamma radiation. This is used as the basis for a powerful technique called pulse shape discrimination (PSD). The separation between gamma and neutron peaks is evaluated by a figure-of-merit (FOM), which is a mathematical equation of the distance between the centroids divided by the sum of the width at half-maximum of neutron and gamma peaks.

Liquid and crystal scintillators have been widely used to achieve PSD. The reason for this is due to two opposing reasons. In the case of liquid crystals, the chromophores are dissolved inside a mobile phase that makes migration of triplet-excited state electrons easier and hence more accessible for collision and subsequent annihilation, which is the basis of PSD. On the other hand, the close proximity and rigidity of crystals allows triplet-triplet annihilation to happen efficiently. On the contrary, plastic scintillators are typically not capable of discriminating the pulse difference between neutrons and gamma radiation. However, there have been recent literature reports exhibiting PSD in plastic scintillators. The reports employ two methods to induce PSD: over-doping primary dopants and ligand-to-metal charge-transfer (MLCT). The over-doping method was first reported by Zaitseva et al. By varying the concentration of PPO (primary dopant) up to 30% in PVT matrix, the signal difference between neutron and gamma radiation widened as the concentration of PPO increased, as shown in Figure 5. The rise in PSD with higher PPO loading is attributed to increased density and migration of triplet excited states that in turn increases the likelihood of triplet-triplet annihilation. However, the light output of these samples was 20% relative to liquid scintillators due to concentration fluorescence quenching. The low light output was improved by 3.5-fold by incorporating 0.2% DPA to the PPO-PVT mix. The addition of DPA as the wavelength shifter didn’t cause statistical change of the FOM (1.27-3.31) for the various PPO loadings.

The mechanical integrity of a plastic scintillator with 30% PPO is compromised and this could hinder its potential field deployment. Another report using the over-doping method used unspecified amount of m-terphenyl in PMMA. Pei et al recently synthesized a copolymerizable derivative of
diphenylanthracene and explored its PSD efficiency. Even though the PSD or light output wasn’t on par with corresponding concentrations of PPO, it demonstrated that synthesis could play a crucial part in designing alternative plastic scintillators based on new or improved emissive dopants.

Despite the success of PPO for PSD application in plastics, there have not been similar reports in literature with other readily available primary dopants such as p-terphenyl, stilbene, anthracene and naphthalene. The difficulty of incorporating high loadings of these dopants in PVT or PS polymer is due to solubility issues. It’s believed that attaching solubilizing groups on these dopants could enhance their solubility in the commonly used matrices such as PVT, PS and PMMA. This is explored in detail in Chapter 2. An effective primary dopant would be highly soluble in these matrices without compromising their mechanical integrity.

1.3.4. Identifying Mixed Radiation by Spectral Shape Discrimination

The second method of PSD in plastic scintillators is demonstrated by incorporating luminescent metal-ligand dopants. Metal-ligand dopants harvest triplet excited states via spin-orbit coupling that traditionally are quenched by complex non-radiative processes. The utilization of triplet excited state electrons in plastic scintillators drastically increases the theoretical maximum light yield by three-fold. Such enhancement in light yield has been extensively reported for electroluminescence in Organic Light Emitting Diodes (OLED) and demonstrated for plastic scintillators, for the first time, by Doty and coworkers. Synthesized Ir-complexes were used with various tunable ligands as metal-ligand charge transfer (MLCT) dopants, Coumarin 540 A as a wavelength shifter and PS as the polymer matrix. Tunable ligands around metal ions have been shown to change the lifetime and emission wavelength of the triplet excited states. Figure 1.8 shows the two Ir-complexes used in the study. Note that triplet-harvesting plastic scintillators
employ spectral shape discrimination as opposed to pulse shape discrimination. The difference in mechanism lies in the energy transfer of triplet excited states of iridium to the metal dopant instead of triplet-triplet annihilation. The intensity of the MLCT and prompt fluorescence is counted relative to the respective energy deposition of neutron and gamma radiation. Note that neutrons, by the virtue of their recoil nucleus interaction, produce higher population of triplet electrons than gamma rays. Therefore, as expected, the intensity ratio of delayed fluorescence from the MLCT over the total scintillation will be higher as shown in Figure 1.9.

Figure 1.8 Chemical structures of the Ir(ppy)$_2$(acac) (left) and Ir(ppy-F$_2$)$_2$ (right) dopants. Figure and description taken from reference #59.

Figure 1.9 Spectral shape discrimination with Iridium complex. Graph taken from reference #59.
The advantages of MLCT over the over-doping method is minimal use of metal complexes (<0.5%), simple reaction routes, high yield synthesis and higher mechanical strength of final plastic scintillator. The disadvantages are expensive metal complexes, longer decay times leading to slower response and incompatibility with blue sensitive PMTs due to emission of the Ir complexes being in the sky blue to red range. However, these disadvantages could be improved upon as this area is very new with many options to consider.

1.4. Overview of Dissertation

Radiation detection has had a significant impact in our society over the last few decades. The applications of radiation detection range from energy sustainability via nuclear power plants to medical treatments and diagnosis to protection of the nation’s boundary from nuclear proliferation. Scintillators are the simplest form of radiation detection in which a signal of light is emitted due to interaction of ionizing radiation with a fluorescent organic, hybrid or inorganic molecule. The use of inexpensive and readily available organic molecules incorporated in equally inexpensive polymer matrices have led to the development of plastic scintillators as a form of first line of detection. Over time, plastic scintillators have evolved to serve as a probe to detect neutrons, gamma radiation and discriminate the signals between the two. The incorporation of high Z atoms in plastics have increased the probability of gamma radiation interaction and, has led to the observation of photo peaks via photoelectric absorption. On the other hand, incorporation of high neutron cross section isotopes has made the detection of thermal neutrons possible, which will eventually replace the rare and very expensive \(^{3}\)He gas proportional counters. Further progress has made it possible to discriminate the signals of neutrons from a gamma radiation background, termed pulse shape discrimination. This marks the latest progress of plastic scintillators.

The steady progress of plastic scintillators has increased their functionality but there is still plenty of research to be done. This is especially true in finding synthetic routes to lower the cost of thermal neutron detecting dopants such as m-carboranes, inexpensive high Z dopants for gamma spectroscopy and availability of multiple primary dopants for PSD other than PPO. All this could be possible with further involvement of synthetic chemists in this interdisciplinary field.

In chapter 2, various alkylated \(p\)-terphenyl derivatives are synthesized to evaluate the correlation between the physical properties of these derivatives (such as melting point, solubility limit in PVT and \(\pi-\pi\) stacking) and performance in a mixed radiation sources. The geometrical shapes and excited state energies of the dopants were compared with PPO to gain insight into the elusive mechanism of PSD. These insights were further explored in chapter 3. The mechanical stability of scintillators made from these dopants was also measured to gain an understanding for the softening of plastic scintillators as high concentration of dopants is incorporated. Although Henok A Yemam was the first author on this chapter, various people contributed to this chapter.
Chapter 3 deals with fluorene derivatives as dopants for use in PSD applications. The fluorene derivatives were synthesized from low cost starting materials in high yields using simple chemistry. The photophysical and thermal properties were investigated for their influence on radiation sensitivity/detection performance, and mechanical stability. Select fluorene derivatives produced scintillator samples whose mechanical properties exceeded those of the commercial PPO based scintillators while producing acceptable PSD capabilities. The physical properties of the synthesized dopants were also investigated to examine their effect on the samples. Planar derivatives of fluorene were found to be highly soluble in PVT matrices with little to no aggregation induced effects. The excited state energies (both singlet and triplet) were used to explain the discrimination performance and provide more evidence to the two alternative theorems introduced earlier in chapter 2.

In chapter 4, a different synthetic approach was taken to further investigate the superior mixed radiation discrimination performance of PPO. One of the synthetic approaches intended to change the thermal properties and geometrical shapes of PPO while keeping the optical properties the same. Another approach slightly changed the optical properties while varying the other properties. A third approach changed all the properties by immobilizing PPO on a 3-dimensional inorganic core. The radiation performance is compared to PPO. In some cases, the mechanical stability of the final plastic scintillator doped with PPO derivatives were found to be more enhanced over the corresponding PPO plastic scintillators at the same concentration. The results from this study provide methods to improve mechanical hardness of PSD capable plastic scintillators.

The last chapter, chapter 5, deals with a topic that wasn’t discussed in the previous three chapters. However, this chapter deals with decades old scintillation problem: replacing \(^{3}\)He gas-filled proportional detectors for detection of thermal neutron. Recent literature advances in this area has been thoroughly discussed. The lack of synthetic efforts to prepare better dopants containing high neutron cross section isotopes such as \(^{10}\)B, \(^{6}\)Li and \(^{155}/^{157}\)Gd was highlighted. The ease of preparation and purification have led us to synthesize small molecules containing boron up to 10 %wt. Their thermal neutron detection efficiency was compared with increase \(^{10}\)B content in the plastic and, the effect it had on light output and FoM in case of over-doped PPO samples. Contrary to what was observed for PSD dopants in chapter 2-4, non-symmetrical boron dopants had higher solubility limits and hence better thermal neutron detection. As a proof of concept, \(^{10}\)B enriched aromatic compounds were synthesized, doped in a plastic scintillator and their thermal neutron detection efficiency compared to other boron containing small molecules. Adam Mahl polished and tested plastic samples.
1.5. Thesis Organization

Chapter 1 was the only chapter solely authored by Henok A Yemam. The rest of the chapters required inputs from colleagues and collaborators. In chapter 2, Adam Mahl helped with making plastic samples, polished and analyzed all the samples with radiation sources. Dr. Jonathan Tinkham calculated the excited states energies, Joshua T. Koube calculated the ground state geometries, professor Uwe Greife and Alan Sellinger supervised and supplied the starting ideas. In chapter 3, Adam Mahl helped with making plastic samples, polished and analyzed all the samples with radiation sources, Dr. Jonathan Tinkham calculated the excited states energies, Joshua T. koubek calculated the ground state geometries, professor Uwe Greife and Alan Sellinger supervised and supplied the starting ideas. Chapter 2 and Chapter 3 were just accepted for publication (April 2017) by Chemistry-A European Journal (DOI: 10.1002/chem.201700877).

In chapter 4, Adam Mahl helped with making plastic samples, polished and analyzed all the samples with radiation sources. Joshua T. koubek calculated the ground state geometries, professor Uwe Greife and Alan Sellinger supervised and supplied the starting ideas.

Chapter 5 is a collection of two published articles and soon to be submitted article. These were outlined as ‘the three approaches’ in the chapter. The first approach or published article is published by Nuclear Instruments and Methods in Physics Research Section A; Accelerators, Spectrometers, Detectors and Associated Equipment (http://doi.org/10.1016/j.nima.2016.01.073). In this article, Adam Mahl helped with making the samples, polished them all and characterized their radiation performance. The second approach or published article is published by Scientific Reports (doi: 10.1038/srep13401). In this article, Dr. Unsal Koldemir provided initial experimental conditions and made TBP crystals. Dr. Sean Parkin analyzed TBP crystal using XRD, Tyler Remedes polished some samples and took pictures of samples, professor Uwe Greife and Alan Sellinger supervised and supplied the starting ideas. In the last approach or soon to be submitted article, Joshua T. Koubek calculated the ground state geometries and scaled up MBB synthesis, Dr. Roshan Fernando provided the experimental conditions and proof of concept synthesis for MBB.
CHAPTER 2. HIGHLY SOLUBLE $P$-TERPHENYL AS EFFICIENT DOPANTS IN PLASTIC SCINTILLATORS FOR SENSITIVE NUCLEAR MATERIAL DETECTION

Slightly modified from submitted manuscript to Chemistry - A European Journal (accepted Apr. 2017)

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2.1. Introduction

Special Nuclear Materials (SNM), such as $^{233/235}$U and $^{239}$Pu, are radioactive isotopes classified as specific nuclear materials that could potentially be used in atomic bombs or related ‘dirty’ explosives (Title I of the Atomic Energy Act of 1954). The potential danger of these isotopes in significant quantities makes them strictly regulated and controlled substances throughout the world. Therefore, it would be beneficial if the domestic and international borders, ports of entry, and airports around the world were equipped with radiation detectors to deter possible illicit trafficking of SNM. The current sparsely deployed detectors use a combination of thermalizing plastic scintillators and $^3$He gas proportional chambers for identification of SNM. The widespread application of these combined detector systems has become prohibitive due to the increasing cost of $^3$He gas. As a result, new plastic scintillators are being investigated as a first-line of detectors for ionizing radiation (i.e. gamma and neutron) due to their low-cost, mass reproducibility, ease of handling and installation. Despite these qualities, the current base formulations are not inherently capable of differentiating the signals of neutron and gamma radiation. This property is critical as sources of gamma radiation are significantly more common when compared to neutron radiation; the latter being a key indicator of SNM. Being able to differentiate the two signals will help identify SNM from naturally occurring radioactive materials (NORM) or medical isotopes such as $^{230}$Th and $^{57}$Co.\textsuperscript{62}

The working principle of plastic scintillators is the absorption of incoming radiation by an inexpensive polymer matrix [e.g. poly(vinyltoluene) (PVT)] followed by the subsequent cascade of energy transfers to a primary fluorescent dopant and an optional wavelength shifter. Then finally the emitted photons are collected by a photodetector such as a photomultiplier tube (PMT) or photodiode.\textsuperscript{14, 16} A pulse is generated that is proportional to the type and energy of the incident radiation. In recent years, research groups have begun investigating and describing methods to enhance the sensitivity of plastic scintillators for distinguishing fast neutron signals from background radiation. A simple, reproducible method has emerged by introducing an increased amount of highly soluble, fluorescent primary dopant (over-doping) into a standard plastic scintillator formulation to induce interactions that allow for pulse shape discrimination (PSD) analysis.\textsuperscript{56} PSD analysis makes use of the slight difference in decay signatures between signals induced by different types of incident radiation. Gamma radiation, converted to electrons in the plastic, inherently deposits less energy over the same distance relative to neutron radiation that
produces proton recoils.\textsuperscript{63} As a result, neutrons scattering through the plastic will result in higher atomic excitation density distributed in singlet and triplet excited states.\textsuperscript{13} The singlet state electrons decay promptly via fluorescence whereas the triplet state, that is populated at a higher ratio through the protons, decays via phosphorescence: a quantum-mechanically forbidden transition that results in different emission wavelength with a much longer decay signature. However, another interaction can occur when excited triplet states are allowed to interact with each other. These triplet states can combine into a higher triplet state, or annihilate (referred to as triplet-triplet annihilation (TTA)).\textsuperscript{64} The resulting singlet states from this process then decay via fluorescence, but on a longer time scale (delayed fluorescence) due to the nature of the interaction. The signals of the collected wave forms can be differentiated by how much of the collected light was generated by delayed fluorescence, thus discriminating neutron from gamma signals.

At lower primary dopant concentrations (<5.0 wt%), the signals from neutron and gamma radiation appear identical (due to the lack of any significant delayed fluorescence) and hence identifying the incident radiation is not possible without employing more complex and expensive inorganic solid state detectors (such as NaI, HPGe, CsI, BaF\textsubscript{2}).\textsuperscript{65} However, when samples were produced that contained highly soluble primary dopants that were admixed at >10.0 wt% concentration, the resulting spectra were found to allow for meaningful PSD analysis. Currently, the accepted theory for PSD capabilities at higher primary dopants concentrations is that the migration and annihilation of first excited triplet states increases, that leads to increased delayed fluorescence (Scheme 2.1).\textsuperscript{66} To our knowledge, only PPO, a diphenylanthracene (DPA) derivative, and \textit{m}-terphenyl have been reported in literature to show PSD capabilities when doped at high concentrations in common polymer matrices.\textsuperscript{57, 67} Furthermore, PPO is the only primary dopant capable of PSD used in a commercial plastic scintillator product.

At higher concentrations of PPO, the mechanical properties of the final plastics soften, making it challenging to process into final form/shape, as well as transportation and field deployment. There is no definitive explanation as to why over-doping PPO leads to enhanced PSD capabilities compared to other dopants such as \textit{m}-terphenyl or the DPA derivative in plastic scintillators. The main reason for this is due
to the lack of highly soluble fluorescent dopants in order to systematically study the parameters that affect the PSD efficiency. If efficient TTA is the driving mechanism, then over-doping other highly emissive primary dopants should introduce similar PSD capabilities as well.

In this chapter, alkylated $p$-terphenyl derivatives were synthesized that could be admixed into common plastic matrices at high concentrations to: 1. to explore PSD with $p$-terphenyl derivatives; and 2. help identify the PSD mechanism. Therefore, we have prepared highly luminescent alkylated $p$-terphenyl with the intent of identifying the main parameters that affect the onset and efficiency of PSD. To systematically study these parameters. The effects of attaching alkyl/solubilizing groups onto $p$-terphenyl were explored in relation to the melting point, solubility limit in PVT, and PSD performance of the final plastic.

2.2. Experimental Section

The synthesis, characterization of small molecules and description of their properties were done by Henok A Yemam whereas the plastic scintillator samples were prepared by both Adam Mahl and Henok A Yemam. The radiation testing and analysis were solely performed by Adam Mahl. The computational results were provided by Dr. Jonathan Tinkham and Joshua T. Koubek.

2.2.1. Instrumentation

All reagents were purchased from either Sigma-Aldrich, Frontier Scientific, or TCI America unless otherwise noted. $^1$H and $^{13}$C NMR spectra were obtained on a JEOL ECA 500 liquid-state NMR spectrometer and data obtained was manipulated in ACD/NMR processor software. Gas-chromatography mass spectra (GC/MS) was acquired on a 1200L Varian GC/MS system with a triple Quad analyzer, MS/MS capabilities and two modes of ionization. Thermal properties were measured on Q2000 TA Instruments DSC: Differential Calorimetry Instrument. Photo absorption was measured by Beckman Coulter DU 800 spectrometer with a xenon light source combined with an optical monochromator that allows scanning of wavelength from 200-800nm. Photoluminescence was recorded by Fluorolog Spectrofluorometer FL 1057.

2.2.2. Preparation of Samples, Radiation Set-up and Testing

An alumina column plug was used to remove the inhibitor from 4-vinyltoluene monomer (TCI America). The radical initiator azobisisobutyronitrile (AIBN) (Aldrich) was recrystallized twice from methanol and stored in a freezer. A stock solution of 0.01 wt% AIBN in 4-vinyltoluene was prepared and stored in a freezer. Glass jars from VWR were used as molds to make 4.7 cm diameter by 1.1-1.3 cm thickness samples (approximately 20.0 g). The sample compositions are X wt% primary dopant, 0.1 wt% POPOP and (99.9-X) wt% 4-vinyltoluene unless otherwise noted. For samples above 10 wt% primary dopant, the glass vial was silanized with dichlorodimethylsilane (Sigma-Aldrich) in accordance with a
After the dopant solutions were prepared in 4-vinyltoluene, argon gas was gently bubbled in the solutions for 20 minutes to displace oxygen. The glass jars were then capped and put in an argon filled vacuum oven under slight vacuum (Fisher Scientific isotemp 280A) and left to cure for 4 days at 80 °C and 24hr at 90 °C. Once the samples were cured and slowly air cooled to room temperature, the glass jars were broken and the plastic discs were collected (Figure 2.6).

The samples were machined down to one flat side (meniscus side) using 100 grit sandpaper by hand or by belt depending on its mechanical and thermal stability. Then, the sample was polished using 150, 220, 300, 400, 600 and 600 wet-grit sandpapers. The final touches of polishing were done on a loose-cotton buffer wheel using white abrasive polishing compound and finished with blue buffing compound. Each sample has 4.7 cm diameter and 1.1-1.3 cm thickness. Solid scintillator samples were tightly wrapped in white Teflon tape on all sides but one and attached to a Hamamatsu PMT (H2431-50) with silicone optical grease. The whole assembly was wrapped in aluminum foil and sealed with light-tight electrical tape. The PMT was biased using standard electronics and read out with a custom built waveform digitizer and DAQ system controlled by a MIDAS interface.

Samples were first exposed to a $^{137}$Cs source (gamma emission of 662 keV) in order to quantify general light output properties. Examining the position of the Compton Edge (C.E.) feature (at 477 keV) in this output spectra allowed us to calibrate each sample individually and establish an individual sample energy scale (in keV$_{ee}$). By comparing each sample’s C.E. location to a commercial control sample’s C.E. location on an absolute scale, we determined a relative light yield output. Next, the samples were exposed to a $^{244}$Cm/$^{13}$C source in two different shielding configurations, which produce different mixed neutron and gamma fields. First a “lead castle” setup was used to shield the detector and samples from the gamma flux and transmits a ‘fast’ neutron spectrum at the detector location, which allowed us to test fast neutron response as well as test and quantify the samples n/$\gamma$ PSD capabilities.

Once enough statistics were obtained, the collected waveforms were analyzed using the ROOT data analysis framework, to develop relevant output spectra for extracting light output and pulse shape response information. The stored pulse is integrated over 2 different integration times where the full integration time period (“Pulse Area”) is proportional to the deposited energy in the sample which is converted to scintillation photons. The integral over a delayed time period (“Delayed Area”) can be used to describe the pulse shape. The ratio of “Delayed Area” and “Pulse Area” is the “Delayed Area Fraction” and is used later to display and quantify pulse shape discrimination.

2.2.3. Computation Set-up

NWchem 6.5 was used to perform DFT computations on single molecules, and Avogadro was used to both construct the initial starting geometries, analyze the resulting geometries, and export the ray-tracing images using the POV-Ray export option. Ground state geometries were computed using B3LYP/6-
31G*, and all energies were computed using CAM-B3LYP/6-31G**. Singlet and triplet state energies were computed by optimizing the excited state geometry of the target state using CIS at the CAM-B3LYP/6-31G** level. The energy of the singlet and triplet states were taken as the difference in total energy between the optimized excited state, and the optimized ground state. This general approach to computing excited state energy levels has previously been established.73

Ground state geometries and energies can quickly be calculated using the hybrid function B3LYP with a decent basis set, and there is an overwhelming amount of literature that utilizes this. Excited state approaches can be more sensitive to other effects and require more care to calculate correct energies. For example, normal DFT functionals all incorrectly approximate the asymptotic behavior of electron density. While negligible for small molecules in the ground state, the effect becomes more appreciable when dealing with conjugated aromatic molecules in the excited state where large changes in electron density can occur.74 To this end we have utilized the range-separated hybrid (RSH) functional, CAM-B3LYP, which offered a good balance of accuracy and computing time.

We initially attempted to utilize TD-DFT to model the excited state electronic structure, but these calculations failed to converge due to instability in calculating the intermediate triplet states. However, we found CIS was capable of converging on the singlet and triplet state geometries. While TD-DFT is capable of more accurate energies in open-shell systems, CIS is a more efficient technique capable of similar accuracy in closed-shell systems. For stilbene and PPO, our T1 and S1 numbers match well with previous experimental and computational numbers.74-76

2.2.4. Synthesis Procedures

Generally, the synthesis of PTP derivatives were achieved with Suzuki coupling between an arylhalide (1.0 equivalent) and an arylboronic acid or ester (1.2-1.5 equivalent) with potassium carbonate (3M) as the base, tetrakis(triphenylphosphine)palladium(0) [4.0 mol %] as the catalyst and tetra-n-butylammonium bromide as the transfer-phase catalyst while toluene and water serve as the solvents.

2.2.4.1. Synthesis of p-alkylated PTP derivatives

2-(4-(tert-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

In oven-dried Schlenk flask under argon atmosphere, 1-bromo-4-(tert-butyl)benzene (4.90 mL, 28.2 mmol) and 8.58 g bis(pinacolato)diboron (33.8 mmol) were dissolved in 60 mL 1,4-dioxane. Oven-dried potassium acetate (4.14 g, 42.2 mmol) was added quickly to the mixture followed by [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride (923 mg, 1.13 mmol). The mixture was heated at 90°C overnight. Once the reaction was complete, the mixture was cooled to room temperature and 100 mL ethyl acetate was added to quench the reaction. DI water (30 mL) was added to extract the aqueous
phase, 50 mL brine (2X) was used to wash the organic phase, and it was dried over anhydrous MgSO₄ and filtered. After concentrating down the filtrate, silica column chromatography with hexanes as eluent gave 5.57 g white powder (76%). ¹H NMR (500.0 MHz, CDCl₃): δ 7.81 (s, 2H), 7.42 (s, 2H), 1.34 (s, 21H). ¹³C {¹H} NMR (125.8 MHz, CDCl₃): δ 154.40, 135.39, 125.27, 123.98, 83.54, 34.83, 30.64, 24.26.

4-(tert-butyl)-1,1′:4′,1″-terphenyl (tBuPTP)

In oven-dried 150 mL Schlenk flask under argon atmosphere, 4-bromobiphenyl (4.48 g, 19.2 mmol) was added to 18 mL anhydrous toluene followed by 6.0 g of 2-(4-(tert-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23.1 mmol). Then, a mixture of 7.97 g oven-dried potassium carbonate (57.7 mmol) in 18 mL degassed DI water and 620 mg tetra-n-butylammonium bromide (1.92 mmol) were added to the mixture. Tetrakis(triphenylphosphine)palladium(0) (888 mg, 0.77 mmol) was added and the mixture was heated to 90°C overnight. The mixture was checked for completion by TLC (hexanes). After completion, the mixture was cooled to room temperature and dumped into 150 mL cold methanol and left overnight in a flammable freezer. It was then filtered and dried and passed through a small silica column chromatography with hexanes as eluent to yield 4.4 g white powder (80%). ¹H NMR (500 MHz, CDCl₃) δ 7.69 (m, 6H), 7.60 (d, 2H), 7.55 – 7.44 (m, 4H), 7.38 (t, 1H), 1.40 (s, 9H). ¹³C {¹H} NMR (125.8 MHz, CDCl₃): δ 150.20, 140.73, 139.64, 137.64, 129.35, 127.88, 127.53, 127.22, 126.68, 126.31, 125.91, 125.01, 34.43, 30.77.

2-(4-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

In oven-dried Schlenk flask under argon atmosphere, 5.0 mL 1-bromo-4-butylbenzene (28.2 mmol,) and 8.58 g bis(pinacolato)diboron (33.8 mmol) were dissolved in 60 mL 1,4-dioxane. Oven-dried 4.14 g potassium acetate (33.8 mmol) was added quickly to the mixture followed by 923 mg [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride (923 mg, 1.13 mmol). The mixture was heated at 90°C overnight. Once the reaction was complete, the mixture was cooled to room temperature and 100 mL ethyl acetate was added to quench the reaction. DI water was added to extract the aqueous phase, 50 mL brine (2X) was used to wash the organic phase, and it was dried over anhydrous MgSO₄ and filtered. After concentrating down the filtrate, silica column chromatography with hexanes as eluent gave 6.02 g white powder (82%). ¹H NMR (500.0 MHz, CDCl₃): δ 7.71 (d, 2H), 7.17 – 7.08 (m, 2H), 2.57 (d, 2H), 1.55 (s, 2H), 1.28 (s, 28H), 0.88 (d, 3H). ¹³C {¹H} NMR (125.8 MHz, CDCl₃): δ 146.20, 135.26, 127.23, 83.55, 35.89, 33.57, 25.59, 24.58, 14.54.
In oven-dried 150 mL Schlenk flask under argon atmosphere, 4-bromobiphenyl (4.48 g, 19.2 mmol) was added to 18 mL anhydrous toluene followed by 2-(4-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6 g, 23.10 mmol). Then, 8.0 mL aqueous solution of potassium carbonate (16 mmol, 2.0 M) and 619 mg tetra-n-butylammonium bromide (1.92 mmol) were added to the mixture. Tetrakis(triphenylphosphine)palladium(0) (888 mg, 0.77 mmol, 4.0% eq) was added and the mixture was heated to 90°C overnight. The mixture was checked for completion by TLC (hexanes). After completion, the mixture was cooled to room temperature and dumped into 150 mL cold methanol and left overnight in a flammable freezer. It was then filtered and dried and passed through a small silica column chromatography with hexanes as eluent to yield 4.81 g white powder (87.3%). 1H NMR (500 MHz, CDCl3) δ 7.67 (m, 6H), 7.58 (d, 2H), 7.47 (t, 2H), 7.37 (t, 1H), 7.29 (d, 2H), 2.68 (t, 2H), 1.73 – 1.59 (m, 2H), 1.41 (m, 2H), 0.98 (t, 3H). 13C {1H} NMR (125.8 MHz, CDCl3): δ 142.00, 140.62, 139.97, 139.58, 137.84, 129.32, 128.00, 127.76, 127.37, 126.54, 126.07, 35.17, 35.50, 22.30, 13.38.

4,4''-di-tert-butyl-1,1':4',1''-terphenyl (ditBuPTP)

In oven-dried 100 mL Schlenk flask under argon atmosphere, 1,4-dibromobenzene (411 mg, 1.74 mmol) and 2-(4-(tert-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (999 mg, 3.84 mmol) were added to 8 mL anhydrous toluene. Then, 8 mL aqueous solution of potassium carbonate (16.0 mmol, 2.0 M) and 56.1 mg tetra-n-butylammonium bromide (0.17 mmol) were added to the mixture. Tetrakis(triphenylphosphine)palladium(0) (80.0 mg, 69.9 µmol) was added and the mixture was heated to 90°C for 24 hr. After checking the completion by TLC (8:2 hexanes to ethyl acetate), the reaction was cooled to room temperature and dumped into 50 mL cold methanol and left in flammable freezer overnight. The mixture was filtered, dried and passed through a plug silica chromatography column with hexanes and 20% ethyl acetate as co-eluents to yield 550 mg white powder (92%). 1H NMR (500 MHz, CDCl3) δ 7.66 (s, 4H), 7.59 (d, 4H), 7.49 (d, 4H), 1.38 (s, 18H). 13C {1H} NMR (125.8 MHz, CDCl3): δ 151.58, 140.59, 129.86, 128.86, 128.54, 128.09, 127.59, 127.16, 126.84, 122.65, 121.42, 100.29, 32.45, 31.45.

4-bromo-4'-(2-ethylhexyl)oxy)-1,1'-biphenyl

In oven-dried 250 mL round bottom flask under argon atmosphere, 2-ethylhexyl bromide (8.5 mL, 48.0 mmol) was added to a solution of 4-bromophenol (9.96 g, 40.0 mmol), 2.80 g potassium hydroxide (50.0 mmol) and 609 mg sodium iodide (4.00 mmol) in 90 mL anhydrous ethanol. The solution was refluxed
for 36 hr and checked for completion with TLC (hexanes). After completion, the solution was concentrated
down and 100 mL ethyl acetate was added, the inorganic layer was extracted with brine solution and dried
over anhydrous magnesium sulfate. It was then concentrated down and passed through a silica column
chromatograph with hexanes and few drops of ethyl acetate as the eluent to yield 12.0 g colorless powder
(83.0%). \(^1\)H NMR (500.0 MHz, CDCl\(_3\)) \(\delta\) 7.54 (d, 6H), 7.03 (s, 2H), 3.94 (s, 2H), 1.39 (d, 11Н), 1.02 (s,
8H). \(^1\)C \(^{1}\)H NMR (125.8 MHz, CDCl\(_3\)) \(\delta\) 159.51, 140.02, 132.79, 131.41, 129.16, 127.94, 121.00,
115.85, 70.85, 39.18, 30.92, 29.47, 24.21, 23.19, 14.99, 10.99

4-((2-ethylhexyl)oxy)-1,1':4',1''-terphenyl (ehPTP)

In oven-dried 150 mL Schlenk flask under argon atmosphere, 4-bromo-4'-((2-ethylhexyl)oxy)-1,1'-
biphenyl (5.80 g, 16.1 mmol) was added to 16 mL anhydrous toluene, followed by 2.35 g of phenylboronic
acid (19.3 mmol). Then, 16.0 mL aqueous solution of potassium carbonate (32.0 mmol, 2.0 M) and 517 mg
tetra-n-butylammonium bromide (1.60 mmol) were added to the mixture. Tetrakis(triphenylphosphine)palladium(0) (742 mg, 642 \(\mu\)mol) was added and the mixture was heated to
90°C for 24 hr. The mixture was checked for completion by TLC (hexanes). The reaction was cooled to
room temperature, precipitated in cold methanol and left overnight in flammable freezer. It was then
filtered, dried and passed through a small silica column chromatography with hexanes as eluent. It was then
reprecipitated in cold methanol and stored in flammable freezer overnight. The white powder was filtered
and dried (4.03 g, 70.0%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.72 – 7.62 (m, 6H), 7.59 (d, 2H), 7.48 (t, 2H),
7.37 (t, 1H), 7.03 (d, 2H), 3.92 (d, 2H), 1.78 (m, 1H), 1.64 – 1.25 (m, 8H), 0.96 (m, 6H). \(^1\)C \(^{1}\)H NMR
(125.8 MHz, CDCl\(_3\)) \(\delta\) 158.98, 140.65, 139.18, 132.77, 129.32, 128.50, 127.95, 127.72, 127.48, 127.18,
126.69, 126.22, 115.38, 114.08, 70.41, 39.82, 38.80, 30.37, 23.74, 14.50, 13.51, 10.51.

4-heptyl-1,1':4',1''-terphenyl (heptylPTP)

In oven-dried 150 mL Schlenk flask under argon atmosphere, 4.0 g 4-bromo-4'-heptyl-1,1'-
biphenyl (12.1 mmol) and 1.77 g phenylboronic acid (14.5 mmol) were added to 14 mL anhydrous toluene.
Aqueous solution of 14.0 mL potassium carbonate (28.0 mmol, 2.0 M), 389 mg tetra-n-butylammonium
bromide (1.21 mmol) and 558 mg tetrakis(triphenylphosphine) palladium(0) (480 \(\mu\)mol) were added to the
mixture. The mixture was heated to 90°C for 48 hr. It was then cooled down to room temperature,
precipitated in cold methanol and left overnight in flammable freezer. The filtered mixture was dried and
passed through a silica column chromatography with hexanes as eluent to yield 3.5 g static white powder
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(88.4%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.73 (m, 6H), 7.65 (d, 2H), 7.53 (t, 2H), 7.44 (t, 1H), 7.36 (d, 2H), 2.74 (d, 2H), 1.75 (t, 2H), 1.42 (m, 9H), 1.00 (t, 3H). $^{13}$C $^1$H NMR (125.8 MHz, CDCl$_3$): δ 142.67, 141.12, 140.54, 140.15, 138.35, 129.92, 128.33, 127.89, 127.08, 36.04, 31.99, 29.66, 28.67, 23.07, 15.04, 14.11.

2.2.4.2. Synthesis of $m$-alkylated PTP derivatives

1-bromo-3-(pentyloxy)benzene 

In oven-dried 250 mL round bottom flask under argon atmosphere, 1-bromopentane (5.45 mL, 44.0 mmol) was added to a solution of 3-bromophenol (7.0 g, 40.0 mmol), 2.80 g potassium hydroxide (50.0 mmol) and 610 mg sodium iodide (4.0 mmol) in 90 mL anhydrous ethanol. The solution was refluxed overnight and checked for completion with TLC 9:1 hexanes to ethyl acetate. After completion, the solution was concentrated down and 100 mL ethyl acetate was added and the inorganic layer was extracted with brine solution and dried over anhydrous magnesium sulfate. It was then concentrated down and passed through a silica column chromatograph with hexanes as the eluent to yield 9.0 g colorless oil (92.6%). $^1$H NMR (500.0 MHz, CDCl$_3$): δ 7.12 (s, 1H), 7.05 (s, 2H), 6.83 (s, 1H), 3.92 (s, 2H), 1.77 (s, 2H), 1.40 (s, 4H), 0.94 (s, 3H). $^{13}$C $^1$H NMR (125.8 MHz, CDCl$_3$): δ 159.73, 130.94, 122.62, 118.19, 112.64, 67.99, 28.68, 22.33, 14.38, 13.39

3-(pentyloxy)-1,1':4',1''-terphenyl (mopPTP)

In oven-dried 150 mL Schlenk flask under argon atmosphere, 1-bromo-3-(pentyloxy)benzene (5.0 g, 21.6 mmol,) was added to 40 mL anhydrous toluene, followed by 7.5 g of 4-biphenylboronic acid (22.6 mmol). Then, 20 mL aqueous solution of potassium carbonate (40.0 mmol, 2.0 M) and 662 mg tetra-n-butylammonium bromide (2.06 mmol) were added to the mixture. Tetrakis(triphenylphosphine)palladium(0) (997 mg, 0.862 µmol) was added and the mixture was heated to 90°C for 24hr. The mixture was checked for completion with 9:1 hexanes to ethyl acetate. After completion, the mixture was cooled to room temperature and dumped into 150 mL cold methanol and left overnight in a flammable freezer. It was then filtered and dried and passed through a small silica column chromatography with hexanes and few intermittent drops of ethyl acetate as eluent to yield 6.0 g white powder (88%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.68 (m, 6H), 7.48 (t, 2H), 7.37 (t, 2H), 7.24-7.19 (m, 2H), 6.93 (dd, 1H), 3.93 (t, 2H), 1.77 (m, 1H), 1.43 (m, 8H), 0.97 (t, 6H). $^{13}$C $^1$H NMR (125.8 MHz, CDCl$_3$): δ 159.52, 141.98, 140.56, 139.84, 130.27, 129.34, 129.00, 128.01, 127.51, 126.65, 126.21, 119.91, 118.58, 113.85, 112.47, 67.91, 28.89, 28.16, 22.33, 13.47.
In oven-dried 150 mL Schlenk flask under argon atmosphere, 1-bromo-3-(tert-butyl)benzene (2.74 g, 12.9 mmol) was added to 26 mL anhydrous toluene, followed by 4-biphenylboronic acid (5.13 g, 15.4 mmol). Then, 13.0 mL aqueous solution of potassium carbonate (26.0 mmol, 2.0 M) and 415 mg tetra-n-butylammonium bromide (1.29 mmol) were added to the mixture. Tetrakis(triphenylphosphine)palladium(0) (595 mg, 515 µmol) was added and the mixture was heated to 90°C overnight. The mixture was checked for completion with 9:1 hexanes to ethyl acetate. After completion, the mixture was cooled to room temperature and dumped into 150 mL cold methanol and left overnight in a flammable freezer. It was then filtered and dried and passed through a small silica column chromatography with hexanes as eluent to yield 2.80 g white powder (76%). {\textsuperscript{1}H NMR (500 MHz, DMSO-\text{d}_6) δ 7.72 (m, 4H), 7.69 (d, 2H), 7.64 (s, 1H), 7.46 (t, 3H), 7.32-7.40 (m, 3H), 1.35 (s, 9H).} 

In oven-dried 150 mL Schlenk flask under argon atmosphere, 1-bromo-3,5-di-tert-butylbenzene (3.46 g, 12.9 mmol) was added to 26 mL anhydrous toluene, followed by 4-biphenylboronic acid (5.13 g, 15.4 mmol). Then, 13.0 mL aqueous solution of potassium carbonate (26.0 mmol, 2.0 M) and 415 mg tetra-n-butylammonium bromide (1.29 mmol) were added to the mixture. Tetrakis(triphenylphosphine)palladium(0) (595 mg, 515 µmol) was added and the mixture was heated to 90°C overnight. The mixture was checked for completion with 9:1 hexanes to ethyl acetate. After completion, the mixture was cooled to room temperature and dumped into 150 mL cold methanol and left overnight in a flammable freezer. It was then filtered and dried and passed through a small silica column chromatography with hexanes as eluent to yield 3.0 g white powder (68%). {\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.65-7.70 (m, 6H), 7.48 (m, 5H), 7.38 (t, 1H), 1.42 (s, 18H).}
1-bromo-3-((2-ethylhexyl)oxy)benzene

In oven-dried 250 mL round bottom flask under argon atmosphere, 2-ethylhexyl bromide (7.90 mL, 44.0 mmol) was added to a solution of 3-bromophenol (7.0 g, 40.0 mol), 2.80 g potassium hydroxide (50.0 mmol) and 610 mg sodium iodide (4.0 mmol) in 90 mL anhydrous ethanol. The solution was refluxed for 36 hr and checked for completion with TLC 9:1 hexanes to ethyl acetate. After completion, the solution was concentrated down and 100 mL ethyl acetate was added, the inorganic layer was extracted with brine solution and dried over anhydrous magnesium sulfate. It was then concentrated down and passed through a silica column chromatograph with hexanes as the eluent to yield 10.8 g colorless oil (94.3%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.16 – 7.11 (m, 1H), 7.09 (s, 2H), 6.86 (s, 1H), 3.83 (s, 2H), 1.85 – 1.66 (m, 1H), 1.61 – 1.21 (m, 12H), 1.08 – 0.78 (m, 9H). $^{13}$C {$^1$H} NMR (125.8 MHz, CDCl$_3$): δ 160.37, 129.88, 122.94, 118.49, 112.90, 70.73, 38.91, 30.64, 23.96, 14.72, 10.71.

3-((2-ethylhexyl)oxy)-1,1′:4′,1″-terphenyl (mehPTP)

In oven-dried 100 mL Schlenk flask under argon atmosphere, 1-bromo-3-((2-ethylhexyl)oxy)benzene (3.67 g, 12.9 mmol) was added to 26 mL anhydrous toluene, followed by 4-biphenylboronic acid (5.13 g, 15.4 mmol). Then, 13.0 mL aqueous solution of potassium carbonate (26.0 mmol, 2.0 M) and 415 mg tetra-n-butylammonium bromide (1.29 mmol) were added to the mixture. Tetrakis(triphenylphosphine)palladium(0) (595 mg, 515 µmol) was added and the mixture was heated to 90°C overnight. The mixture was checked for completion by TLC (hexanes). The reaction was quenched by 100 mL ethyl acetate and washed with 50 mL DI water followed by 50 mL brine solution twice. It was then filtered, dried and passed through a small silica column chromatography with hexanes as eluent. It was then precipitated in cold methanol and stored in flammable freezer overnight. The white powder was filtered and dried (3.50 g, 76.1%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.68 (m, 6H), 7.48 (t, 2H), 7.41 – 7.3 (m, 2H), 7.20 (m, 2H), 6.93 (d, 1H), 3.93 (d, 2H), 1.77 (m, 1H), 1.43 (m, 8H), 1.02 – 0.87 (m, 6H). $^{13}$C {$^1$H} NMR (125.8 MHz, CDCl$_3$): δ 159.66, 141.95, 139.87, 130.24, 130.24, 129.33, 128.97, 127.89, 127.50, 126.63, 126.20, 119.83, 118.49, 113.92, 112.68, 70.38, 39.80, 30.57, 23.80, 14.50, 13.51, 11.52, 10.53.

2.3. Results and Discussion

PTP has been used as a primary fluorescent dopant together with 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP) as a wavelength shifter in basic plastic scintillator formulations by several groups
including commercial producers of scintillators, eg. Saint Gobain Crystals. Its high fluorescence quantum yield (93%), fast decay lifetime (1.05 ns) and high photospectral overlap with PVT and POPOP makes it an efficient dopant. However, due to its limited solubility in current plastic scintillator formulations, it has never been investigated for PSD application in plastics outside of the early attempts by Birks. Birks had used 2.5 wt% \( p \)-terphenyl in polystyrene as a proof of concept to show how fast neutron signals could be separated from gamma radiation, though exhibiting only weak PSD. We here attempt to increase the solubility of PTP to further study this promising family of fluorescent dopants.

### 2.3.1. Synthesis and Physical Characterization of PTP Derivatives

The solubility of PTP in PVT was increased by changing the position and length of alkyl substituents on PTP. As expected, this minimally affected the photophysical properties (Figures 2.2-2.5) and yielded a more useful form of the dopant for possible PSD properties in plastic scintillators via overdoping. Finkelstein and modified Miyaura borylation reactions were used to synthesize precursors from inexpensive starting materials, whereas Suzuki coupling of the precursors afforded the final products with good to excellent reaction yields (Schemes 2.2 and 2.3, Figure 2.1). The choice of the alkylated substituents was made based on the price of starting materials, as well as the ease of scale up and purification schemes.

**Scheme 2.2** Synthesis of para-alkylated \( p \)-terphenyl derivatives

\[
\begin{align*}
\text{Br} & \quad + \quad \begin{array}{c}
\text{BPin or B(OH)}_2 \\
R_1 \\
\end{array} \\
\begin{array}{c}
\text{Br} \\
R_2
\end{array} \\
\end{align*}
\]

\[
\begin{array}{c}
Pd(PPh_3)_4, K_2CO_3 \\
\text{Toluene/H}_2\text{O (1:1), 90°C}
\end{array}
\]

\[
\begin{align*}
\text{R}_1 &= \text{H}, \text{R}_2 = \text{tBu} \\
\text{R}_1 &= \text{H}, \text{R}_2 = \text{nBu} \\
\text{R}_1 &= \text{(2-ethylhexyl)}, \text{R}_2 = \text{H} \\
\text{R}_1 &= \text{heptyl}, \text{R}_2 = \text{H}
\end{align*}
\]

**Scheme 2.3** Synthesis of meta-alkylated \( p \)-terphenyl derivatives

\[
\begin{align*}
\text{Br} & \quad + \quad \begin{array}{c}
\text{B(OH)}_2 \\
R_1 \\
\end{array} \\
\begin{array}{c}
\text{Br} \\
R_2
\end{array} \\
\end{align*}
\]

\[
\begin{array}{c}
Pd(PPh_3)_4, K_2CO_3 \\
\text{Toluene/H}_2\text{O (1:1), 90°C}
\end{array}
\]

\[
\begin{align*}
\text{R}_1 &= \text{H}, \text{R}_2 = \text{tBu} \\
\text{R}_1 &= \text{tBu}, \text{R}_2 = \text{tBu} \\
\text{R}_1 &= \text{tBu}, \text{R}_2 = \text{OPenty1} \\
\text{R}_1 &= \text{H}, \text{R}_2 = \text{2-ethylhexyl}
\end{align*}
\]
The synthesis of PTP derivatives didn’t require the use of toxic or flammable reagents and most of these derivatives are reported here for the first time in literature. The exception are tBuPTP, hepPTP and ditBuPTP. None of these, apart from PTP and hepPTP in plastic scintillator and liquid scintillator respectively, have been reported for use as a primary dopant in plastic scintillator. The alkylated PTP derivatives showed nearly identical absorption and emission properties as the parent PTP, as seen in Figures 2.2-2.5. The relative photoluminescent quantum yields (PLQY) of these derivatives are also very similar (>90%), as shown in Table 2.1, and these deviations are within the systematic error of the relative quantum yield measurement. The thermal properties of PTP derivatives was studied using differential scanning calorimetry (DSC) and results shown in Table 2.1. The Tm vary greatly from one another and as expected, the m-alkylated PTP derivatives showed much lower values compared to their p-alkylated counterparts. Interestingly, some of these derivatives appear to have multiple thermal transitions (Table 2.1), suggesting liquid crystalline (LC) phases (that has been previously reported for terphenyl molecules), but we found no correlation between the existence of the LC-phases and the position of the solubilizing group. In addition, the existence and position of the LC-phase did not noticeably affect scintillation efficiency of the dopants. Results for PPO is shown for comparison.

Table 2.1 p-terphenyl derivatives and their physical properties.

<table>
<thead>
<tr>
<th>Primary dopants</th>
<th>Tm (°C)</th>
<th>LC-phase (°C)</th>
<th>UV-max (nm)</th>
<th>PL-max (nm)</th>
<th>Relative PLQY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO</td>
<td>72</td>
<td>N/A</td>
<td>304</td>
<td>367</td>
<td>100</td>
</tr>
<tr>
<td>PTP</td>
<td>213</td>
<td>N/A</td>
<td>281</td>
<td>341</td>
<td>93</td>
</tr>
<tr>
<td>tBuPTP</td>
<td>187</td>
<td>N/A</td>
<td>277</td>
<td>344</td>
<td>93</td>
</tr>
<tr>
<td>nBuPTP</td>
<td>180</td>
<td>126-180</td>
<td>277</td>
<td>345</td>
<td>91</td>
</tr>
<tr>
<td>chPTP</td>
<td>179</td>
<td>N/A</td>
<td>285</td>
<td>353</td>
<td>93</td>
</tr>
<tr>
<td>hepPTP</td>
<td>174</td>
<td>121-174</td>
<td>278</td>
<td>344</td>
<td>98</td>
</tr>
<tr>
<td>ditBuPTP</td>
<td>255</td>
<td>245-255</td>
<td>280</td>
<td>349</td>
<td>-</td>
</tr>
<tr>
<td>mtBuPTP</td>
<td>94</td>
<td>N/A</td>
<td>274</td>
<td>342</td>
<td>90</td>
</tr>
<tr>
<td>mtBuPTP</td>
<td>136</td>
<td>N/A</td>
<td>275</td>
<td>345</td>
<td>97</td>
</tr>
<tr>
<td>mopPTP</td>
<td>64</td>
<td>57-62</td>
<td>275</td>
<td>346</td>
<td>95</td>
</tr>
<tr>
<td>mehPTP</td>
<td>11</td>
<td>N/A</td>
<td>274</td>
<td>346</td>
<td>100</td>
</tr>
</tbody>
</table>

Melting Point (Tm) was determined by TA Instruments Q2000 Differential Scanning Calorimetry; UV-VIS was run in spectral grade cyclohexane with Beckman Coulter DU 800 Spectrometer; Photoluminescence (PL) was run with Fluorolog Spectrofluorimeter FL1057 excited at 290 nm. PL Quantum Yield (PLQY) was run with PTP as the reference dye and excitation wavelength at 270 nm.
Figure 2.1 PTP derivatives and their reaction yields. [ditBuPTP is not shown on Schemes 2.2/2.33 as a matter of convenience.]
Figure 2.2 Photoabsorption of p-alkylated PTP

Figure 2.3 Photoemission of p-alkylated PTP
2.3.2. Solubility Test and Radiation Performance

The solubility limit of PTP in PVT was determined to be 2.0-3.0 wt% in agreement with literature\textsuperscript{14}. The \textit{p}-alkylated derivatives (Figure 2.1) solubility in PVT were determined to be between 5.0-7.0 wt% with the exception of tBuPTP (Figure 2.1) and ditBuPTP (Figure 2.1). The higher melting points of PTP, tBuPTP and ditBuPTP when compared to the rest of the \textit{p}-alkylated derivatives correlate to the lower solubility.
ditBuPTP had the highest melting point and lowest solubility in PVT (<1.0 wt%). The relationship between high melting points of the dopants and low solubility in PVT were directly correlated and provided motivation to synthesize lower melting point PTP derivatives (to increase the solubility within PVT), through the synthesis of \( m \)-alkylated PTP derivatives (Table 2.1, Scheme 2.3). \( m \)-alkylated PTP derivatives had much higher solubility limits; up to 20.0 wt% in PVT. The increase in solubility correlates with the lower melting points of the derivatives. The high solubility allowed for testing of PSD capabilities via over-doping. Note, mehPTP (Figure 2.1) has a melting point lower than room temperature and thus was not explored further for over-doping due to extreme softening (gel-like) of the final plastic at concentrations of 10.0 wt%.

Figure 2.6 Plastic scintillators doped with the new p-terphenyl derivatives. [Each square is 1cm x 1cm]
Figure 2.7 Compton edge comparison of commercial scintillator and \textit{p}-alkylated PTP derivatives.

Figure 2.8 Compton edge comparison of commercial scintillator and \textit{m}-alkylated PTP derivatives.
To test their radiation response, each sample was polished (Figure 2.6), coupled to a PMT (Hamamatsu H2431-50) and then exposed to various radiation sources. First, a $^{137}$Cs gamma source was used to measure the gamma response. The dominant photoelectric interaction in plastic scintillators is via the Compton effect. Therefore, the collected spectra are analyzed for the Compton edge feature, the location of which can be used to quantify the light yield (LY) and generate an energy calibration unique to each sample (Figure 2.7 and 2.8). Light yield is a general property of plastic scintillators that describe their scintillation or energy transfer efficiency. In literature, light yields are often presented by comparing with signals from commercial scintillators such as Saint Gobain Crystals (BC-408) and Eljen Technology. The $^{137}$Cs response spectra of all the samples are shown in Figures 2.7 and 2.8. In this study, the light outputs of the samples are compared to a similarly sized sample of BC 408 acquired from Saint Gobain Crystals. The CE of PTP derivatives containing plastic scintillators are divided by the CE of BC-408. The result is reported as a percentage (in Table 2.2).

Table 2.2 Radiation response of plastic scintillator with soluble derivatives of PTP

<table>
<thead>
<tr>
<th>Primary Dopants</th>
<th>1.0 wt%</th>
<th>5.0 wt%</th>
<th>10.0 wt%</th>
<th>15.0 wt%</th>
<th>20.0 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>LY (%)</td>
<td>LY (%)</td>
<td>FOM</td>
<td>LY (%)</td>
<td>FOM</td>
<td>LY (%)</td>
</tr>
<tr>
<td>PTP</td>
<td>97.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>t-buPTP</td>
<td>85.4</td>
<td>71.0</td>
<td>0.58</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>n-buPTP</td>
<td>87.5</td>
<td>69.0</td>
<td>0.67</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ehPTP</td>
<td>89.6</td>
<td>65.0</td>
<td>0.52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>hepPTP</td>
<td>77.1</td>
<td>55.0</td>
<td>0.56</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>mtBuPTP</td>
<td>86.0</td>
<td>94.0</td>
<td>0.79</td>
<td>90.0</td>
<td>0.81</td>
</tr>
<tr>
<td>mtBuPPT</td>
<td>79.0</td>
<td>68.0</td>
<td>0.57</td>
<td>88.0</td>
<td>0.79</td>
</tr>
<tr>
<td>mopPTP</td>
<td>63.3</td>
<td>62.0</td>
<td>0.64</td>
<td>76.0</td>
<td>0.71</td>
</tr>
<tr>
<td>PPO</td>
<td>90.0</td>
<td>80.0</td>
<td>0.65</td>
<td>87.0</td>
<td>1.10</td>
</tr>
</tbody>
</table>

In comparison for light yield, $p$-alkylated PTP derivatives are similar to PTP at 1.0 wt%. Note that the systematic error of the light yield (LY) measurements of this experiment is estimated to be $\pm 5.0\%$ (Table 2.2). The variation in LY outside of the experimental error is believed to be due to the morphological changes within the plastic as the solubilizing chain of the derivatives increases, that in turn decreases the $\pi-\pi$ stacking of the derivatives. This leads to a decrease in non-radiative energy transfer from the PVT matrix to the primary dopant. Similar trends were observed with 1.0 wt% $m$-alkylated PTP derivatives, with mopPTP (Figure 2.1) showing the lowest light yield as shown in Table 2.2. The steric hindrance affects the $\pi--\pi$ stacking of the derivatives and decreases the homogeneity of the solution. This lowers the likelihood of Förster Resonance Energy Transfer (FRET) between PVT to dopants, resulting in lower scintillation efficiency or light output.
Next, a $^{244}\text{Cm}/^{12}\text{C}$ source was used to generate a mixed neutron and gamma radiation field. The individual samples response was energy calibrated using the $^{137}\text{Cs}$ spectrum, and then analyzed for any indication of n/γ PSD. The efficiency of PSD is quantified by a figure-of-merit (FoM) measuring the separation of the two types of signals at a given energy. $p$-alkylated PTP derivatives did not have high enough solubility in PVT (≤7.0 wt%) to generate sufficient TTA, resulting in a low FoM (Table 2.2). Thus, only the initial onset of PSD was demonstrated close to the solubility limit. The drop in the light yield from 1.0 to 5.0 wt% is expected due to concentration fluorescence quenching (Table 2.2). The results of PPO are shown as the last entry in Table 2 for comparison.

The increased solubility of the $m$-alkylated PTP derivatives allowed for more significant PSD analysis. mtBuPTP showed promising PSD at 5.0 wt% with a FoM value higher than the corresponding PPO at 5%, but the FoM stopped increasing with higher concentrations, showing even a decrease at 15.0 wt%. This was counterintuitive to our expectation as higher concentrations of primary dopants should lead to efficient TTA and hence better PSD. However, the same trend was also observed with mtBu$_2$PTP in which there was not a significant increase in FoM as the concentration increased from 10.0 to 15.0 wt%. Due to this trend, samples with higher concentrations were not pursued. The reason for the leveling PSD performance with increasing dopant concentration could be attributed to morphological effects allowing the energy transfer from triplet excited states to be quenched because of vibrational dissipation.$^{91}$ The effect of morphology on triplet excited state migration and density within a non-conjugated system such as PVT needs to be investigated further. In addition, the light yield of the dopants with respect to concentration shows no discernable pattern, which is currently being investigated.

Figure 2.9 Onset of Pulse Shape Discrimination (PSD) of 5.0 wt% mopPTP and 0.1 wt% POPOP in PVT
Figure 2.9 and 2.10 show the n/γ PSD analysis of 5.0 wt% and 20.0 wt% mopPTP respectively. The increase in FoM as the amount of mopPTP increases is thought to be due to enhanced triplet state migration that leads to higher concentration of TTA and subsequent delayed fluorescence.\textsuperscript{56} The 5.0 wt% sample showed onset of discrimination at higher energies where the discrimination in the 20.0 wt% sample becomes better resolved at lower energies. However, the increased FoM compared to corresponding PPO concentration wasn’t on par. This made us question whether there was any relationship between geometrical shapes of dopants and PSD performance in plastic. It’s a well-known fact that excessive rotation or vibration of molecules quenches triplet state electrons via vibrational dissipation. Therefore, comparing the ground geometrical shapes of PPO and PTP derivatives might helped us understand the lack of drastic increase in FoM for m-alkylated PTP derivatives from 10 to 20 wt%. As shown in Figure 2.11, the molecules have been color coded for visual clarity. Oxygen is red, nitrogen is a light blue, and carbons are purple, yellow, and green. The three different color carbons show: purple the main plane of the base compound determined by most number of carbon atoms in a single plane, yellow are part of the base molecule but are twisted slightly out of plane as compared to the purple and the angle that is twisted is shown in the picture, and the green carbons are solubilizing functional group carbons. Hydrogens, are not shown but were accounted for in the DFT calculations. PPO is a perfectly planar molecule with the three aromatic rings sitting flat on the plane of conjugation at 180°. On the other hand, both m-alkylated/p-alkylated PTP derivatives have a
slightly twisted phenyl ring from the other two phenyl rings by 40° from the plane of conjugation. In addition, the solubilizing alkyl chains are out of plane from the plane of conjugation. This discrepancy between PPO and PTP derivatives geometrical shape may contribute to the observed PSD difference between the two.

Figure 2.11 Computational data for geometrical optimization of PTP derivatives and PPO.

2.3.3. Hardness Measurement m-alkylated PTP Derivatives

The mechanical properties were evaluated by using a Shore-D durometer (GxPro model# 560-10D). For this measurement, six equidistance points on the flat side of a sample were measured and averaged. Only m-alkylated PTP samples were measured due to insufficient data points for the p-alkylated derivatives to make a meaningful comparison. The graph shows hardness dropping off with increasing dopant concentration (Figure 2.12). This could be a result of fluorescent dopants retarding polymerization that creates softer plastic scintillators.92-94 mopPTP has the most drastic drop off correlating with the lower melting point. Addition of cross-linkers such as 1,4-divinyl benzene to curb this problem was not attempted but will be investigated in future work.
2.3.4. Possible Mechanisms for Underperformance of PTPs

There are two plausible theories that could be at play here, perhaps both might be responsible for the observed PSD of PPO and other primary dopants. The first one is based on direct cascade of triplet energy transfers in which the triplet state of the matrix directly transfers its energy to the primary dopant which then transfers it to the wavelength shifter. This could only be if the triplet states are coupled, that essentially is an overlap of the wavefunction that describes the triplet states. Therefore, the main requirement for this theory is the energetic matching (overlap of wavefunction) between the matrix and the fluorescent dopants. Assuming this theory to be true and triplet state energies between PS and PVT are equal, there is a 340 meV difference between the first triplet state energies ($T_1$) of PPO and PTP. For example, PPO having a lower $T_1$ would make it more energetically favorable than PTP (Figure 2.13). Additionally, as eluded to earlier, its planar structure may lead to micro-crystalline domains that could allow for enhanced mobility of triplet state electrons and therefore higher probability for triplet-triplet annihilation to create delayed fluorescence. Because the wavelength shifter (POPOP) is only 0.1 wt% in the plastic, the probability of the triplet state energy being quenched by POPOP is minimal. However, the primary dopant in PSD experiments is usually between 10-30 wt% and hence the triplet energy will eventually get trapped by the primary dopant $T_1$. One might ask why triplet-triplet annihilation doesn’t happen with the $T_1$ of PVT. The answer lies on the high energy of the first singlet excited state that is about 5.35 eV compared to 4.30 eV for PPO or 4.52 eV for PTP and hence the probability of annihilation leading to delayed fluorescence is minimal. In addition, the non-crystalline nature of the polymer could inhibit triplet mobility that is why quenching by a neighboring primary dopant is a dominant route.
The major drawback of this theory is that it assumes that the mixed radiation solely interacts with the matrix to create excited states. This assumption is wrong as it was debunked by over-doping PPO in PMMA that showed a lower PSD compared to corresponding concentrations of PPO in PVT. This means the mixed radiation is directly interacting with the primary dopant and creating the triplet excited states without the need for triplet energy transfer from the matrix. Hence the need for a second theory. The second theory emphasizes on how triplet excited states are created and is thoroughly discussed by Birks.

Essentially the population of triplet excited states is due to ion recombination which was observed for fluorescent molecules (naphthalene and anthracene) dissolved in a hydrocarbon solvent such as cyclohexane. Ion recombination populates more triplet states than singlet excited states due to the availability of three relatively stable degenerate triplet states than singlet state (statistical reasoning). Assuming this theory to be true, the variation in the density of triplet excited state for PPO and PTP is essentially constant due to their similar triplet energies. Therefore, the difference lies in the mobility and eventual annihilation of triplet excited state which heavily depends on the symmetry of the fluorescent dopant as shown by the massive discrepancy in FoM between a naphthalene (negligent) and a pendant naphthalene derivative crystal, tris(1-naphathalenylethyl)amine, with FoM over two.

To evaluate this theory, we made two 6.0 g samples with 20 wt% mopPTP and 20 wt% PPO in PMMA with 0.1 wt% POPOP as the wavelength shifter. If theory two is true, then both mopPTP and PPO in PMMA should lead to similar FoM since the ion recombination should lead to similar population of triplet state electrons in both. As shown in Figure 2.14, the FoM for PPO sample isn’t significantly different from mopPTP. This shows that the matrix plays a significantly role in determining the PSD performance of fluorescent primary small molecules. It’s also worth noting that 20 wt% mopPTP in PMMA has similar hardness compared to 20 wt% PPO in PMMA which is why its non-planar ground state geometry didn’t inhibit (via vibrational dissipation) the formation of delayed fluorescence. The light output of the two samples came out to be 70% compared to BC-406.
To validate the size of the sample was independent of the radiation performance differences between mopPTP and PPO, we made two 6.0 g samples with 20 wt% of the dopants and 0.1 wt% POPOP in PVT. Similar to the 20.0 g samples, the difference in PSD between mopPTP and PPO were significantly different (Figure 2.15). The light output of 20 wt% mopPTP and 20 wt% PPO were 92% and 97% respectively.

Figure 2.14 Pulse Shape Discrimination of mopPTP and PPO in PMMA

Figure 2.15 Pulse Shape Discrimination of mopPTP and PPO in PVT
2.4. Conclusion

The softening of plastics when over-doped with high concentration of primary dopants is a critical problem in the development and commercialization of new, next generation plastic scintillators with PSD properties. It appears that the melting point of primary dopants is a predictive factor that affects the solubility limit in PVT and the mechanical strength of the resultant plastic. Select \textit{m}-alkylated PTP derivatives showed encouraging PSD capabilities with enhanced mechanical properties compared to corresponding concentration of PPO. The exception to this was mopPTP that showed a drastic decline in hardness when over-doped in PVT in addition to showing little to negligible increase in FoM. This was attributed to the lack of symmetry and high probability of vibrational/rotational energy dissipation of PTP derivatives due to their geometry.

Although we were successful in preparing PTP derivatives with enhanced solubility, over-doping did not lead to a significant PSD in all cases. While we achieved comparable FoM \textit{m}-alkylated PTP derivatives relative to PPO at concentration \( \leq 10.0 \text{ wt}\% \), the FoM plateaued at 15.0 and 20.0 wt\%. In addition, despite the geometrical similarity between mopPTP and mtBuPTP, the discrepancy between the observed FoM implies that triplet exciton migration has a preferred morphological pathway to achieve efficient TTA. This observation was further supported by the planarity of PPO that shows a much better FoM after > 10.0 wt\% despite having similar optical properties as PTP derivatives. In addition, the discrimination performance of 20 wt\% mopPTP and 20 wt\% PPO in PMMA were similar emphasizing the significance of the polymer matrix.

The exact physics responsible for efficient PSD is still elusive, however; we believe it could be explained by a mix of the two plausible theories presented here. We will further explore these theories in chapter 3 using fluorine derivatives. Our future work will focus on these investigations along with computational modeling of excited states as well as the effect of plastic mechanical properties on PSD performance.
CHAPTER 3. FLUORENE DERIVATIVES FOR PULSE SHAPE DISCRIMINATION

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3.1. Introduction

Plastic scintillation is crucial in the identification of special nuclear materials (SNM). It provides the initial detection of ionizing radiation by attenuating the incident radiation energy through a thermoplastic matrix and converting it to visible light via a cascade of energy transfers. The moderation of incident radiation energy could also be done by a primary dopant if it is present in the plastic at high concentrations. In this case, the primary dopant has to be stable optically in the presence of radicals during polymerization so that the cascade of energy transfer is uninterrupted and reaches the photomultiplier tube (PMT). As discussed in chapter 2, there are very few alternative primary dopants geared towards specific applications when it comes to plastic scintillators. In continuing the search for alternative primary dopants and achieving a better understanding of the mechanism behind pulse shape discrimination, we explore the parameter space of fluorene derivatives.

Fluorene derivatives have been frequently used in Organic Light Emitting Diode (OLED) research due to ease of chemical manipulation, efficient and predictable photophysical properties, thermal stability, efficient light output, and relatively low cost. Early on, there were multiple literature reports on fluorene derivatives as additives in liquid scintillators. The reports focusing on fluorene derivatives as primary dopants in plastic scintillators were all substituted at the C-2 and C-7 position but not substituted at the C-9 position (Figure 3.1). However, the methylene hydrogens at the C-9 position (being doubly benzylic) are susceptible to oxidation and possible attack by radicals. This might explain why the scintillators made from unsubstituted fluorene at the 9th position develop a yellow to green color depending on the substitution at the 2 and 7 positions.

Figure 3.1 Unsubstituted fluorene molecule
The ease of substituting at these three positions was key in deciding to explore fluorene derivatives as these positions could be used to add solubilizing alkyl chains and/or extending conjugation length depending on the range of absorption/emission target (260-500nm). Other researchers have explored fluorescent small molecules such as substituted pyrazoline and naphthalimide due to their ease of synthetic modification.\(^{36,110}\) Both of these small molecules have heteroatoms (N, O) and the authors have suggested that might be the reason for the improved emission in plastic scintillators with these dopants. In addition, heteroatoms could increase the effective nuclear charge (Z) of the molecule. Increased Z, on the other hand, is directly related to spin-orbit coupling as shown by the Hamiltonian operator in Equation 3.1.\(^{111}\) Therefore, attaching heteroatoms such as halogens or group V/VI containing aromatic rings (such as thiophene, furan or pyrrole) may lead to increased density of triplet state electrons due to the heavy atom effect (Z) or due to weak coupling between the excited triplet state and the non-bonded ground state. For the latter scenario, benzophenone is the popular example in which ISC is nearly 100% and phosphorescence could be observed at 77K.\(^{111}\)

\[
H_{S-o} = -\frac{Z^4 e^2}{8\pi \varepsilon_0 m_e^2 c^2} l_s
\]  

(3.1)

Equation 3.1 Hamiltonian operator for spin-orbit coupling [Z is effective nuclear charge, e is the charge of an electron, \(\varepsilon_0\) is the permittivity of vacuum, \(m_e\) is the mass of an electron and \(c\) is the speed of light, \(l\) is the angular momentum quantum number.]

As discussed in chapter 2, triplet-triplet annihilation (TTA) is the basis for PSD. TTA is a complex process that requires population of triplet state electrons, sufficient triplet mobility, and their collision to produce a “delayed” singlet. In simple hydrocarbon fluorescent molecules, the population of triplet state electrons is minimal due to the lack of high-Z atoms capable of promoting intersystem crossing (ISC) via spin-orbit coupling. In addition, longer lifetime of triplet state electrons makes them vulnerable to vibrational dissipation and attack by molecular oxygen.\(^{112-113}\)

In this chapter, fluorene derivatives were synthesized that could be admixed into common plastic matrices at high concentrations to: 1. find alternatives to PPO that lead to efficient PSD with enhanced mechanical properties; and 2. help identify the PSD mechanism. Similar to chapter 2, three parameters were systematically studied. First, fluorene derivatives with varied absorption and emission were compared to PPO based on their general scintillation characteristics in PVT and PSD performance. Second, the effect of geometrical shape on the solubility limit, PSD capability and light yield is explored.
3.2. Experimental Section

The synthesis, characterization of small molecules and description of their properties were done by Henok A Yemam whereas the plastic scintillator samples were prepared by both Adam Mahl and Henok A Yemam. The radiation testing and analysis were solely performed by Adam Mahl. The computational results were provided by Dr. Jonathan Tinkham and Joshua T. Koubek.

3.2.1. Instrumentation

The same instrumentations used in section 2.2.1. were used here as well with the exception that GC-MS was used quantitatively to evaluate the ratio of geometrical isomers of SF and the effectiveness of the purification method utilized.

3.2.2. Preparation of Samples, Radiation Set-up and Testing

Same as section 2.1.2 except for production of 6.0 g samples in addition to the 20.0 g samples shown in chapter 2. The dimensions for 6.0 g samples are 2.25 cm in diameter and approximately 14.0 mm tall. All sample polishing, testing and analysis of samples radiation performance was done by our collaborators.

3.2.3. Computation Set-up

The same set-up was used as section 2.2.3. The goal in this section was to identify planar and non-planar fluorene derivatives so that their radiation performance could be correlated with their ground state geometries.

3.2.4. Synthesis Procedures

9,9-dimethyl-2-phenyl-9H-fluorene (PhF)

In oven dried 150 mL Schlenk flask under argon atmosphere, 2.68 g phenylboronic acid (22.0 mmol) was added to 4.0 g 2-bromo-9,9-dimethylfluorene (14.6 mmol) in 15 mL anhydrous toluene. Aqueous solution of cesium carbonate (15.0 mL, 45.0 mmol, 3.0 M) was added to the mixture, followed by 472 mg tetra-n-butylammonium bromide (1.46 mmol) and 675 mg tetrakis(triphenylphosphine) palladium(0) (584 µmol). The mixture was heated to 90°C overnight and TLC (hexanes) was used to check for completion. Once completed, the reaction was quenched by 50 mL ethyl acetate and washed by 50 mL DI water and 50 mL brine solution twice. Silica chromatography with hexanes as eluent was used to purify product mixture and then recrystallized in methanol resulting in 3.25 g white powder (82%).$^1$H NMR (500 MHz, DMSO-D$_6$) δ 7.84 (m, 2H), 7.81 (d, 2H), 7.73 (d, 3H), 7.62 (dd, 1H), 7.51 (d, 3H), 7.47 (t, 2H), 7.28-7.39 (m, 3H), 1.49 (s, 6H). $^{13}$C {$^1$H} NMR (125.8 MHz, CDCl$_3$): δ 154.58, 141.87, 140.66, 139.16, 138.72,
9,9-dimethyl-2,7-diphenyl-9H-fluorene (PFP)

In oven dried 250 mL Schlenk flask under argon atmosphere, 12.2 g phenylboronic acid (100 mmol) was added to 16.0 g 2,7-dibromo-9,9-dimethylfluorene (45.4 mmol) in 45 mL anhydrous toluene. Aqueous solution of potassium carbonate (45.0 mL, 3.0 M) was added to the mixture, followed by 1.46 g tetra-n-butylammonium bromide (4.54 mmol) and 2.10 g tetrakis(triphenylphosphine) palladium(0) (1.82 mmol). The mixture was heated to 90°C overnight and TLC (hexanes) was used to check for completion. Once the reaction was done, the mixture was dumped into cold methanol and left in the freezer overnight. Then, it was filtered and dried. Silica chromatography with 10% activated carbon and eluted with hexanes to get 13.0 g white product (82.6%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.89 (d, 2H), 7.81 (d, 6H), 7.71 (d, 2H), 7.59 (t, 4H), 7.48 (t, 2H), 1.71 (s, 6H). $^{13}$C $^1$H NMR (125.8 MHz, CDCl$_3$): $\delta$ 154.58, 141.47, 138.22, 129.57, 128.24, 127.94, 128.24, 127.94, 126.64, 121.11, 121.14, 120.87, 119.87, 47.16, 26.94.

9,9-dimethyl-2-styryl-9H-fluorene (SF)

In 150 mL oven-dried Schlenk flask under argon atmosphere, 4.04 ml styrene (35.16 mmol, 1.2 eq) was added to a solution of 2-bromo-9,9-dimethyfluorene (29.3 mmol, 1.0 eq) and 40 mL anhydrous toluene. N,N-dicyclohexylmethylamine (7.5 mL, 35.16 mmol, 1.2 eq) was added to the mixture, followed by 449.2 mg bis(tri-tert-butylphosphine)palladium(0) (0.88 mmol, 3.0% eq) and the mixture was heated to 80°C overnight. The mixture was checked by TLC (hexanes) for completion and quenched by 50 mL ethyl acetate followed by 50 mL brine solution twice and concentrated down. The white powder (7.0 g, 80.6%) was purified by silica chromatography with hexanes as eluent and recrystallized in methanol. $^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ 7.85 (s, 1H), 7.80 (d, 2H), 7.62 (d, 2H), 7.55 (q, 2H), 7.39 (t, 2H), 7.35 – 7.26 (m, 5H), 1.47 (s, 6H). $^{13}$C $^1$H NMR (125.8 MHz, CDCl$_3$): $\delta$ 154.46, 139.32, 137.80, 136.81, 130.12, 129.72, 129.09, 128.86, 128.39, 127.83, 127.43, 126.93, 126.73, 126.17, 125.63, 123.55, 122.36, 121.24, 119.99, 47.07, 27.05.
In 250 mL oven-dried Schlenk flask under argon atmosphere, 10.7 ml styrene (93.7 mmol) was added to a solution of 2,7-dibromo-9,9-dimethylfluorene (42.6 mmol) and 80 mL anhydrous toluene. N,N-dicyclohexylmethylamine (11.0 mL, 51.1 mmol) was added to the mixture, followed by 435 mg bis(tri-tert-butylphosphine)palladium(0) (850 µmol) and the mixture was heated to 80°C overnight. The mixture was checked by TLC(hexanes) for completion and purified the same way as SF resulting in bright yellow powder (14.0 g, 82.5%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.79 (d, 2H), 7.70 (s, 2H), 7.66 (d, 4H), 7.60 (d, 2H), 7.48 (t, 4H), 7.37 (m, 2H), 7.32 (d, 4H), 1.64 (s, 6H). $^{13}$C {$^1$H} NMR (125.8 MHz, CD$_2$Cl$_2$): δ 154.94, 141.00, 139.00, 137.83, 136.97, 129.76, 129.03, 127.30, 126.14, 121.23, 111.97, 47.11, 27.93.

9,9-dimethyl-2-(naphthalen-2-yl)-9H-fluorene (NapF)

In oven dried 50 mL Schlenk flask under argon atmosphere, 140 mg naphthalen-2-ylboronic acid (820 µmol) was added to 190 mg 2-bromo-9,9-dimethylfluorene (680 µmol) in 6 mL anhydrous toluene. Aqueous solution of potassium carbonate (3.00 ml, 6.00 mmol) was added to the mixture, followed by 22.1 mg tetra-n-butylammonium bromide (70 µmol) and 31.7 mg tetrakis(triphenylphosphine) palladium(0) (27.0 µmol). The mixture was heated to 90°C overnight and TLC (hexanes) was used to check for completion. Once completed, the reaction was quenched by 50 mL ethyl acetate and washed by 50 mL DI water and 50 mL brine solution twice. Silica chromatography with hexanes as eluent was used to purify product mixture and then recrystallized in methanol resulting in 200 mg white powder (91%).

3.3. Results and Discussion

We tested five fluorene derivatives that could potentially be used as emissive dopants to better understand the scintillation process as related to PPO. Dimethyl fluorene (Me$_2$F) and PPO were directly purchased from Sigma-Aldrich. Me$_2$F was tested both as purchased and then after further purification. 9,9-dimethyl-2-phenylfluorene (PhF), 9,9-dimethyl-2,7-diphenylfluorene (PFP), 9,9-dimethyl-2-styrylfluorene (SF) and 9,9-dimethyl-2,7-di((E)-styryl)fluorene (SFS) were synthesized from the respective 2-bromo-9,9-dimethylfluorene and 2,7-dibromo-9,9-dimethylfluorene precursors via Suzuki and Heck coupling. The fluorene derivatives (Figure 3.2) were designed to evaluate the effect of both blue- and red-shifting the photo-absorption and emission spectra as compared to PPO as shown in Figure 3.4 and 3.5. Scintillation samples for this study were prepared and tested in the same manner as the PTP derivative based samples.
3.3.1 Optical and Physical Properties of Fluorene Derivatives

Figure 3.2 Fluorene derivatives for use as dopants in plastic scintillators in this study

![Figure 3.2](image1)

Figure 3.3 Absorption of fluorene derivatives.

![Figure 3.3](image2)

Figure 3.4 Emission of fluorene derivatives.

![Figure 3.4](image3)
Melting points and optical properties of the fluorene derivatives and PPO are outlined in Table 3.1. The range in values of these properties will be key in determining the parameter(s) that affects their scintillation efficiency in PVT. PPO is used as a control to compare FoM values for PSD capabilities and thermomechanical properties of the final plastic scintillator. BC-408 from Saint Gobain Crystals was used for light yield comparison.

Table 3.1 Photophysical properties and melting points of fluorene derivatives and PPO.

<table>
<thead>
<tr>
<th>Primary dopants</th>
<th>Tm (°C)</th>
<th>UV-max (nm)</th>
<th>PL-max (nm)</th>
<th>PLQY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO</td>
<td>72</td>
<td>304</td>
<td>367</td>
<td>100</td>
</tr>
<tr>
<td>Me$_2$F</td>
<td>96</td>
<td>264</td>
<td>304, 317</td>
<td>45</td>
</tr>
<tr>
<td>PhF</td>
<td>86</td>
<td>289</td>
<td>330, 346</td>
<td>64</td>
</tr>
<tr>
<td>PFP</td>
<td>175</td>
<td>342</td>
<td>390</td>
<td>89</td>
</tr>
<tr>
<td>SF</td>
<td>113</td>
<td>338</td>
<td>387</td>
<td>72</td>
</tr>
<tr>
<td>SFS</td>
<td>125</td>
<td>371</td>
<td>411, 436</td>
<td>100</td>
</tr>
</tbody>
</table>

$p$-terphenyl was used as a reference dye for PLQY measurement of Me$_2$F and PhF, excitation wavelength at 270 nm whereas PPO was used as a reference dye for PFP and SF PLQY measurement, excitation wavelength at 320nm. 9,10-diphenylanthracene was used as a reference dye for SFS, excitation wavelength at 350nm. Cyclohexane was used as a solvent for all UV/VIS and PL measurements. Melting point was measured using the same DSC procedure as used for the PTP.

3.3.2. Radiation Performance of Fluorene Derivatives

The photoemission of Me$_2$F (Figure 3.3) is blue-shifted from PPO by 60 nm so the overlap with the absorption of POPOP is decreased relative to PPO, and the expected light output should decrease as well due to less energy transfer. As predicted, 1.0 wt% Me$_2$F shows lower light output compared to the same PPO sample (Table 3.2). The purified 1.0 wt% Me$_2$F showed a drastic increase in light output, nearly 1.5-fold compared to as received Me$_2$F. Therefore, the purity of materials (>99% by GC) is a key parameter for the optimization of energy transfer (light output) as impurities may quench fluorescence.

The photoemission of PhF is also blue-shifted from PPO, but only by 22 nm and a 1.0 wt% PhF showed similar light output compared to PPO. Similar light output was observed for 1.0 wt% PFP as well. The photoemission from SF is red-shifted from PPO by 20 nm and a 1.0 wt% SF sample has comparable light output to a corresponding PPO control. This indicates that the optimization of the overlap between primary dopant emission and secondary absorption is not a dominant factor for efficient scintillation in agreement with literature. SFS absorbs and emits within the same region as POPOP so as expected,
showed a high light output as a stand-alone dopant (Table 3.2). This again indicates the effectiveness of non-radiative energy transfer (or FRET) between optically uncoupled matrix and dopant. We have used SFS as a wavelength shifter and showed equivalent performance as DPA and POPOP, two of the most commonly used wavelength shifters. Currently, there is no correlation observed between light output and PLQY of the fluorene based dopants. This is due to a secondary effect of optical mismatching between the matrix and the primary dopants caused by the blue/red shifting.

Table 3.2 Radiation responses of fluorene derivatives plastic scintillators and PPO.

<table>
<thead>
<tr>
<th>Primary Dopants</th>
<th>1.0wt%</th>
<th>5.0 wt%</th>
<th>10.0 wt%</th>
<th>15.0 wt%</th>
<th>20.0 wt%</th>
<th>25.0 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LY (%)</td>
<td>LY (%)</td>
<td>FOM</td>
<td>LY (%)</td>
<td>FOM</td>
<td>LY (%)</td>
</tr>
<tr>
<td>Me₂F</td>
<td>53.0</td>
<td>52.0</td>
<td>0.41</td>
<td>37.0</td>
<td>0.49</td>
<td>42.0</td>
</tr>
<tr>
<td>Me₂F*</td>
<td>77.0</td>
<td>85.0</td>
<td>0.53</td>
<td>70.0</td>
<td>-</td>
<td>64.0</td>
</tr>
<tr>
<td>PhF</td>
<td>96.0</td>
<td>83.0</td>
<td>0.62</td>
<td>90.0</td>
<td>0.97</td>
<td>66.0</td>
</tr>
<tr>
<td>PFP</td>
<td>92.0</td>
<td>89.0</td>
<td>0.69</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SF</td>
<td>88.0</td>
<td>76.0</td>
<td>0.43</td>
<td>61.0</td>
<td>0.63</td>
<td>63.0</td>
</tr>
<tr>
<td>SFS†</td>
<td>82.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PPO</td>
<td>90.0</td>
<td>80.0</td>
<td>0.65</td>
<td>87.0</td>
<td>1.10</td>
<td>88.0</td>
</tr>
</tbody>
</table>

* As received Me₂F was purified by passing through a silica column with 10% activated carbon. † Sample was made without a POPOP wavelength shifter.

Three out of the five tested fluorene dopants can be overdoped in PVT to a significant degree (Table 3.2). Despite increased purity, the PSD for all over-doped Me₂F was negligible, that we are further investigating (Table 3.2). However, it proves that not all soluble fluorescent dopants could produce PSD in a mixed radiation environment. Similar results were observed when trans-stilbene was over-doped in polystyrene. This could possibly be due to unmatched triplet excited states between the matrix and fluorescent dopant leading to non-radiative quenching.⁹⁶

PhF also has a high solubility limit in PVT at over 20.0 wt% with a comparable light output relative to corresponding PPO samples. Purified crystals of PhF were crushed and used to make samples that showed a 1.16 FoM for 20% PhF, to our knowledge the highest FoM reported for a non-PPO derivative (Table 3.2, Figures 3.5).³⁷

Even though, NapF precipitated out at 10.0 wt% in 6.0 g sample, it showed a promising PSD (~0.8 FoM) similar as PPO at the same concentration. It also showed high light output similar to PPO at the same concentration at 91% relative to BC-406. The light output marginally changed as we increased the amount doped in PVT from 1.0 to 5.0 to 10.0 wt% staying within 85-91% of BC-406. Future work in this area will include introducing longer alkyl chains at the 9-position in order to prepare more soluble derivative of NapF.
Figure 3.5 Pulse Shape Discrimination (PSD) of 20 wt% PhF and 0.1 wt% POPOP in PVT.

Figure 3.6 Plastic scintillators doped with fluorene derivatives and PPO. [Each square is 1cm x 1cm]
3.3.3. Effect of Geometrical Isomers on Radiation Performance

SF, on the other hand, showed >25.0 wt% solubility in PVT with good light output and mechanical properties. However, the increase in FoM from 5.0 to 25.0 wt% SF was unexpectedly minimal (Table 3.2). The reason for the low PSD at high SF concentrations is proposed to be attributed to the small percentage of cis-isomer present in SF as shown in GC/MS data (Figure 3.7). The first excited triplet state for cis-SF (1.93eV) was found to be lower than that of trans-SF (2.21eV) via our computational modeling data. Hence, it could be acting as a trap site to the first excited triplet states of trans-SF in agreement with what others have observed in a mixed crystal scintillator system. In addition to the negligible increase in FoM, samples with a higher concentration of SF developed a fluorescent yellow color during polymerization that is attributed to aggregation effect at higher concentrations (Figure 3.6).

![Geometrical isomers of SF chromatogram and corresponding MS.](image)

To validate this hypothesis, the trans-isomer was selectively precipitated out via fractional precipitation in cold methanol (Figure 3.8). This resulted in a significantly whiter powder with the filtrate being a yellow oil, indicating the optical difference between the two isomers. Twelve samples (6.0 g each
sample) were made as shown in Table 3.3 in PVT. Each sample contained 0.1 wt% POPOP. As shown, the trans-SF samples were noticeably yellower than the isomerically impure SF samples. We speculate this to be a result of aggregation induced effect since the trans-SF is a planar molecule, capable of pi-pi stacking, possibly forming J-aggregates. This might seem to be in direct conflict from PPO’s behavior at high concentration that results in a colorless plastic. However, the emission of trans-SF is redshifted from PPO by 20 nm that might be why it developed a yellow color in aggregates.

![Chromatogram of SF after column (top) and the 5th precipitation in cold methanol (bottom).](image)

As shown in Table 3.3, both the isomerically pure samples (Trans-SF) and impure samples (SF) showed statistically insignificant difference in both light output and FoM contrary to what we expected. This could perhaps be due to the small size of the samples that was 6.0 g for each sample. Scale up of the both molecules are currently underway and larger samples (20.0 g) will be explored.
3.3.4. Effect of Ground State Geometry on Radiation Performance

Generally, fluorene derivatives and PPO had higher solubility in PVT than PTP derivatives regardless of melting point or photophysical properties. For instance, SF has a higher melting point than mtBuPTP but also a higher solubility in PVT (~25.0 vs ~20.0 wt%). The same is true for SF and PPO vs mopPTP. To investigate this, the molecular geometry and angle measurements were modeled with Density Functional Theory (DFT) based code using the PBE generalized gradient approximations and TZ2P basis set in an all electron calculation. These calculations were made using the Slater type orbitals of Amsterdam Density Functional 2016.104 (ADF2016). The models showed that dopants with the highest solubility (SF and PPO) were completely planar whereas the less soluble PTP derivatives had one of the phenyl rings out of plane from the other two phenyl rings by 142.0°. Optimized geometry for all the dopants can be found in Figure 3.9. Going forward we believe that computation can play an important role in understanding how dopants work so that we can predict and design more efficient dopants.

It’s important to note that fluorene derivative samples have shown no noticeable physical change or degradation for over ten months. We would also like to emphasize that these samples were made via bulk radical polymerization that has its drawbacks with regards to incomplete termination of propagating radicals and long reaction time.26

As shown in Figure 3.9, the molecules have been color coded for visual clarity. Oxygen is red, Nitrogen is a light blue, and carbons are purple, yellow, and green. The three different color carbons show: purple the main plane of the base compound determined by most number of carbon atoms in a single plane, yellow are part of the base molecule but are twisted slightly out of plane as compared to the purple and the angle that is twisted is shown in the picture, and the green carbons are solubilizing functional group carbons. Hydrogens, are not shown but were accounted for in the DFT calculations.

<table>
<thead>
<tr>
<th>Primary Dopants</th>
<th>1.0wt%</th>
<th>5.0 wt%</th>
<th>10.0 wt%</th>
<th>15.0 wt%</th>
<th>20.0 wt%</th>
<th>25.0 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LY (%)</td>
<td>LY (%)</td>
<td>FOM</td>
<td>LY (%)</td>
<td>FOM</td>
<td>LY (%)</td>
</tr>
<tr>
<td>SF</td>
<td>87</td>
<td>85</td>
<td>-</td>
<td>81</td>
<td>0.67</td>
<td>82</td>
</tr>
<tr>
<td>Trans-SF</td>
<td>87</td>
<td>84</td>
<td>-</td>
<td>87</td>
<td>0.56</td>
<td>85</td>
</tr>
</tbody>
</table>

Each sample is 6.0 g
Figure 3.9 Ground state geometrical optimization of fluorene derivatives.

3.3.5. Hardness Measurement

Hardness measurements were done using the shore durometer as done with the PTP derivatives. Selected fluorene derivatives showed similar FoM values (PhF) as compared to the corresponding PPO samples at 10 wt% loadings, and also displayed similar light output (SF) and stronger thermomechanical material properties. As shown in Figure 3.10, as the concentration of PPO is increased, the hardness of the final plastic scintillator decreases dramatically. The same was true for purchased Me$_2$F and purified Me$_2$F$^*$. The discrepancy in hardness between purified Me2F$^*$ and purchased Me2F is worth noting since it might help us understand the influence of impurities on hardness. PhF and SF both had much lower drop off in hardness as concentration increased. PFP and NapF precipitated out at 10 wt%, and were thus not studied further for PSD. This suggests that the inverse relationship between melting points of dopants and solubility in PVT generally holds true for fluorene derivatives as well as PTP derivatives.
As discussed at the end of chapter 2, two theories were discussed. Both emphasized the importance of triplet energy transfer from the matrix to the primary dopant’s triplet state. Assuming this to be true, Figure 3.11 below shows the first excited triplet state (T_1) energies of PS (assumed to be similar as PVT) and primary dopants. The T_1 of Me2F and PhMe2F are both higher than T_1 of PPO. Therefore, we would expect a more efficient energy transfer from T1 of PS (or PVT) to PPO than both Me2F and PhF. This is supported by actual discrimination of neutron and gamma radiation (due to TTA) observed and hence reported in Table 3.2. The high T_1 of Me2F, despite its planar geometry (Figure 3.9), might be the reason why there was no discrimination observed despite incorporating up to 25.0 wt% in PVT. The non-planar geometry PhF (Figure 3.9) could also inhibit its triplet mobility, allowing non-radiative triplet state quenching. Following the same reasoning, the T_1 of trans-SF is lower than all the primary dopants and wavelength shifter (POPOP). Therefore, the T_1 PVT energy transfer could easily be quenched by POPOP or be susceptible to quenching before it reaches T_1 of trans-SF. Hence why the FoM for highly doped trans-SF samples didn’t result in impressive FoM despite its planar geometry.
3.4. Conclusion

The softening of plastics when over-doped with high concentration of primary dopants is a critical problem in the development and commercialization of new, next generation plastic scintillators with PSD properties. It appears that the melting point of primary dopants is a predictive factor that affects the solubility limit in PVT and the mechanical strength of the resultant plastic. In addition, planar dopants such as SF and PPO had higher solubility in PVT than the non-planar PTP derivatives. Select \( m \)-alkylated PTP and fluorene derivatives showed encouraging PSD capabilities with enhanced mechanical properties compared to corresponding concentration of PPO.

We were successful in preparing derivatives with enhanced solubility, and were able to show that over-doping any fluorescent dopants does not lead to high PSD. The synthesized fluorene derivatives with varied optical properties had no direct correlation between spectral overlap of dopants with the wavelength shifter, and final scintillating light output. Overdoped samples showed PSD, but not to the same degree as PPO. PhF at 20 wt% showed the highest reported FoM (1.16) for a non-PPO derivative. Furthermore, the hardness of this sample compared to the corresponding 20 wt% PPO sample was much harder (Shore D of 81 vs 69) resulting in a final plastic that could be easily handled and polished.

The exact physics responsible for efficient PSD is still elusive, however we are able to conclude that planar molecules heavily influence how triplet states migrate, collide and annihilate each other. In addition, the energy states of triplets relative to the matrix triplets state is crucial in determining the final PSD measured.
CHAPTER 4. THERMALLY AND MECHANICALLY SUPERIOR PLASTIC SCINTILLATORS FOR PULSE SHAPE DISCRIMINATION USING 2,5-DIPHENYLOXAZOLE DERIVATIVES

4.1. Introduction

As described in chapters 1-3, plastic scintillators are a century old technology that still have plenty of use for the advancement of science and security of our society. Currently, they are mainly being utilized for identifying the mere presence of ionizing radiation. The radiation detection mechanism relies on the absorption of incoming radiation by inexpensive plastic base/matrix (such as polyvinyltoluene (PVT) and polystyrene (PS)) and then a cascade of energy transfers to a primary fluorescent dopant and a wavelength shifter. A photomultiplier tube (PMT) photosensitivity is aligned within the maximum photoemission of a wavelength shifter in order to maximize the collection of emitted photons by the plastic scintillator. Advances in this field have been incremental at enhancing the detection capabilities of plastic scintillators to gamma radiation via incorporation of heavy metals\textsuperscript{41,43,115}, fast neutron via introduction of dense plastic matrices\textsuperscript{21}, thermal neutron via introduction of plastic compatible boron or lithium dopants\textsuperscript{50,116} and, discrimination of fast neutron in gamma background radiation via Spectra Shape discrimination using iridium complexes or pulse shape discrimination (PSD) using over-doped fluorescent dopants\textsuperscript{59,117}. PSD, first demonstrated by Zaitsev et al in 2012, has been the gold standard technique for plastic scintillators when it comes to discrimination of ionizing radiation.\textsuperscript{56} This technique relies heavily on highly soluble fluorescent dopants to increase the migration and collision of triplet states to result in particle dependent delayed fluorescence. As of now, 2,5-diphenyloxazole (PPO) is the only commercialized dopant for PSD capable plastic scintillators with excellent figure-of-merit (FOM). However, over-doped PPO (>15% by mass) leads to soft and thus mechanically useless samples. In order to mitigate this problem, alternative derivatives have been explored as a fluorophore for plastic scintillators. Recently, DeVol et al explored polymerizable 2-(1-naphthyl)-5-phenyloxazole to make a PS scintillating resin beads.\textsuperscript{38} Although the performance of the resins wasn’t on par with PPO doped beads, the polymerizable derivative led to a more stable resin beads.

In the previous chapters, we have showed that over-doped p-terphenyl and fluorene derivatives with higher melting points exhibit better mechanical properties when over-doped than PPO; even though PPO demonstrated superior discrimination capabilities. We hinted that the superior discrimination capabilities of PPO at higher concentration may not be inherent to PPO but the softness of plastic matrix allowing triplet mobility and migration that results in a better PSD. To prove this hypothesis, here we have prepared PPO derivatives with nearly identical optical properties as PPO for PSD application but lead to plastic scintillators with superior thermal and mechanical properties.
4.2. Experimental Section

The synthesis, characterization of small molecules and description of their properties were done by Henok A Yemam whereas the plastic scintillators samples were prepared by both Adam Mahl and Henok A Yemam. The radiation testing and analysis were solely performed by Adam Mahl. The computational results were provided by Dr. Jonathan Tinkham and Joshua T. Koubek.

4.2.1. Instrumentation

The same instrumentations used in section 2.2.1. were used here as well with the exception that GC-MS was used quantitatively to evaluate the ratio of geometrical isomers of SPO.

4.2.2. Preparation of Samples, Radiation Set-up and Testing

Same as section 2.2.2. All sample polishing, testing and analysis of samples radiation performance was done by our collaborators.

4.2.3. Synthesis Procedures

4-bromophenyl)-2-phenyloxazole (BrPPO)

Iodine (1.86 g, 7.33 mmol) was added to the mixture of α2,4'-dibromoacetophenone (3.33 mmol, 926 mg), benzylamine (0.50 ml, 3.99 mmol) and oven-dried K$_2$CO$_3$ (2.44 g, 13.3 mmol) in 20.0 mL of DMF, and then the mixture was stirred at 80 °C. After the reaction was complete by TLC analysis (9 hexanes: 1 ethyl acetate), 30 mL ethyl acetate was added to dilute the reaction mixture, followed by the treatment of saturated sodium thiosulfate solution to quench the reaction. The organic layer was separated, washed in water (3 × 10 mL), and dried over anhydrous sodium sulfate. Silica column chromatography eluted with hexanes–ethyl acetate (9:1) gave a yellow powder (870 mg, 87%). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.09 (s, 1H), 7.52 (d, $J = 49.0$ Hz, 4H). $^{13}$C {1H} NMR (125.8 MHz, CDCl$_3$): δ 150.16, 132.03, 130.41, 128.75, 126.22, 125.51, 123.85, 122.18.

5-(4-bromophenyl)-2-(p-tolyl)oxazole (BrPPOMe)

Iodine (1.86 g, 7.33 mmol) was added to the mixture of α2,4'-dibromoacetophenone (3.33 mmol, 926 mg), 4-methylbenzylamine (510 µL, 3.99 mmol) and oven-dried K$_2$CO$_3$ (2.44 g, 13.3 mmol) in 20.0 mL of DMF, and then the mixture was stirred at 80 °C. After the reaction was complete by TLC analysis (9 petroleum ether: 1 ethyl acetate), 30 mL ethyl acetate was added to dilute the reaction mixture, followed by the treatment of saturated sodium thiosulfate solution to quench the reaction. The organic layer was separated, washed in water (3 × 10 mL), and dried over anhydrous sodium sulfate. Silica column
chromatography eluted with petroleum ether–ethyl acetate (9:1) gave a pale yellow powder (500 mg, 50%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.98 (s, 2H), 7.56 (s, 4H), 7.42 (s, 1H), 7.28 (s, 2H), 2.41 (s, 3H). $^{13}$C $\{^1$H$\}$ NMR (125.8 MHz, CDCl$_3$): $\delta$ 150.34, 141.28, 132.49, 129.96, 127.42, 126.69, 125.95, 124.93, 124.24, 122.53, 21.97.

5-(4-bromophenyl)-2-(4-(tert-butyl)phenyl)oxazole (BrPPOtBu)

Iodine (1.86 g, 7.33 mmol) was added to the mixture of $\alpha$-2,4'-dibromoacetophenone (3.33 mmol, 926 mg), 4-tertbutylbenzylamine (710 µL, 3.99 mmol) and oven-dried K$_2$CO$_3$ (2.44 g, 13.3 mmol) in 20.0 mL of DMF, and then the mixture was stirred at 80 °C. After the reaction was complete by TLC analysis (9 petroleum ether: 1 ethyl acetate), 30 mL ethyl acetate was added to dilute the reaction mixture, followed by the treatment of saturated sodium thiosulfate solution to quench the reaction. The organic layer was separated, washed in water (3 × 10 mL), and dried over anhydrous sodium sulfate. Silica column chromatography eluted with petroleum ether–ethyl acetate (9:1) gave a pale yellow powder (750 mg, 75%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.01 (d, 2H), 7.57 (s, 4H), 7.49 (d, 2H), 7.43 (s, 1H). $^{13}$C $\{^1$H$\}$ NMR (125.8 MHz, CDCl$_3$): $\delta$162.02, 154.42, 152.53, 150.39, 132.52, 127.44, 126.58, 126.24, 125.98, 124.27, 122.55, 100.31, 35.38, 31.58.

OVS-PPOMe (SSQ-PPOMe)

To a vacuum dried and degassed 50 mL Schlenk flask, octavinylsilsequioxane (200 mg, 318 µmol) was added, followed by 5-(4-bromophenyl)-2-(p-tolyl)oxazole (800 mg, 2.55 mmol) and bis(tri-tert-butylphosphine)palladium(0) catalyst (1.64 mg, 3.20 µmol). The flask was evacuated and refilled with nitrogen three times. Anhydrous toluene (10.0 mL) was added, followed by addition of N,N-dicyclohexylmethylamine (550 µL, 2.55 mmol). The reaction was left to stir overnight at 80°C. Once there was no starting material detected by TLC, the product was cooled to room temperature and precipitated in acidic methanol and left in the freezer overnight. The mixture was gravity filtered and dried. It was then dissolved in minimal THF and reprecipitated in cold methanol and gravity filtered. A plug silica column chromatography was used to remove residual catalyst eluted with ethyl acetate. It was an off-white powder with deep blue fluorescence under UV light lamp.

SSQ-PPOtBu

To a vacuum dried and degassed 50 mL Schlenk flask, mixed T-8, T-10 and T-12 silsesquioxane (160 mg, 210 µmol) was added, followed by 5-(4-bromophenyl)-2-(4-(tert-butyl) phenyl)oxazole (590 mg, 1.66 mmol) and bis(tri-tert-butylphosphine)palladium(0) catalyst (1.10 mg, 2.10 µmol). The flask was evacuated and refilled with nitrogen three times. Anhydrous toluene (10 mL) was added, followed by addition of N,N-dicyclohexylmethylamine (360 µL, 1.68 mmol). The reaction was left to stir overnight at
80°C. Once there was no starting material detected by TLC, the product was cooled to room temperature and precipitated in acidic methanol and left in the freezer overnight. The mixture was gravity filtered and dried. It was then dissolved in minimal THF and reprecipitated in cold methanol and collected by gravity filtration. A plug silica column chromatography was used to remove residual catalyst eluted with ethyl acetate. The product is an off-white powder with deep blue fluorescence under UV light lamp.

4-bromo-2,5-diphenyloxazole (PPO-Br)

In oven and vacuum-dried 500 mL schlenk flask, 2,5-diphenyloxazole (40.0 g, 180 mmol) was added to 200 mL degassed chlorform. N-bromosuccinimide (48.3 g, 270 mmol) was added to the flask followed by few drops of hydrobromic acid. The reaction was stirred for a day at 65°C. Reaction was cooled down to room temperature after confirming completion by TLC (9 hexanes: 1 ethyl acetate). The mixture was precipitated in cold methanol and left in the freezer overnight. The product was collected by gravity filtration and dried resulting in white fluffy powder (50.0 g, 92%), precipitation in cold methanol could be done few times. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.09 (dd, 2H), 8.00 (d, 2H), 7.53 – 7.43 (m, 5H), 7.39 (t, 1H). $^{13}$C $^1$H NMR (125.8 MHz, CDCl$_3$): δ 159.85, 145.95, 131.47, 130.19, 129.38, 129.30, 129.24, 126.86, 126.25, 125.84, 125.51, 124.51, 112.56

2,4,5-triphenyloxazole (TPO)

In oven dried 100 mL Schlenk flask under argon atmosphere, 100 mg phenylboronic acid (820 µmol) was added to 210 mg 4-bromo-2,5-diphenyloxazole (690 µmol) in 6 mL anhydrous toluene. Aqueous solution of potassium carbonate (2.00 mL, 3.0 M) was added to the mixture, followed by 22.1 mg tetra-n-butylammonium bromide (70.0 µmol) and 31.7 mg tetrakis(triphenylphosphine) palladium(0) (30.0 µmol). The mixture was heated to 90°C overnight and TLC (hexanes) was used to check for completion. Once the reaction was complete as determined by TLC, liquid-liquid extraction was done with 30 mL ethyl acetate and 30 mL DI water. The product mixture as then passed through anhydrous magnesium sulfate, concentrated down and purified by silica chromatography with 10% activated carbon and eluted with hexanes to get 160 mg white powder (78.5%). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.18 (s, 2H), 7.72 (d, 4H), 7.48 (s, 3H), 7.45 – 7.30 (m, 6H). $^{13}$C $^1$H NMR (125.8 MHz, CDCl$_3$): δ 160.18, 145.55, 136.88, 132.67, 131.04, 129.83, 129.35, 129.05, 128.85, 128.14, 127.44, 127.15, 125.92
4-(4-methylstyryl)-2,5-diphenyloxazole (VPO)

In 150 mL oven-dried Schlenk flask under argon atmosphere, 1.05 mL 4-methylstyrene (mmol) was added to a solution of 2.00 g 4-bromo-2,5-diphenyloxazole (6.67 mmol) and 20.0 mL anhydrous toluene. N,N-dicyclohexylmethylamine (1.70 mL, 7.99 mmol) was added to the mixture, followed by 136 mg bis(tri-tert-butylphosphine)palladium(0) (270 µmol) and the mixture was heated to 80°C overnight. The mixture was checked by TLC (1 hexanes: 1 dichloromethane) for completion and quenched by 50 mL ethyl acetate followed by 50 mL brine solution twice and concentrated down. The off-white powder (7.00 g, 80.6%) was purified by silica chromatography (10% activated carbon) with hexanes as eluent with a small amount of dichloromethane and recrystallized in methanol. VPO $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.17 - 8.23 (m, 3H), 7.79 (d, 2H), 7.63 (d, 2H), 7.46 - 7.56 (m, 7H), 7.39 - 7.45 (t, 1H), 7.18 - 7.25 (t, 2H), 2.39 (s, 3H).

2,5-diphenyl-4-styryloxazole (SPO)

Same procedure as VPO apart from using styrene instead of 4-methylstyrene, yellow powder (84% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ ppm 8.23 (dd, 2H), 7.79 - 7.83 (d, 2H), 7.70 (d, 1H), 7.61 - 7.65 (d, 2H), 7.49 - 7.59 (m, 5H), 7.40 - 7.47 (m, 3H), 7.29 - 7.37 (m, 3H). $^{13}$C $^1$H NMR (125.8 MHz, CDCl$_3$): $\delta$ 159.95, 146.26, 136.97, 135.29, 132.42, 130.99, 129.71, 129.91, 129.48, 129.18, 128.66, 128.20, 127.97, 127.57, 125.84, 125.61, 117.58, 116.36.

4.3. PPO Variants

These variants are substituted at the 4 position on the oxazole ring that characteristically makes the variants optically similar to PPO while altering their physical properties such as melting point and decomposition temperatures.

4.3.1. Synthesis and Physical Properties of PPO Variants Type-1

2,4,5-triphenyloxazole (TPO) was synthesized through a two-step route as shown in Scheme 4.1. PPO was brominated in the first step with 96% yield and then the brominated PPO was coupled with
phenylboronic acid via normal Suzuki coupling conditions yielding a white powder with 75% yield. On the other hand, the synthesis of 2,5-diphenyl-4-styryloxazole (SPO) and 4-(4-methylstyryl)-2,5-diphenyloxazole (VPO) were achieved via normal Heck coupling conditions with styrene and 4-methylstyrene respectively (Scheme 4.1).

![Scheme 4.1 Synthesis of PPO derivatives.](image)

Figure 4.1 shows the comparison of UV-Vis and photoluminescence (PL) of PPO and PPO derivatives. As for TPO, from ground state geometrical computational optimizations (using ADF), the phenyl ring in the fourth position is orthogonal to the plane of phenyl rings in the second and fifth position as well as the core oxazole itself. Hence the reason for the near identical photo-absorption and photoemission of PPO and TPO. This indicates that there is minimal orbital overlap between the phenyl ring in the fourth position and the rest of the molecule. This is in agreement with a well-known practice in thermally activated delayed fluorescence OLEDs.\(^{118}\) We believe the rotational and vibrational freedom at the 4\(^{th}\) position might be the reason for the drop in PLQY from PPO’s 100% to TPO’s 67% as a result of vibrational dissipation (Table 4.1).\(^{119}\) The UV-Vis/PL of SPO and VPO are redshifted by about 20 nm. The reason for this is also explained by the ground state geometrical shape that shows the (phenyl ring in the second position) for both SPO and PPO getting pushed out of the plane of conjugation slightly and therefore the styryl group in the fourth position locks the oxazole and the phenyl ring in the fifth position in plane.
Figure 4.1 UV-Vis and PL of PPO and TPO.

The physical and optophysical properties of PPO and its derivatives are summarized in Table 1. Both melting and decomposition temperatures (T_d) of PPO derivatives are higher than PPO’s which will be key for use in high-temperature areas/borders. It’s possible that the T_d could possibly be the temperature at which these small molecules sublime.

Table 4.1 Physical properties of PPO and its derivatives.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Tm (°C)</th>
<th>Td (°C)</th>
<th>UV-Vis (nm)</th>
<th>PL max (nm)</th>
<th>Relative PLQY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO</td>
<td>72</td>
<td>132</td>
<td>304</td>
<td>364</td>
<td>100</td>
</tr>
<tr>
<td>TPO</td>
<td>115.11</td>
<td>169</td>
<td>308, 309</td>
<td>375</td>
<td>67</td>
</tr>
<tr>
<td>SPO</td>
<td>114</td>
<td>196</td>
<td>328</td>
<td>395</td>
<td>-</td>
</tr>
<tr>
<td>VPO</td>
<td>139</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Tm-Melting point, Td-decomposition temperature.

4.3.2. Radiation Performance of PPO Variants Type-1

In total, six plastic scintillator samples of 6.0 g each were made with TPO. The photoabsorption and photoemission similarities between PPO and TPO was important in deciding the effect of symmetry, melting point and PLQY have on radiation performance. As described earlier, PPO is perfectly planar whereas TPO is not. In terms of solubility, both PPO and TPO have high solubility in vinyl toluene exceeding 25 wt%. Figure 4.2 shows the relationship between the light output of PPO and TPO doped PVT
samples as the concentration increases. Both maintained nearly constant light output despite change in concentration. For PPO, the light output was nearly 100% compared to BC-406 commercial scintillator whereas TPO’s light output stayed constant at around 65%. These light output values are identical to the PLQY of PPO and TPO indicating the direct correlation between scintillation light output and PLQY. It’s noteworthy that both dopants showed a slight increase in light output as the concentration increased in PVT. This is contrary to our expectations of concentration fluorescence quenching due to dopant aggregation at higher concentrations. However, it is possible that the first non-radiative energy transfer from PVT to these dopants could be increasing more dramatically compared to the radiative energy transfer to the wavelength shifter (POPOP), outweighing concentration fluorescence quenching. Figure 4.2 shows the excellent discrimination TPO demonstrate even at low energies.

Figure 4.2 Pulse Shape Discrimination of 20 wt% TPO, 0.1 wt% POPOP in PVT (6g sample)
Figure 4.3 shows the correlation between these dopants and mixed radiation discrimination performance. Both dopants showed identical discrimination (FoM) up to 10 wt%. However, after 10 wt% PPO’s discrimination increased drastically with increase in concentration whereas the increase in FoM of TPO samples stopped below 1.0 FoM. If we were to assume that PSD is a result of triplet-triplet annihilation, the symmetry of these dopants must come in play with discrimination performance. PPO being planar is prone to aggregation via $\pi-\pi$ stacking and in contrary, TPO’s lack of symmetry inhibits formation
of aggregation domains. If the density of triplet state electrons is the same in over-doped PPO and TPO, the mobility of these states will determine their eventual annihilation. Therefore, the lack of symmetry in TPO could perhaps be the reason for the reduced discrimination performance due to lower triplet state mobilities in TPO vs PPO.\(^\text{97}\)

**4.3.3. Hardness of Over-doped PPO Variant Type-1**

There were noticeable mechanical differences among samples with varying amounts of dopants and these differences were qualitatively measured by thermal analysis using DSC. High glass temperatures of plastic scintillators are assumed to produce samples with enhanced mechanical properties. A razor blade was used to cut 15-20 mg from each sample to be used to measure glass transition temperature by DSC. As shown in Figure 4.4, PPO doped plastic showed a drastic decrease in glass transition relative to TPO doped plastic scintillator. This correlate well to the physical ‘softness’ of PPO samples confirming our hypothesis.

![Figure 4.5 Correlation between glass transition of plastic scintillators and amount of primary dopant as measured by differential scanning calorimetry (DSC).](image)

**4.4. Silesquioxanes Doped Plastic Scintillators (PPO Variant Type-2)**

The synthesis of rigid 3-D dopants potentially alleviates the issue of dopant aggregation versus concentration. For example, it is well known that increasing the concentration of fluorescent dopants beyond just 1% results in concentration quenching and red shifted PL.\(^\text{120}\) As PSD generally requires an excess of 15% dopant, there will clearly be some aggregation and red shifted PL. Normally one mechanism for the concentration quenching is the \(\pi-\pi\) aggregation of the dopants due to their planar aromatic molecular structure. The goal of the 3-D dopant study is to prepare non-aggregating highly fluorescent dopants and study the effects of concentration on scintillation and PSD. Silesquioxanes (SSQs) are three-dimensional
cores which have been used as a versatile reactive intermediate to immobilize fluorescent dopants to decrease aggregation induced effects, increase thermal stability and glass transition temperature. Octa, deca, dodeca vinyl SSQ mixtures have excellent reactivity with commonly available brominated fluorescent molecules via Heck coupling. The ease of purification via precipitation followed by short silica chromatography, and high solubility in common organic solvents makes them good candidates as a primary dopant for scintillation.

Scheme 4.2 Synthesis of brominated oxazole derivatives

Figure 4.6 Chemical structure of brominated PPO derivatives

To date we have prepared 3-D dopants based on octavinyl-T8-silsesquioxane (OVS) and a mixture of 5% octavinyl-T8-, 65% decavinyl-T10- and 30% dodecavinyl-T12 (40%) SSQ cores. In order to explore SSQs for scintillation application, brominated PPO derivatives were synthesized using a domino reaction with iodine as a co-catalyst in Scheme 4.2 which uses dibromo-acetophenone and alkyl substituted primary benzylamine with yields ranging from 50-87%.

As shown in Figure 4.5, three brominated PPO derivatives were synthesized. Their proton NMRs are overlayed as shown in Figures 4.7. As expected, the absorption and emission of brominated PPO derivatives were nearly identical to each other and redshifted from PPO (Figure 4.8). The slight difference among the brominated PPO derivatives is attributed to contribution by the addition of the alkyl chains (-Me and -tBu). The brominated PPO’s are redshifted from PPO albeit less than 15 nm (Figure 4.8). However, the shift becomes more pronounced once brominated PPO’s are attached to the OVS cage. The immobilization of PPO derivatives was achieved via normal Heck coupling conditions (Scheme 4.3). It was difficult controlling the number of PPO derivatives attached to the OVS core despite varying catalyst,
equivalence of BrPPO derivative relative to vinyl cages, reaction time and type of base used. Multiple purifications including silica column chromatography, precipitation and recrystallization techniques were attempted to separate the fractions without success.

Figure 4.7 $^1$H NMR of BrPPO, BrPPOMe and BrPPOtBu

Figure 4.9 shows the MALDI mass spectra of the immobilized PPOMe (OVS-PPOMe) with 1,8,9-trihydroxyanthracene as the matrix in dichloromethane. The fragments shown in Figure 4.9 indicate that more than eight PPOMe (Ligand-L) were attached. In this case up to 11 substitutions were achieved which means more than one ligand was attached per vinyl group on the OVS. Other researchers have observed similar results.$^{122, 124}$
Figure 4.8 UV-VIS/PL of PPO and PPO derivatives

Scheme 4.3 Heck coupling synthesis of immobilized PPO derivatives.
As shown in Figure 4.10, both photoabsorption and photoemission of OVS-PPOMe were redshifted from PPO by 40nm. The stoke shift of OVS-PPOMe is nearly 55nm relative to PPO’s 35nm which theoretically makes it more suitable for scintillation use due to its limited light reabsorption. Notice that maximum photoemission of OVS-PPOMe is within the photosensitivity of blue PMT, therefore use of wavelength shifter is not needed. Unlike PPO, there are no peak features for both absorption and emission of OVS-PPOMe indicating fixed transitions with little to no vibrational modes or dissipation.
Figure 4.11 shows the change in mass response of PPO and OVS-PPOMe with temperature. PPO starts decomposing/subliming at around 130°C and completely decomposes/sublimes by 250°C whereas OVS-PPOMe is stable up to 300°C (<5% mass loss). The gradual mass loss seen in OVS-PPOMe thermal profile is evident of multiple ligands attached to the core. The superior thermal property and large stoke-shift encouraged us to make a 20g sample with 1.0 wt% OVS-PPOMe in PVT without a wavelength shifter. Surprisingly, as the polymerization progressed, the sample developed a dark color despite the low concentration, we have no idea where the dark color comes from. However, it emitted bright blue color under illumination with a 365nm lamp which meant the ligand attached (PPOMe) is still intact during polymerization. The scintillation result from $^{22}$Na gamma source (1.27 MeV) was the bare minimum-1% light output.

In case the issue is somehow related to the OVS core, we have prepared another 3-D SSQ as shown in Scheme 4.4. The yield of this reaction was similar to OVS-PPOMe of around 90%, white powder with bright blue fluorescence under 365nm hand lamp. The MALDI with 1,8,9-trihydroxyanthracene in CH$_2$Cl$_2$ (Figure 4.12) shows that all the three cage cores reacted successfully with BrPPOtBu.
Like OVS-PPOMe, the distribution of ligand attachment per vinyl is still random with up to 9 ligands per 8 vinyl groups. There were two samples made with the mixed cage-PPOtBu but it developed the same dark color as OVS-PPOMe during polymerization. As a result, cyclophosphazene-PPO was synthesized as alternative immobilized PPO and doped 1.0 wt% in PVT without a wavelength shifter and observed scintillation approximately 40% of commercial scintillation. This proof of concept result suggests that SSQ’s have instability issues during the radical polymerization.

More investigation is needed to explore the parameter space for the development of dark color during polymerization. In general, the sample quality needs to improve and the reason for negligible scintillation from gamma radiation also needs further study. Going forward, altering the method of polymerization and the polymer matrix might both suitable routes.
4.5. Conclusion

Mechanically and thermally stable plastic scintillators allow the deployment of radiation detectors in remote areas due to its inherent capability to withstand high temperatures. The synthesis of PPO derivatives at the 4th position with a simple bromination of PPO and subsequent Heck or Suzuki coupling at high yields and simple purification schemes allowed us to synthesize thermally stable dopants. Plastic scintillators made from these dopants were mechanically superior compared to PPO doped plastic scintillators. We also synthesized immobilized PPO derivatives at high yields with relatively high thermal decomposition. However, the plastics made from these dopants developed dark color during polymerization and scintillated poorly despite bright blue emission under 365 nm irradiation. The reason for this is attributed to the core cage somehow being affected by radicals since a different core (cyclicphosphazenes) attached with PPO showed scintillation (35% LY) with a gamma source.
CHAPTER 5. BORON CONTAINING SMALL ORGANIC MOLECULES FOR DETECTION OF THERMAL NEUTRON

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Additional data to be submitted shortly. Additional authors are Joshua T Koubek and Roshan Fernando.

5.1. Introduction

Plastic scintillators are polymer-based detector materials for gamma radiation, fast neutrons and other charged particles.\textsuperscript{61,125} Its low cost, fast-timing resolution and ease of large-scale production make it a first-line detection method compared to inorganic crystal scintillators.\textsuperscript{10,126} However, due to the absence of high neutron capture isotopes in plastic scintillators, they are unable to detect thermal neutrons and are therefore concurrently used with \textsuperscript{3}He gas detectors at international borders and airports to detect illicit trafficking of special nuclear materials (SNM).\textsuperscript{127} Due to \textsuperscript{3}He scarcity and increasing demand, alternative isotopes such as \textsuperscript{10}B and \textsuperscript{6}Li with comparable thermal neutron capture cross sections and higher natural abundances have been investigated.\textsuperscript{49,128} Current developments of neutron sensitive plastic scintillators mainly rely on commercially available carboranes as a boron source due to their high boron content.\textsuperscript{52} Thermal neutrons are detected via the capture reaction on the nucleus of \textsuperscript{10}B and measuring the scintillation light produced by the alpha particles (\textsuperscript{4}He) released by this reaction, shown in Equation 5.1.\textsuperscript{13} The neutron induced reaction on \textsuperscript{10}B has a thermal cross section of 3837 barns (\textsuperscript{3}He is 5333 barns) and results in low mass ions (alpha and \textsuperscript{7}Li) as the products that carry significant kinetic energy to be easily detected.\textsuperscript{129}

\begin{equation}
\textsuperscript{10}B + n = \begin{cases} \textsuperscript{7}Li + \textsuperscript{4}He, & Q = 2.792\text{MeV}, 6\% \\ \textsuperscript{7}Li + \textsuperscript{4}He + \gamma(480\text{keV}), & Q = 2.310\text{MeV}, 84\% \end{cases}
\end{equation}

Equation 5.1 Boron capture reaction with thermal neutron. Carboranes (~75% wt.) are currently the state-of-the-art boron dopant for detection of thermal neutron. Although carboranes have high boron content, they have limited solubility in plastic scintillator formulations, are very expensive, and the cost is significantly higher in their \textsuperscript{10}B enriched form. Alternatives to carboranes need to be produced with efficient synthesis methods and inexpensive reagents. However, organic scintillators suffer in light ion detection from a type of pulse height defect, named alpha quenching, that reduces the number of emitted scintillation photons to a small fraction of the quantity emitted in detection of gamma photons of the same energy. It has been observed that the addition of higher concentrations of additives (fluorescent or neutron sensitive)
can lower the overall light output of a scintillator and/or worsen the alpha quenching effect. The combination of light output and alpha quenching determines the overall performance of a scintillator in how well one can separate the neutron reaction signal from gamma backgrounds and electronic noise.

Alternative methods of thermal neutron detection include boron containing semiconductor crystals, enriched boron-10 fluoride ($^{10}\text{BF}_3$) gas filled proportional counters, and boron lined tube counters along with liquid scintillators doped with boron compounds such as trimethyl borate. However, growing crystals in large quantities for significant area coverage is difficult and $^{10}\text{BF}_3$ has severe limitations in deployment due to its gaseous form at ambient conditions and toxicity. While boron lined tubes are physically similar to $^3\text{He}$ tubes, they suffer from reduced efficiencies due to the energy loss effects from having a solid boron wall coverage. Trimethyl borate mixed into liquid scintillators of many varieties has been reported, however this molecule is hydrolytically unstable, has a very low flash point and is required to be very well sealed from oxygen in order to reduce quenching effects and maintain efficiency. Other isotopic candidates for scintillators such as $^6\text{Li}$ or $^{155}\text{Gd}/^{157}\text{Gd}$ are not as attractive as $^{10}\text{B}$ due to higher cost, lack of availability, and reduced compatibility with inexpensive polymer matrices. Furthermore, the price of $^{10}\text{B}$ containing additives to these matrices needs to be comparable to that of the polymers in order to achieve neutron sensitivity in a cost-effective manner.

Detection of neutron plays an important role in the identification of illicit trafficking of special nuclear materials. With increasing demand, the current state-of-the-art neutron detectors deployed, which are based on $^3\text{He}$ gas proportional counters surrounded by thermalizing materials, have become significantly more expensive. Therefore, alternatives with lower cost and similar efficiency as well as comparable signal to background ratio are sought. Recent advances in $^3\text{He}$ alternatives have used plastic or liquid scintillator compounds that contain high neutron cross-section isotopes such as $^6\text{Li}$, $^{10}\text{B}$, and $^{155}\text{Gd}/^{157}\text{Gd}$ isotopes. Our group is focusing on the incorporation of boron containing organic compounds because of the significant natural abundance (~20%) of $^{10}\text{B}$, its high thermal neutron reaction cross section and easy availability in highly enriched isotopic concentrations. Previous work incorporating boron in the chemical form of carboranes into plastic matrices achieved promising results and has been used in some commercial products. However, the price of the neutron sensitive scintillator product is still dominated by carboranes price tag and would need to be lowered to allow widespread deployment in large portal type monitor applications. Additionally, the signal to background ratios achieved are not yet competitive to $^3\text{He}$ based detectors motivating further research on boron containing scintillator systems.

We hereby present three simple approaches to detect thermal neutrons using simple small organic molecules containing boron.
5.2. Experimental Section

The synthesis, characterization of small molecules and description of their properties were done by Henok A Yemam whereas the samples were prepared by both Adam Mahl and Henok A Yemam. The radiation testing and analysis were solely performed by Adam Mahl. The computational results were provided by Dr. Jonathan Tinkham and Joshua T. Koubek.

5.2.1. Instrumentation

All reagents were purchased from either Sigma-Aldrich, Frontier Scientific, or TCI America unless otherwise noted. $^1$H and $^{13}$C NMR spectra were obtained on a JEOL ECA 500 liquid-state NMR spectrometer and data obtained was manipulated in ACD/NMR processor software.

X-ray data were collected on a Bruker-Nonius X8 Proteum CCD diffractometer using Cu $K\alpha$ radiation. The structures were solved using SHELXT and refined using SHELXL programs. Molecular fragment editing, including the construction of suitable disorder models was performed using the XP program of SHELXTL. Hydrogen atoms were included using a riding model. The final models were checked using an R-tensor, and by validation routines of the Platon program as implemented in the IUCr checkCIF facility.

Mass spectrometric measurements were acquired in positive-ion and negative-ion modes with a Bruker Ultraflextreme MALDI-TOF mass spectrometer (Bruker Daltonics, Billerica, MA) equipped with a 355 nm Nd:YAG laser. Spectra were collected in reflector mode with a grid voltage of 50.3%, and a low mass cutoff of 200 Da. Five replicate spectra were collected for each analysis as 100 shot composites at a sampling frequency of 1 kHz using automated laser rastering.

Molecular weight and molecular weight distributions of polymer samples were determined by gel permeation chromatography (GPC) using stabilized tetrahydrofuran (THF) as the eluent with a flow rate of 1.0 mL/min (Viscotek GPC pump; PLgel 5µm MIXED-C and MIXED-D columns: molecular weight range 200-2,000,000 and 200-400,000 g/mol (PS equiv), respectively.

5.2.2. Preparation of Samples, Radiation Set-up and Testing

Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. The inhibitor in 4-vinyltoluene was removed by filtering through a 100 mg plug of a potassium carbonate and basic alumina mixture. An example of a typical plastic scintillator disc preparation is as follows. In a 120 mL clear glass bottle, the calculated amounts of 2,5-diphenyl oxazole (PPO), 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP), boron based materials, and AIBN were dissolved in the liquid 4-vinyltoluene monomer. The clear solution was degassed by gently bubbling with argon gas for 15-30 min to displace and remove oxygen. The presence of oxygen inhibits polymerization, causes significant light emission quenching, and sample discoloration. Therefore, the atmosphere inside the vacuum oven was exchanged from air to argon.
via a few cycles of evacuation followed by argon refill. The solution was then bulk polymerized in an oil bath or an argon-filled vacuum oven at 80°C for 96 hours, followed by 90°C for 12 hours. The sample was cooled to room temperature and the glass bottle was broken with a mallet, giving a clear polymer disk of scintillating polymer. The sample was machined down to one flat side (meniscus side) using 100 grit sandpaper by hand or by belt depending on its mechanical and thermal stability. Then, the sample was polished using 150, 220, 300, 400, 600 and 600 wet-grit sandpapers. The final touches of polishing was done on a loose-cotton buffer wheel using white abrasive polishing compound and finished with blue buffing compound. Each sample has 4.7 cm diameter and 1.1-1.3 cm thickness.

Solid scintillator samples were tightly wrapped in white Teflon tape on all sides but one and attached to a Hamamatsu PMT (H2431-50) with silicone optical grease. The whole assembly was wrapped in aluminum foil and sealed with light-tight electrical tape. The PMT was biased using standard electronics and read out with a custom built waveform digitizer and DAQ system controlled by a MIDAS interface.

Samples were first exposed to a $^{137}$Cs source (gamma emission of 662 keV) in order to quantify general light output properties. Examining the position of the Compton Edge (C.E.) feature (at 477 keV) in this output spectra allowed us to calibrate each sample individually and establish an individual sample energy scale (in keV$_{ee}$). By comparing each sample's C.E. location to a commercial control sample’s C.E. location on an absolute scale, we determined a relative light yield output.

Next, the samples were exposed to a $^{244}$Cm/$^{13}$C source in two different shielding configurations, which produce different mixed neutron and gamma fields. First a “lead castle” setup was used to shield the detector and samples from the gamma flux and transmits a ‘fast’ neutron spectrum at the detector location, which allowed us to test fast neutron response as well as test and quantify the samples n/γ PSD capabilities. Next the sample and source were placed in a similar castle built out of poly(ethylene) bricks that would alter the neutron spectrum producing a more thermalized flux. This allowed us to test low energy neutron response and identify the $^{10}$B neutron reaction occurring in the sample. Finally, the detector was wrapped in a cadmium shield within the poly(ethylene) cave. Due to the high cadmium, thermal neutron capture cross section, this exposure of our samples eliminated the thermal neutron flux and allowed us to collect gamma background spectra that could be subtracted from the non-cadmium shielded spectra, exposing more clearly the samples’ response to thermal neutrons.

Once enough statistics were obtained, the collected waveforms were analyzed using the ROOT data analysis framework, to develop relevant output spectra for extracting light output and pulse shape response information. The stored pulse is integrated over 2 different integration times where the full integration time period (“Pulse Area”) is proportional to the deposited energy in the sample that is converted to scintillation photons. The integral over a delayed time period (“Delayed Area”) can be used to describe the
pulse shape. The ratio of “Delayed Area” and “Pulse Area” is the “Delayed Area Fraction” and is used later to display and quantify pulse shape discrimination.

5.2.3. Synthesis Procedures

Two approaches were taken for the synthesis of borylated benzene and pyrene molecules. One, conventional heating using slightly modified Miyaura condition. Second, microwave heating at elevated temperature was used to achieve decent yields in just 40 minutes.

5.2.3.1. Conventional Heating Experimental Conditions

4,4,5,5-tetramethyl-2-(pyren-1-yl)-1,3,2-dioxaborolane (MBP)

In a flame-dried Schlenk tube under argon atmosphere, 1-bromopyrene (200 mg, 0.71 mmol) and B₂Pin₂ (270 mg, 1.07 mmol) were dissolved in 20 mL 1,4-dioxane. Flame dried KOAc (210 mg, 2.13 mmol) was added quickly to the mixture followed by PdCl₂(dppf) (17 mg, 0.021 mmol). The mixture was heated at 90°C overnight. Once the reaction was complete, the mixture was cooled to room temperature and 20-30 mL ethyl acetate was added to quench the reaction. 30 mL DI water was added to extract the aqueous phase, 30 mL brine (2X) was used to wash the organic phase, and it was dried over anhydrous MgSO₄ and filtered. After concentrating down the filtrate, silica column chromatography with hexanes as eluent gave a yellow powder (175 mg, 75%). ¹H NMR (500.0 MHz, CDCl₃): δ 9.16 (d, 1H; CH), δ 8.02-8.28 (m, 7H; CH), δ 1.54 (s, 12H; CH₃).

13C {¹H} NMR (125.8 MHz, CDCl₃): δ 124.02-136.41 (CH), δ 83.82 (CCH₃), δ 25.00 (CH₃), n.o. (CB).

1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (BBP)

In a flame-dried Schlenk tube under argon atmosphere, 1,6-dibromopyrene (200 mg, 0.56 mmol) and B₂Pin₂ (420 mg, 1.67 mmol) were dissolved in 20 mL 1,4-dioxane. Flame dried KOAc (327 mg, 3.32 mmol) was added quickly to the mixture followed by PdCl₂(dppf) (13.6 mg, 0.017 mmol). The mixture was heated at 90°C overnight. A scoop of catalyst (5 mg) was added to complete the reaction. Once the reaction was complete, the mixture was cooled to room temperature and 20-30 mL ethyl acetate was added to quench the reaction. 30 mL DI water was added to extract the aqueous phase, 30 mL brine (2X) was used to wash the organic phase, and it was dried over anhydrous MgSO₄ and filtered. After concentrating down the filtrate, silica column chromatography with hexanes:dichloromethane (1:1) mixture as eluent gave a yellow powder (200 mg, 79%). ¹H NMR (500.0 MHz, CDCl₃): δ 9.12 (d, 2H; CH), δ 8.56 (d, 2H; CH), δ 8.21 (d, 2H;
CH), δ 8.15 (d, 2H; CH), δ 1.51 (s, 24H; CH<sub>3</sub>).<sup>13</sup>C <sup>1</sup>H NMR (125.8 MHz, CDCl<sub>3</sub>): δ 133.77 (CH), δ 133.20 (CH), δ 129.22 (CH), δ 127.99, δ 124.55 (CH), δ 83.96 (CCH<sub>3</sub>), δ 25.12 (CH<sub>3</sub>), n.o. (CB). MALDI TOF MS: m/z 455 (M<sup>+</sup>), 353, 326 (M-Bpin<sup>+</sup>).

1,3,6,8-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (TBP)

\[
\text{Bpin} \quad \text{Bpin} \\
\text{Bpin} \quad \text{Bpin}
\]

In a flame-dried Schlenk tube under argon atmosphere, 1,3,6,8-tetrabromopyrene (500 mg, 0.97 mmol) and B<sub>2</sub>Pin<sub>2</sub> (1.47 g, 5.79 mmol) were dissolved in 20 mL 1,4-dioxane. Flame dried KOAc (1.14 g, 11.6 mmol) was added quickly to the mixture followed by PdCl<sub>2</sub>(dppf) (24 mg, 0.029 mmol). The mixture was heated at 90°C overnight. At the 16hr mark, 10 mg catalyst was added to complete the reaction. Once complete, the mixture was cooled to room temperature and 20-30 mL ethyl acetate was added to quench the reaction. 30 mL DI water was added to extract the aqueous phase, 30 mL brine (2X) was used to wash the organic phase, and it was dried over anhydrous MgSO<sub>4</sub> and filtered. After concentrating down the filtrate, silica column chromatography with hexanes:ethyl acetate (8:2) mixture as eluent gave a yellow powder (592 mg, 87%). MALDI TOF MS: m/z 707 (M<sup>+</sup>), 581 (M-Bpin<sup>+</sup>), 454(M-2Bpin)<sup>+</sup>, 227 (M-3Bpin)<sup>+</sup>.

1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (135TrBB)

In a flame-dried Schlenk tube under argon atmosphere, 1,3,5-tribromobenzene (200 mg, 0.64 mmol) and B<sub>2</sub>Pin<sub>2</sub> (807 mg, 3.18 mmol) were dissolved in 20 mL 1,4-dioxane. Flame dried KOAc (500 mg, 5.08 mmol) was added quickly to the mixture followed by PdCl<sub>2</sub>(dppf) (15.5 mg, 0.029 mmol). The mixture was heated at 90°C overnight. The progress of reaction was tracked by TLC (9 hexanes: 1 ethyl acetate) and visualization was achieved in an iodine chamber. Two spots (Rf 0.20 and Rf 0.25) were observed and heating was stopped and allowed to cool down to room temperature. 20-30 mL ethyl acetate was added to extract the aqueous phase and 30 mL brine (2X) was used to wash the organic phase, dried over anhydrous MgSO<sub>4</sub> and filtered. After concentrating down the filtrate, hexanes:ethyl acetate (9:1) mixture was used to elute Rf 0.25 in silica column chromatography to yield white powder [69%, 200 mg]. <sup>1</sup>H NMR (500.0 MHz, CDCl<sub>3</sub>): δ 8.36 (s, 3H; CH), δ 1.32 (s, 36H; CH<sub>3</sub>). <sup>13</sup>C <sup>1</sup>H NMR (125.8 MHz, CDCl<sub>3</sub>): δ 144.14 (CH), δ 83.79 (CCH<sub>3</sub>), δ 24.96 (CH<sub>3</sub>), n.o. (CB).
2,2',2''-(benzene-1,2,4-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (124TrBB)

\[
\begin{align*}
\text{Bpin} & \quad \text{Bpin} \\
\text{Bpin} & \quad \text{Bpin}
\end{align*}
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In a flame-dried Schlenk tube under argon atmosphere, 1,2,4-tribromobenzene (200 mg, 0.64 mmol) and B\textsubscript{2}Pin\textsubscript{2} (810 mg, 3.18 mmol) were dissolved in 20 mL 1,4-dioxane. Flame dried KOAc (500 mg, 5.08 mmol) was added quickly to the mixture followed by PdCl\textsubscript{2}(dppf) (15.5 mg, 0.029 mmol). The mixture was heated at 90°C overnight. The progress of reaction was tracked by TLC (9 hexanes: 1 ethyl acetate) and visualization was achieved in an iodine chamber. Two spots (R\textsubscript{f} 0.20 and R\textsubscript{f} 0.25) were observed and heating was stopped to allow cooling to room temperature. 20-30 mL ethyl acetate was added to quench the reaction. 30 mL DI water was added to extract the aqueous phase, 30 mL brine (2X) was used to wash the organic phase, and it was dried over anhydrous MgSO\textsubscript{4} and filtered. After concentrating down the filtrate, hexanes:ethyl acetate (9:1) mixture was used to elute R\textsubscript{f} 0.2 by silica column chromatography to yield a white powder (280mg, 96%). \textsuperscript{1}H NMR (500.0 MHz, CDCl\textsubscript{3}): δ 8.06 (s,1H; CH), δ 7.80 (dd,1H; CH), δ 7.62 (d,1H; CH), δ 1.36 (s, 12H; CH\textsubscript{3}), δ 1.33 (s, 12H; CH\textsubscript{3}), δ 1.26 (s, 12H; CH\textsubscript{3}). \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (125.8 MHz, CDCl\textsubscript{3}): δ 139.48 (CH), δ 135.47 (CH), δ 132.41 (CH), δ 83.44 (CCH\textsubscript{3}), δ 83.69 (CCH\textsubscript{3}), δ 83.480 (CCH\textsubscript{3}), δ 25.02 (CH\textsubscript{3}), n.o. (CB).

1,2,4,5-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (TBB)

\[
\begin{align*}
\text{Bpin} & \quad \text{Bpin} \\
\text{Bpin} & \quad \text{Bpin}
\end{align*}
\]

In a flame-dried Schlenk tube under argon atmosphere, 1,2,4,5-tetrabromobenzene (380 mg, 0.97 mmol) and B\textsubscript{2}Pin\textsubscript{2} (1.47g, 5.79mmol) were dissolved in 20 mL 1,4-dioxane. Flame dried KOAc (1.14 g, 11.6 mmol) was added quickly to the mixture followed by PdCl\textsubscript{2}(dppf) (23.6 mg, 0.030 mmol). The mixture was heated at 90°C overnight. The progress of reaction was tracked by TLC (9 hexanes: 1 ethyl acetate) and visualization was achieved in an iodine chamber. Two spots (Rf 0.20 and Rf 0.25) were observed and heating was stopped to allow cooling to room temperature. 20-30 mL ethyl acetate was added to quench the reaction. 30 mL DI water was added to extract the aqueous phase, 30 mL brine (2X) was used to wash the organic phase, and it was dried over anhydrous MgSO\textsubscript{4} and filtered. After concentrating down the filtrate, hexanes:ethyl acetate (9:1) mixture was used to elute R\textsubscript{f} 0.25 in silica column chromatography to yield a white powder. Alternatively, after concentration of the filtrate, both fractions were collected by filtering through a silica chromatography column, with elution by hexanes: ethyl acetate (7: 3) mixture. The mixture was vacuum dried and 20 mL hexanes was added and left in the fridge overnight. The precipitate was collected by filtration (202mg, 36%). \textsuperscript{1}H NMR (500.0 MHz, CDCl\textsubscript{3}): δ 7.89 (s,2H; CH), δ 1.36 (s, 36H; CH\textsubscript{3}). \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (125.8 MHz, CDCl\textsubscript{3}): δ 137.90 (CH), δ 83.84 (CCH\textsubscript{3}), δ 24.99 (CH\textsubscript{3}), n.o. (CB).
Vacuum refill a clean and dry 250 mL two arm round bottom flask with a stir bar and a dropping funnel four times. Cannula transfer 50.0 mL tBuLi into the round bottom and add 45.0 mL of anhydrous pentane. Stir mixture at -78°C for 30min or until at room temperature. In a clean dry 50 mL round bottom flask add 8.45 mL bromobenzene and vacuum refill 3 times followed by 10-15min of bubbling Ar through the solution followed by an additional vacuum refills 4 times. Add 10 mL of anhydrous THF to the tBuLi solution and to the bromobenzene. Transfer the bromobenzene solution into the dropping funnel. Allow the bromobenzene solution to drip slowly (over about 1h) into the tBuLi solution while under Ar. The solution will go from pale yellow to off white after approx. 2h. Then add 15.87 g of dry isoproxyBpin to the dropping funnel and slowly drop into the reaction over 30m. Allow the reaction to continue at -78°C for 24h. Afterwards the reaction vessel was removed from the cold bath and allow to warm to room temperature while being stirred over approx. 5h. The reaction was then extracted with Et2O, dried with MgSO4 and rotovapped down to remove the majority of the solvents. Following this, the product was vacuum distilled to remove the remaining volatile materials and the product was then collected as a white solid and stored in the freezer until needed. (yield 46%, 7.54 g). 1H NMR (500.0 MHz, CDCl3) δ 1.34 (s, 12 H), 7.34 - 7.38 (t, 2 H), 7.44 - 7.47 (t, 1 H), 7.80 - 7.81 (d, 2 H). 13C {1H} NMR (125.8 MHz, CDCl3): δ 135.13 (CH), δ 131.65 (CH), δ 128.10 (CH), δ 84.15 (CCH3), δ 25.24 (CH3), n.o. (CB).

5.2.3.2. Microwave Synthesis Experimental Conditions

4,4,5,5-tetramethyl-2-(pyren-1-yl)-1,3,2-dioxaborolan-2-yl)pyrene (BBP)

1-bromopyrene (500 mg, 1.78 mmol) and B2Pin2 (900 mg, 3.56 mmol) were added to a 20 mL microwave flask. Flame dried KOAc (524 mg, 5.33 mmol) and PdCl2(dppf) (58 mg, 0.071 mmol) were added quickly to the flask. After adding 12 mL 1,4-dioxane, the flask was capped tightly and run at 130°C for 40min. Once the reaction was complete, the mixture was cooled to room temperature and 15 mL ethyl acetate was added to quench the reaction. 20 mL DI water was added to extract the aqueous phase and 20 mL brine (2X) was used to wash the organic phase. It was dried over anhydrous MgSO4 and filtered. After concentrating down the filtrate, silica column chromatography with hexanes as eluent gave a yellow powder (396 mg, 68%).

1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (BBP)

1,6-dibromopyrene (500 mg, 1.39 mmol) and B2Pin2 (1.76 g, 6.94 mmol) were added to a 20 mL microwave flask. Flame dried KOAc (818 mg, 8.33 mmol) and PdCl2(dppf) (45.4 mg, 0.056 mmol) were added quickly to the flask. After adding 12 mL 1,4-dioxane, the flask was capped tightly and run at 130°C for 40min. Once the reaction was complete, the mixture was cooled to room temperature and 15 mL ethyl
Acetate was added to quench the reaction. 20 mL DI water was added to extract the aqueous phase and 20 mL brine (2X) was used to wash the organic phase. It was dried over anhydrous MgSO₄ and filtered. After concentrating down the filtrate, silica column chromatography with a mixture of hexanes and dichloromethane (1:1) as eluent yielded a yellow powder (400 mg, 63%).

1,3,6,8-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (TBP)

1,3,6,8-tetrabromopyrene (500 mg, 0.97 mmol) and B₂Pin₂ (1.47 g, 5.79 mmol) were added to a 20 mL microwave flask. Flame dried KOAc (947 mg, 9.65 mmol) and PdCl₂(dppf) (31.5 mg, 0.039 mmol) were added quickly to the flask. After adding 12 ml 1,4-dioxane, the flask was capped tightly and run at 130°C for 1 hr. Once the reaction was complete, the mixture was cooled to room temperature and 15 mL ethyl acetate was added to quench the reaction. 20 mL DI water was added to extract the aqueous phase and 20 mL brine (2X) was used to wash the organic phase. It was dried over anhydrous MgSO₄ and filtered. After concentrating down the filtrate, silica column chromatography with a mixture of hexanes and ethyl acetate (8:2) as eluent yielded a yellow powder (579 mg, 85%).

1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (135TrBB)

1,3,5-tribromobenzene (500 mg, 1.59 mmol) and B₂Pin₂ (1.82 g, 7.15 mmol) were added to a 20 mL microwave flask. Flame dried KOAc (1.17 g, 11.9 mmol) and PdCl₂(dppf) (52 mg, 0.064 mmol) were added quickly to the flask. After adding 12 mL 1,4-dioxane, the flask was capped tightly and run at 130°C for 1 hr. TLC (9 hexanes: 1 ethyl acetate) showed there were two spots Rf 0.2 and Rf 0.25. The mixture was cooled to room temperature and 30 ml ethyl acetate was added to quench the reaction. 30 mL DI water was added to extract the aqueous phase, 30 mL brine (2X) was used to wash the organic phase, and it was dried over anhydrous MgSO₄ and filtered. After concentrating down the filtrate, hexanes:ethyl acetate (9:1) mixture was used to elute Rf 0.25 by silica column chromatography to yield a white powder (440 mg, 61%).

2,2',2''-(benzene-1,2,4-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (124TrBB)

1,3,5-tribromobenzene (500 mg, 1.59 mmol) and B₂Pin₂ (1.82 g, 7.15 mmol) were added to a 20 mL microwave flask. Flame dried KOAc (1.17 g, 11.9 mmol) and PdCl₂(dppf) (51.9 mg, 0.064 mmol) were added quickly to the flask. After adding 12 mL 1,4-dioxane, the flask was capped tightly and run at 130°C for 1 hr. TLC (9 hexanes: 1 ethyl acetate) showed there were two spots Rf 0.2 and Rf 0.25. The mixture was cooled to room temperature and 30 ml ethyl acetate was added to quench the reaction. 30 mL DI water was added to extract the aqueous phase and 30 mL brine (2X) was used to wash the organic phase, dried over anhydrous MgSO4 and filtered. After concentrating down the filtrate, hexanes:ethyl acetate (9:1) mixture was used to elute Rf 0.2 in silica column chromatography to yield a white powder (600 mg, 83%).

1,2,4,5-tetakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (TBB)
1,2,4,5-tetrabromobenzene (500 mg, 1.27 mmol) and B₂Pin₂ (1.94 g, 7.63 mmol) were added to a 20 mL microwave flask. Flame dried KOAc (1.25 g, 12.7 mmol) and PdCl₂(dppf) (41.6 mg, 0.051 mmol) were added quickly to the flask. After adding 12 ml 1,4-dioxane, the flask was capped tightly and run at 130°C for 1 hr. TLC (9 hexanes: 1 ethyl acetate) showed there were two spots Rf 0.2 and Rf 0.25. The mixture was cooled to room temperature and 30 mL ethyl acetate was added to quench the reaction. 30 mL DI water was added to extract the aqueous phase, 30 mL brine (2X) was used to wash the organic phase, and it was dried over anhydrous MgSO₄ and filtered. After concentrating down the filtrate, hexanes:ethyl acetate (9:1) mixture was used to elute Rf 0.25 by silica column chromatography to yield a white powder. Alternatively, after filtrate concentration, both fractions were collected by filtering through a silica chromatography column, with elution by hexanes: ethyl acetate (7: 3) mixture. The mixture was vacuum dried, and 20 mL hexanes was added and left in the fridge overnight. The precipitate was collected by filtration to yield a white powder (250 mg, 41%).

5.3. Methods used to Detect Thermal Neutron

As hinted earlier in this chapter, three approaches were taken to detect thermal neutron. The first approach utilized a commercially available dopant that contains boron but not UV-absorbing chromophore. The second approach used boron containing benzene (UV-absorbing) and pyrene (visible light absorbing) moieties. The third approach was unique in that it solely used ¹⁰B enriched benzene molecule.

5.3.1. Thermal Neutron Detection by Commercially Available Neutron (Approach #1)

Bis(pinacolato)diboron (B₂Pin₂) (Figure 5.1) as an affordable/simple, off the shelf chemical and plastic compatible boron dopant for detection of thermal neutrons. B₂Pin₂ was first used in organic reactions by Miyuara et al to create an intermediate for the very important Suzuki C-C bond forming cross-coupling reaction.¹⁴³ The conversion of arylhalides to arylboronates using an inexpensive and readily available borylating reagent such as B₂Pin₂ has been extensively used in the pharmaceutical and organic electronics industries.¹⁴³-¹⁴⁵

![Chemical structure of B₂Pin₂](image)

Chemical Formula: C₁₂H₂₄B₂O₄
Molecular Weight: 253.94
Elemental Analysis: C, 56.76; H, 9.53; B, 8.51; O, 25.20

Figure 5.1 Molecular weight and elemental composition (%) of bis(pinacolato)diboron (B₂Pin₂).
Plastic scintillators generally consist of an inexpensive polymer matrix that absorbs incoming radiation. The matrix becomes “excited” and transfers this energy to fluorescent dopants within the sample that then emit photons in a spectral region matching the photodetector’s response function. In order to provide thermal neutron sensitivity, another dopant containing $^{10}\text{B}$ is added to the formulation; $\text{B}_2\text{Pin}_2$ for instance. The compatibility of these dopants is essential in creating optically clear, mechanically stable and efficient plastic scintillator samples capable of discriminating neutron signals from a gamma field. We chose the commonly used PPO and POPOP as primary and secondary dopants respectively in order to be able to allow direct comparison with previous literature reports. The initial set of samples (Table 5.1) was intended to test the solubility limit of $\text{B}_2\text{Pin}_2$ in PVT, holding the fluorescent dopant concentrations constant. As for $\text{B}_2\text{Pin}_2$, it has a smaller boron content per molecule than carboranes, the achievable boron concentrations are lower than commercially available products which advertise up to 5% natural boron content. For comparison, a typical $^3\text{He}$ proportional counter with 10 atm gas pressure corresponds to a cross section weighted $^{10}\text{B}$ content in polymers of app. 0.6 wt%.

5.3.1.1. Solubility Limit and Radiation Performance of $\text{B}_2\text{Pin}_2$

The increase in $\text{B}_2\text{Pin}_2$ concentration from 2 to 15 wt% did not result in significant physical change or a decrease in optical clarity (Figure 5.2). However, some slight opaqueness could be observed in the 15 wt% sample and when increased to 20 wt% $\text{B}_2\text{Pin}_2$ (~1.7 wt% B), the sample showed significant $\text{B}_2\text{Pin}_2$ precipitation that did not allow further machining and testing. Higher dopant concentration usually leads to softening of the polymer matrix, however, this was not noticeable until total dopant concentration was above 15%. Light yield and thermal neutron $^{10}\text{B}$ capture results are detailed below in Figures 5.3-5.4.

![Figure 5.2 Sample and UV irradiated 1 wt% PPO, 0.1% POPOP and 11.75% $\text{B}_2\text{Pin}_2$ in PVT](image)
Table 5.1 Optimizing boron additive in PVT.

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Matrix</th>
<th>Primary dopant</th>
<th>Wavelength shifter</th>
<th>B$_2$Pin$_2$ content</th>
<th>Nat-B content</th>
<th>$^{10}$B content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Name wt%</td>
<td>Name wt%</td>
<td>wt%</td>
<td>wt%</td>
<td>wt%</td>
</tr>
<tr>
<td>1</td>
<td>PVT</td>
<td>PPO 1</td>
<td>POPOP 0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>PVT</td>
<td>PPO 1</td>
<td>POPOP 0.1</td>
<td>2</td>
<td>0.17</td>
<td>0.03</td>
</tr>
<tr>
<td>3</td>
<td>PVT</td>
<td>PPO 1</td>
<td>POPOP 0.1</td>
<td>5</td>
<td>0.43</td>
<td>0.09</td>
</tr>
<tr>
<td>4</td>
<td>PVT</td>
<td>PPO 1</td>
<td>POPOP 0.1</td>
<td>10</td>
<td>0.85</td>
<td>0.17</td>
</tr>
<tr>
<td>5</td>
<td>PVT</td>
<td>PPO 1</td>
<td>POPOP 0.1</td>
<td>11.75</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>6</td>
<td>PVT</td>
<td>PPO 1</td>
<td>POPOP 0.1</td>
<td>15</td>
<td>1.28</td>
<td>0.25</td>
</tr>
<tr>
<td>7</td>
<td>PVT</td>
<td>PPO 1</td>
<td>POPOP 0.1</td>
<td>20</td>
<td>1.7</td>
<td>0.34</td>
</tr>
</tbody>
</table>

*Total mass of each sample is app. 20.0g

The B$_2$Pin$_2$ concentration appears to have little effect on light output when added at the 10 wt% level as shown in Figure 5.3; most samples produce a Compton Edge at 92-94% that of a commercial control sample (Saint Gobain BC408; 10,000 photons/1 MeV e$^-\$). There is a slight decrease at 15 wt% that is suspected to be due to the approaching solubility limit of B$_2$Pin$_2$ in PVT.

Figure 5.3 Number of counts vs uncalibrated pulse area in scintillating PVT based samples as measured through exposure to a 137Cs $\gamma$-source using the same PMT bias value.
5.3.1.1. Optimization of Sample Formulation

Thermal neutrons in the $^{244}$Cm/$^{13}$C “Poly Cave” setup were captured by the naturally occurring $^{10}$B isotope within $\text{B}_2\text{Pin}_2$. As described earlier, although the reaction produces light ions with kinetic energies in the MeV range, the signal registered in the detector samples was, due to alpha quenching, around 90 keV$_{ee}$, only slightly varying with $\text{B}_2\text{Pin}_2$ concentration. In order to extract the neutron capture peaks clearly, the cadmium shielded spectra were subtracted from the “Poly Cave” capture spectra as shown in Figure 5.4. The results here reported on the position (keV$_{ee}$) of the $^{10}$B neutron capture peak are similar to previously reported values on boron loaded plastic scintillators using carboranes.\textsuperscript{52,140-141} It should be noted that raising the $\text{B}_2\text{Pin}_2$ concentration up to the solubility limit of the compound in PVT appears to have only a minor impact on both light output and alpha quenching. This indicates a good match of the neutron sensitive dopant to the plastic matrix in terms of scintillation relevant properties.

![Boron Capture Peak (PVT+1%PPO+0.1%POPOP+x%B2PIN2)](image)

Figure 5.4 Number of counts versus calibrated pulse area (keVee) for 10B thermal neutron reaction spectra with gamma response subtracted via cadmium shielded measurement. The keVee sample scale adjusts all samples to the $^{137}$Cs Compton edge position of each sample.

A second set of samples was prepared and tested with the intent of achieving PSD in our samples using the scintillating fluor over-doping method originally developed by Brooks et al.\textsuperscript{16} that in recent years
inspired further work in several laboratories.\textsuperscript{18, 21, 56} The compositions used in this sample set are provided in Table 5.2. The 11.75 wt\% B\textsubscript{2}Pin\textsubscript{2} concentration is equivalent to 1 wt\% natural boron content, and was selected to be well below the solubility limit of the B\textsubscript{2}Pin\textsubscript{2}/PVT system. The plastic samples were polished and prepared as described earlier and their detector response properties analyzed with the same radioactive source configurations. In our tests significant PSD was not quantifiable until the sample contains at least 10\% PPO. Meaningful separation between neutrons and gammas in our energy range of interest (of order 100 keV\textsubscript{ee}) was not seen until higher concentrations (~20\%). The B\textsubscript{2}Pin\textsubscript{2} content combined with the high amount of PPO necessary to achieve PSD leads to the polymerization kinetics being significantly altered producing plastic samples that are too soft for radiation detection analysis. In order to address this concern, divinylbenzene (DVB), a crosslinking agent, was introduced into the sample solution prior to polymerization. With the crosslinking agent added, the plastic sample containing 20 wt\% PPO 0.1 wt\% POPOP and 11.75 wt\% B\textsubscript{2}Pin\textsubscript{2} was at a “hardness” level that could be cut and prepared for our standard detector test. The Compton Edge of the $^{137}$Cs spectrum was 98\% light output of our commercial plastic scintillator (Saint Gobain Crystals, BC-408). However, the PPO over-doping method appeared to worsen the alpha quenching significantly and the $^{10}$B thermal neutron capture peak was located at app. 60 keV\textsubscript{ee}. The resulting spectrum from the thermalized $^{244}$Cm/$^{13}$C neutron source is detailed in Figure 5.5 and various PSD figures of merit (FoM) numbers using the fast neutron spectrum are shown in Figure 5.6. The measured FoM at 100 keV\textsubscript{ee} of 1.04 compares well to the published value of 0.9 at 120 keV\textsubscript{ee} for the commercial EJ-299-33, which is based on the addition of carboranes and also presumably uses the PPO over-doping method [8].

Table 5.2 Plastic compositions with over-doped PPO and 1\% “boron” additive.

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Matrix</th>
<th>Primary dopant</th>
<th>Wavelength shifter</th>
<th>B\textsubscript{2}Pin\textsubscript{2}</th>
<th>Crosslinker</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>wt%</td>
<td>wt%</td>
<td>wt%</td>
<td>wt%</td>
</tr>
<tr>
<td>1</td>
<td>PVT</td>
<td>PPO</td>
<td>10</td>
<td>POPOP</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>PVT</td>
<td>PPO</td>
<td>15</td>
<td>POPOP</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>PVT</td>
<td>PPO</td>
<td>20</td>
<td>POPOP</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>PVT</td>
<td>PPO</td>
<td>25</td>
<td>POPOP</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*11.75\% B\textsubscript{2}Pin\textsubscript{2} is equivalent to 1\% boron content.
In addition to the thermal neutron capture peak a band between the fast neutron and gamma bands becomes tentatively visible which contains events originating from the exited state of the $^7$Li reaction product with an alpha and gamma emission detected in coincidence (Figure 5.5).

Figure 5.6 PSD Figure of Merit values resulting from various energy cuts (spectrum shown from 200 keV<sub>ee</sub> cut) using the same sample as in Fig. 5 in the “lead cave” setup and projecting the Full PSD Spectrum after the energy cut onto the y-axis.
To assess the aging effects, we retested the scintillator samples 9 months later after storage in ambient conditions without humidity control. There was some slight visual yellowing/clouding of the $\text{B}_2\text{Pin}_2$ doped samples (e.g. Figure 5.7) with average decrease of approximately 20% in light yield. However, $^{10}\text{B}$ thermal neutron reaction signals could still be detected from in the samples containing PPO at the 1 wt% level. The over-doped PPO samples while still displaying n/γ PSD, had turned opaque with negligible light output (~10% of BC408). The yellowing in our samples is likely due to oxidation of residual radicals remaining from the radical bulk polymerization method used in our production process. Future work will need to be devoted to employ radical quenchers, antioxidants or thermal annealing procedures to achieve the long (~years) lifetimes expected from plastic scintillator products.

![Figure 5.7 Plastic scintillator sample containing 1 wt% PPO, 0.1% POPOP and 11.75% B2Pin2 in PVT (same as Figure 5.2) after 9 months’ ambient storage.](image)

5.3.1. Boron Containing Pyrene and Benzene Molecules for Detection of Thermal Neutron (Approach #2)

With regard to boron containing organic materials, recently direct borylation of activated C-H bonds of aromatic compounds has been reported using iridium-based catalysis.\textsuperscript{146-151} However, high Ir catalyst loadings, lack of regioselectivity and longer reaction times hinder its applicability and scale up potential. In order to counter these disadvantages, the synthesis of 1,3,6,8-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene was reported by Yamada and coworkers by nickel catalyzed direct borylation achieving a yield of 74% in two days.\textsuperscript{152} Furthermore, synthesis of 1,2,4,5-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene was reported by Wagner and coworkers with an overall yield of 64%; however, their synthetic process was a two-step reaction system achieving only partial borylation
and the use of highly pyrophoric and toxic reagents such as n-butyllithium and Grignard reagents.Both Aubert et al. and Gandon et al. utilized cobalt-catalyzed [2+2+2] cycloaddition of ethynyl pinacol borate to yield a mixture of 2,2',2''-(benzene-1,2,4-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) and 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene with a yield of 63%. Their use of an expensive borylating reagent (ethynyl pinacol borate - $650/g) and a difficult separation of the product mixture could be detrimental to using this reaction system. Compared to cobalt-catalyzed cycloaddition reactions, Wang et al. achieved 85% yield by direct borylation of 1,3,5-tribromobenzene using Miyuara conditions.

5.3.1.1. Synthetic Methodology

We report here the borylation of multi-halo functionalized benzene and pyrene derivatives via this $\text{B}_2\text{Pin}_2$ reaction using the very efficient and mature Suzuki chemistry to afford soluble materials with boron content as high as 7.43 wt%. Furthermore, some of these materials also have strong blue luminescence properties that may contribute to scintillation efficiency for detecting both gamma and neutron radiation. Examples of polymer-based scintillators using our new materials demonstrate highly efficient scintillation and thermal neutron detection.

![Scheme 5.1 Conventional heating condition (trad.) and microwave (μW) heating condition for generating tetra-borylated pyrene (TBP). These conditions were used for all the reactions.](image-url)
We have applied traditional and microwave assisted Suzuki conditions to promote the borylation of bromo functionalized aromatics using commercially available and cost effective bispinacolato diborane ($\text{B}_2\text{Pin}_2$). In our efforts to complete these reactions within a reasonable time, we used slight excess equivalents of $\text{B}_2\text{Pin}_2$ for multiple borylations. Increasing the heating to 90°C was crucial for completing these reactions in less than 24 hours (Scheme 5.1) and our microwave assisted conditions resulted in similar reaction yields in much shorter reaction times (40 min vs. 24 hr).

To show applicability of the aforementioned conditions to other aromatic molecules, related boron containing molecules (Figure 5.8) were synthesized using lower catalyst loading, shorter reaction times, simpler purification methods, and comparable synthesis yields as previous literature methods. To our knowledge, use of microwave methods for multiple borylation has only been reported for diborylation, where in our approach we demonstrate multiple borylations (tri and tetra) in a significantly reduced time frame of 40-60 min. Table 5.3 summarizes conditions and percent yield comparison between traditional and microwave assisted reactions.

The synthesis of 1 (Figure 5.8, entry 1) was previously reported by Akhavan-Tafti et. al with a similar procedure to our traditional synthesis (except 85°C, DMSO) affording approximately the same

![Figure 5.8 Boron containing pyrene and benzene derivatives.](image-url)
percent yield (Table 5.3). To our knowledge we are the first to report the synthesis of this molecule by microwave-assisted borylation. Compound 2 synthesis showed the biggest drop in yield when attempting microwave borylation (79% vs 63%). Several attempts were made by varying temperature, amounts of catalyst and B₂Pin₂, and reaction time, however the microwave yield couldn’t be improved. Both MALDI TOF MS (Figure 5.9) and NMR for this compound confirm the product purity.

Table 5.3 Comparison of multiple borylation by conventional heating vs microwave synthesis.

<table>
<thead>
<tr>
<th></th>
<th>B₂Pin₂ [equiv]</th>
<th>KOAc [equiv]</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Microwave</td>
<td>Conventional</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.0</td>
<td>3.0</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
<td>6.0</td>
<td>63</td>
</tr>
<tr>
<td>3</td>
<td>6.0</td>
<td>10.0</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>4.5</td>
<td>7.5</td>
<td>61</td>
</tr>
<tr>
<td>5</td>
<td>4.5</td>
<td>7.5</td>
<td>83</td>
</tr>
<tr>
<td>6</td>
<td>6.0</td>
<td>10.0</td>
<td>41</td>
</tr>
</tbody>
</table>

3-4 mol% Pd catalyst was used to synthesize 1-6.

Figure 5.9 MALDI-TOF-MS spectra for 1,6-diborylatedpyrene.
5.3.1.1. Characterization of Synthesized Molecules for Approach #2

The synthesis of TBP (Figure 5.8, entry 3) appeared straightforward but the characterization was problematic as both $^1$H and $^{13}$C NMR were inconclusive, resulting in broad and featureless peaks in the aromatic region while showing definitive and clear peaks in the aliphatic region. This was thought to be the result of the presence of a paramagnetic ion or of the large difference between the number of aliphatic and aromatic hydrogens (48: 6). As such, many attempts were made to solve this problem by varying deuterated solvents, increasing relaxation time, utilizing chromium(III) acetylacetonate (Cr(acac)$_3$) as a relaxing agent, and attempting solid-state NMR.\textsuperscript{163} Unfortunately, a conclusive NMR confirming the successful synthesis of TBP couldn’t be produced. Even though this problem was not stated explicitly in the literature, we have noticed similar reports confirming our observation.\textsuperscript{149} Despite this shortcoming, we turned our attention to analyzing this molecule by MALDI TOF MS that confirmed the molecule as shown in Figure 5.10. By utilizing 1,8,9-tri hydroxyanthracene as a matrix, all the possible fragments 707.4 (M$^+$), 581.1, 454.8 and 227.3 were observed.

Encouraged by this result, TBP crystals with dimensions of 1-2 mm were prepared by slow introduction of hexanes into a TBP chloroform solution. The crystals had suitable quality for single-crystal x-ray analysis, revealing TBP and n-hexane molecules each sitting on a 2-fold rotation axis as shown in Figure 5.11. The pyrene ring system is essentially flat, but the Bpin rings are non-planar and disordered over two distinct conformations.\textsuperscript{164-166} The crystal structure of TBP coupled with MALDI shows we have unequivocally synthesized this molecule despite our inability to obtain conclusive $^1$H and $^{13}$C NMR.

![Figure 5.10 An ellipsoid plot (50% probability) for TBP.](image-url)
The synthesis of 135TrBB and 124TrBB (Figure 2, entry 4 & 5) had significance in determining if the symmetry of boron containing molecules could have an effect in the detection of thermal neutrons, especially because these two molecules have identical amounts of boron by weight (7.11%).

Generally, the yield for conventional heating was slightly improved (except for entry 6) over the microwave approach (Table 5.3). Entry 6 (Figure 5.8) clarified the lack of accurate NMR spectra for TBP since its aromatic to aliphatic hydrogen ratio is higher (48:2 to 48:6). However, both $^1$H and $^{13}$C NMR unambiguously confirmed the synthesis of this molecule. The crystal structure and two-step reaction synthesis of this molecule was published by Wagner et. al.\textsuperscript{153}

### 5.3.1.2. Results and Discussion for Approach #2

Table 5.4 shows the composition of plastic scintillators prepared incorporating the synthesized boron materials (entry 3-6, Figure 5.8) into the PVT matrix. The first eight samples were colorless with intense blue luminescence under UV excitation. As TBP has a pale yellow color, samples ix-xi were optically clear with a yellowish color and strong blue luminescence under UV excitation.
Table 5.4 Plastic scintillator formulations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vinyl toluene [% wt]</th>
<th>Primary dopant Name</th>
<th>Wavelength shifter [% wt]</th>
<th>Boron source Name</th>
<th>Boron source [% wt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>98.9</td>
<td>PPO</td>
<td>POPOP 0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ii</td>
<td>98.4</td>
<td>PPO</td>
<td>POPOP 0.1</td>
<td>135TrBB 0.1</td>
<td>135TrBB 0.5</td>
</tr>
<tr>
<td>iii</td>
<td>97.9</td>
<td>PPO</td>
<td>POPOP 0.1</td>
<td>135TrBB 0.1</td>
<td>135TrBB 1.0</td>
</tr>
<tr>
<td>iv</td>
<td>93.9</td>
<td>PPO</td>
<td>POPOP 0.1</td>
<td>135TrBB 0.1</td>
<td>135TrBB 5.0</td>
</tr>
<tr>
<td>v</td>
<td>97.9</td>
<td>PPO</td>
<td>POPOP 0.1</td>
<td>124TrBB 0.1</td>
<td>124TrBB 1.0</td>
</tr>
<tr>
<td>vi</td>
<td>93.9</td>
<td>PPO</td>
<td>POPOP 0.1</td>
<td>124TrBB 0.1</td>
<td>124TrBB 5.0</td>
</tr>
<tr>
<td>vii</td>
<td>97.9</td>
<td>PPO</td>
<td>POPOP 0.1</td>
<td>TBB 0.1</td>
<td>TBB 5.0</td>
</tr>
<tr>
<td>viii</td>
<td>93.9</td>
<td>PPO</td>
<td>POPOP 0.1</td>
<td>TBB 0.1</td>
<td>TBB 5.0</td>
</tr>
<tr>
<td>ix</td>
<td>98.9</td>
<td>TBP</td>
<td>POPOP 0.1</td>
<td>TBP 0.1</td>
<td>TBP 1.0</td>
</tr>
<tr>
<td>x</td>
<td>97.9</td>
<td>TBP b</td>
<td>POPOP 0.1</td>
<td>TBP 0.1</td>
<td>TBP 2.0</td>
</tr>
<tr>
<td>xi</td>
<td>97.9</td>
<td>PPO</td>
<td>POPOP 0.1</td>
<td>TBP 0.1</td>
<td>TBP 1.0</td>
</tr>
</tbody>
</table>

a Total mass of each sample: 20.0g
b TBP acting as boron source and primary dopant.

The light output of these samples (4.7 cm diameter x 1.1-1.3 cm thickness) was compared to a commercial scintillator (EJ-204) of approximately the same dimensions prepared by Eljen Technology. Our control (Table 5.4, sample i) resulted in 95% of the light output compared to the commercial scintillator. A summary of light output of samples i-xi compared to EJ-204 and their properties are shown in Table 5.5. The high average molecular weight (Mn and Mw) of the samples (as determined by GPC using poly(styrene) calibration standards) is indicative of complete polymerization of the scintillator samples, hence minimal inhibition of polymerization by the added components. As shown in column 5 (Table 5.5), the signal produced by the 1.48MeV alpha and 0.48 MeV 7Li ion (products of thermal neutron reaction with 10B) is quenched to produce scintillation light equivalent in amplitude from an electron with an energy of 60-100kev depending on sample composition.

Samples ii-iv (Figure 5.12) contain increasing amounts of 135TrBB (Figure 5.8, entry 4). As expected, capture of thermal neutrons was not observed for the 0.5% sample of this compound due to the low concentration of 10B (0.007% wt) (Sample ii). Increasing the amount of 135TrBB to 1% showed thermal capture as well as increased light output (sample iii), while increasing the amount to 5% wt reached the solubility limit of 135TrBB in PVT (sample iv) resulting in an opaque sample. We speculate that the symmetrical nature of the compound was contributing to its crystallization in PVT at higher loadings.
Figure 5.12 Left to right: Sample ii, iii and iv: 0.5, 1.0 and 5 wt% 135TrBB respectively.

Figure 5.13 Left to right: Sample v and vi: 1 and 5 wt% 124TrBB respectively
To address this issue, we prepared and utilized 124TrBB that has a more unsymmetrical structure but the same boron content as 135TrBB. Samples v and vi both had the best optical clarity with 124TrBB (Figure 5.8, entry 5) as the boron additive (Figure 5.13) indicating enhanced solubility of 124 versus 135TrBB. Increasing the concentration of 124TrBB from 1% to 5 % wt increased both the light output as well as thermal neutron capture (Table 5.5, entry v and vi).

To clarify, Table 5.5 provides a detailed overview of the light output, boron capture, and polymer properties of plastic scintillator samples:

<table>
<thead>
<tr>
<th>Samples</th>
<th>Relative PL (Comparison to EJ 204)</th>
<th>B content [%wt]</th>
<th>10B content [%w]</th>
<th>Neutron capture [keVee]</th>
<th>M_n [MDa]</th>
<th>M_w [MDa]</th>
<th>PDI</th>
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<tr>
<td>i</td>
<td>95</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.37</td>
<td>3.52</td>
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<td>ii</td>
<td>74</td>
<td>0.035</td>
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<td>No capture</td>
<td>1.20</td>
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</tr>
<tr>
<td>iii</td>
<td>78</td>
<td>0.070</td>
<td>0.014</td>
<td>78.8 ± 0.8</td>
<td>1.29</td>
<td>3.44</td>
<td>2.66</td>
</tr>
<tr>
<td>iv</td>
<td>78</td>
<td>0.356</td>
<td>0.071</td>
<td>73.1 ± 2.0</td>
<td>0.69</td>
<td>1.54</td>
<td>2.24</td>
</tr>
<tr>
<td>v</td>
<td>77</td>
<td>0.070</td>
<td>0.014</td>
<td>72.1 ± 2.6</td>
<td>0.91</td>
<td>2.49</td>
<td>2.73</td>
</tr>
<tr>
<td>vi</td>
<td>81</td>
<td>0.356</td>
<td>0.071</td>
<td>91.9 ± 0.2</td>
<td>1.34</td>
<td>2.88</td>
<td>2.22</td>
</tr>
<tr>
<td>vii</td>
<td>87</td>
<td>0.075</td>
<td>0.015</td>
<td>74.9 ± 2.0</td>
<td>0.32</td>
<td>0.81</td>
<td>2.58</td>
</tr>
<tr>
<td>viii</td>
<td>76</td>
<td>0.370</td>
<td>0.074</td>
<td>82.6 ± 0.7</td>
<td>1.26</td>
<td>4.39</td>
<td>3.47</td>
</tr>
<tr>
<td>ix</td>
<td>36</td>
<td>0.065</td>
<td>0.013</td>
<td>No capture</td>
<td>1.35</td>
<td>3.38</td>
<td>2.51</td>
</tr>
<tr>
<td>x</td>
<td>31</td>
<td>0.130</td>
<td>0.026</td>
<td>No capture</td>
<td>0.79</td>
<td>1.96</td>
<td>2.49</td>
</tr>
<tr>
<td>xi</td>
<td>70</td>
<td>0.065</td>
<td>0.013</td>
<td>69.8 ± 1.1</td>
<td>1.72</td>
<td>4.72</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Figure 5.14 Thermal neutron capture using a 5 wt% 124TrBB plastic scintillator, sample vi.
Figure 5.14 shows a one minute collection of data using the $^{244}\text{Cm}/^{13}\text{C}$ source for 5% 124TrBB (Table 5.4, entry vi), that already shows distinct neutron capture above the background noise. This sample resulted in a $^{10}\text{B}$ thermal neutron capture signal at approximately 92 keVee with 81% relative light output. To our knowledge, this is the highest thermal neutron capture signal observed from a boron doped plastic scintillator. 124 TrBB also had the highest solubility with approximately 20.0 wt% (0.28 wt% $^{10}\text{B}$) in PVT. As expected, the light output of 124TrBB decreased from 81% at 5.0 wt% to 60% at 20.0 wt% (Not shown in Table 5.5). The boron capture peak also decreased from nearly 91 keVee to 75 keVee (Not shown in Table 5.5). Although there was a slight decrease in radiation performance (both light output and capture signals) as concentration of 124TrBB increased in PVT, the mechanical stability of the samples were sound.

Samples vii and viii both had TBB (Figure 5.8, entry 6) as boron additive. The solubility limit of this compound was the lowest in PVT. For example, 1% wt loadings showed crystallization as shown in Figure 5.15. Despite its poor solubility, it showed a clearly visible boron capture signal even at 1% (Table 5.4, entry vii). Increasing the concentration to 5% wt decreased the optical clarity significantly as shown in Figure 14. We propose that the decrease in light output compared to our standard was due to attenuation of light by increased dopant concentration. This effect is in agreement with literature reports.
Utilizing TBP (Figure 5.8, entry 3) as both a boron source and primary dopant resulted in lower light output and neutron capture likely due to the inefficiency of energy transfer from the matrix to TBP and wavelength shifter (Table 5.5, entry ix and x). The dramatic drop in light output also caused the capture reaction to be buried in the electronic background. The issue was resolved by only utilizing TBP as a boron source and using PPO as the primary dopant (Table 5.4, entry xi). This sample showed a dramatic increase in light output and the thermal neutron induced reaction signal became clearly visible (Table 5, entry xi). All of the samples containing TBP (Figure 5.16) were slightly yellow due to the pale yellow nature of the TBP powder as shown by its photoabsorption and photoemission (Figure 5.17). The same is true for biborylated pyrene (Figure 5.18, entry II).
5.3.2. Synthesis of $^{10}$B enriched Small Molecule (Approach #3)

The detection of thermal neutron is achieved by a capture reaction with B-10 isotopes. Therefore, increasing the B-10 content in plastic would enhance its capture efficiency. So far, the maximum B-10 containing small molecule is TBB with approximately 1.5 wt%. This would mean we would need to incorporate relatively large amounts of TBB in order to detect significant amount of thermal neutron. This is problematic from a materials usage perspective as well as leading to inferior plastic scintillator mechanical and stability issues. It was therefore our focus to synthesize $^{10}$B enriched small molecules with higher $^{10}$B percentage to mitigate this problem. As such, Scheme 5.2 shows a simple route starting with $^{10}$B enriched boric acid that is converted to triisoproxyborate with water as a byproduct, followed by a condensation reaction with pinacol resulting in triisoproxypinacolboron. By reacting triisoproxypinacolboron with the Grignard reagent (lithiated benzene), the final product (MBB) is synthesized in high purity. MBB is very compatible with common plastic scintillator formulations, and we were able to incorporate it in PVT with PPO and POPOP as primary dopant and wavelength shifter respectively.

Scheme 5.2 Synthesis of B-10 containing benzene (MBB).

5.3.2.1. Sample Formulation Optimization for Approach #1

As a proof of concept, $^{10}$B enriched small molecule was synthesized starting from inexpensive boric acid, $^{10}$B(OH)$_3$, and successfully incorporated in PSD capable plastic scintillator. MBB (Scheme 5.2) was used as a thermal neutron sensitive dopant with PPO and POPOP serving as fluorescent dopants in PVT. Similar to the B$_2$Pin$_2$ study, the solubility limit of MBB was first determined before exploring its PSD properties. The samples with the exception of 1.0 wt% MBB, were optically cloudy and their mechanical properties drastically changed as MBB concentration was increased. As shown in Table 5.6, there is a consistent decrease in light output as the concentration of MBB increases, both B$_2$Pin$_2$ and 124TrBB show similar trends. The boron capture is shown in Figure 5.18. The capture signal remains constant for samples 1-6 with an increase in peak intensity as the concentration of MBB increases.
Table 5.6 Plastic scintillator formulations with MBB.

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Matrix</th>
<th>Primary dopant</th>
<th>Wavelength shifter</th>
<th>MBB content</th>
<th>$^{10}$B content</th>
<th>Light output</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Name</td>
<td>wt%</td>
<td>Name</td>
<td>wt%</td>
<td>wt%</td>
<td>% BC-406</td>
</tr>
<tr>
<td>1</td>
<td>PVT</td>
<td>PPO</td>
<td>1</td>
<td>POPOP</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>PVT</td>
<td>PPO</td>
<td>1</td>
<td>POPOP</td>
<td>0.1</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>PVT</td>
<td>PPO</td>
<td>1</td>
<td>POPOP</td>
<td>0.1</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>PVT</td>
<td>PPO</td>
<td>1</td>
<td>POPOP</td>
<td>0.1</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>PVT</td>
<td>PPO</td>
<td>1</td>
<td>POPOP</td>
<td>0.1</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>PVT</td>
<td>PPO</td>
<td>1</td>
<td>POPOP</td>
<td>0.1</td>
<td>5.3</td>
</tr>
<tr>
<td>7</td>
<td>PVT</td>
<td>PPO</td>
<td>20</td>
<td>POPOP</td>
<td>0.1</td>
<td>5.3</td>
</tr>
<tr>
<td>8</td>
<td>PVT</td>
<td>PPO</td>
<td>20</td>
<td>POPOP</td>
<td>0.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Total mass of each sample is approximately 20.0g

5.3.2.1. Radiation Performance of MBB

The over-doped PPO samples with MBB (Table 5.6, 7-8) both showed excellent discrimination between gamma, fast neutrons, and thermal neutrons.

Figure 5.18 Boron capture signal of MBB doped plastic scintillators.
However, sample 7 was an extremely soft sample, so we lowered the concentration of MBB from 5.3 to 1.0 wt%. The hardness and clarity of the sample changed drastically. Figure 5.19 shows the mixed radiation interaction with sample 8 (Table 5.6). Note that MBB has melting point of 15.0°C and therefore the softness and cloudiness of samples with MBB could possibly be a consequence of that. We saw similar result with mehPTP from chapter 2 with a melting point of 10.0 °C that resulted in a jelly-like sample at a 10.0 wt% loading in PVT. Therefore, going forward, synthesizing high melting point B-10 containing small molecules to achieve mechanically suitable plastic scintillators with thermal neutron detection capability will be performed.

![Figure 5.19 Radiation performance of 20 wt% PPO, 1 wt% MBB and 0.1 wt% POPOP in PVT](image)

**5.1. Conclusion**

B$_3$Pin$_2$ can be used as a low cost $^{10}$B additive that is compatible with commonly used plastic scintillator formulations to achieve plastic scintillator detectors with thermal neutron sensitivity. B$_3$Pin$_2$ concentrations up to the solubility limit have little effect on sample light yield and alpha quenching, allowing detectors to be produced with on the order of 1 wt% natural boron content. Thermal neutrons are easily detected with the $^{10}$B neutron capture peak occurring at ~90 keV$_{ee}$ in the basic formulations, and at ~60-65 keV$_{ee}$ in formulations with PPO overdoping to achieve PSD. In the PSD samples, analysis allowed for separation of gamma and proton (or alpha) signals down to low energies providing an additional factor
to distinguish the thermal neutron signal. Further work is necessary to suppress aging effects through improvements in the scintillator formulation and/or production process. The measurements here were performed using B\textsubscript{2}P\textsubscript{i}n\textsubscript{2} with natural boron isotopic distribution.

The traditional and microwave-assisted synthesis of direct multi-borylation of pyrene and benzene derivatives achieved high percent yields and purity of desired products. The simplicity of these synthetic routes together with inexpensive starting materials and ease of scale up production could be highly advantageous in reducing the cost of boron-rich additives for plastic scintillators. These synthesized boron additives doped with commercially utilized PPO and POPOP fluorescent emitters in poly(vinyltoluene) (PVT) matrices have demonstrated successful thermal neutron induced reactions with comparable/improved light output compared to commercial samples using very expensive carborane derivatives. In the case of 124 TrBB, the \(^{10}\text{B}\) neutron capture signal registered a stronger signal than state-of-the-art boron doped plastic scintillators.

Finally, the synthesis of \(^{10}\text{B}\) enriched MBB resulted in scintillation samples with a much stronger B-10 capture signal of thermal neutron. The synthesis was simple with inexpensive starting materials, easy purification scheme and good yield. There was a strong correlation between a decrease in light output of samples and increase in MBB concentration, possibly due to MBB retarding polymerization. In addition, the optical clarity of MBB incorporated plastics became more and more cloudy as concentration increased. The mechanical strength was also negatively affected with more added MBB. In the future, pathways of synthesizing boron containing organic additives from readily available \(^{10}\text{B}\) enriched compounds should be investigated. The synthesis of \(^{10}\text{B}\) enriched boron-rich additives (such as 124TrBB) would be worth looking pursuing to increase thermal neutron capture probability. Additionally, attempting to differentiate the thermal neutron capture and fast neutron scattered signals from gamma radiation signals through pulse shape discrimination (PSD) using over-doping method with fluorescent dopants (other than PPO) that have little to no alpha quenching effect will allow for better boron capture signals. Perhaps all the over-doped experiments in this chapter should be attempted with SF or TPO to further explore alpha quenching effect on boron capture signals.
CHAPTER 6. SUMMARY AND OUTLOOK FOR THE FUTURE

6.1. Summary

Plastic scintillators are crucial first-line of defense for detection of sensitive nuclear materials. Their ease of fabrication, mass scalability and inexpensive price tag makes them attractive for researchers as well as field deployment. The mechanism of plastic scintillators via cascades of energy transfers through its components allows the conversion of radiation to visible light. The type and intensity of light is analyzed to gain insight into the type and source of radiation. Although this technology is old, there is plenty of room for improvement. In addition, the current state of the art radiation detectors, crystal scintillators and $^{3}$He gas proportional counters, are expensive and are failing to meet the increasing demand. This coupled with the growing threats of terrorism and special nuclear material smuggling helps motivate this dissertation work.

Plastic scintillators could be expanded through better understanding of underlying mechanism and continued improvements of their efficiency. The focus in this field so far has been on commercially available small organic molecules for various applications such as pulse shape discrimination (PPO), thermal neutron detection (m-carborane), gamma radiation via photopeak (triphenyl bismuth) and so forth. Except PPO, all the commercially available dopants are expensive to meet deployment needs. Although, other researchers have recently begun to make efforts to curb this problem, this thesis makes a concerted effort in addressing the issue of softening of PSD capable plastics (including PPO over-doped plastic), expanding potential primary dopants through scalable and high yield synthetic routes, exploring possible factors of PSD via systematic design of over-doped plastic scintillators and integrating experimental results with computation.

The ideal plastic scintillator could identify various sources of radiation or radioactive isotopes while maintaining mechanical integrity, aging and price criteria set by Department of Homeland Security. The current method utilizes over-doping primary fluorescent dopants. The general underlying reason behind the over-doped method is presumed to be the increase in migration of triplet excited states and their subsequent annihilation to particle dependent delayed fluorescence. In other words, the relative amount of prompt and delayed fluorescence is used to discriminate the pulse signal difference between fast neutron and gamma radiation. According to this method, any over-doped primary could potentially differentiate signals of fast neutron in gamma background. However, results of various fluorescent dopants (SF) in PVT demonstrated subpar discrimination compared to PPO. This was attributed to many reasons including relative energies of first excited triplet states of matrix and primary dopants, symmetry of the primary dopants and softness of the plastic. Hence the multiple factors contributing to efficiency of triplet-triplet annihilation makes pulse shape discrimination a complex problem.
The various small molecules explored in this thesis have allowed us to solve the softening of overdoped plastic scintillators. Melting point of the dopants is indicative of the solubility limit and the hardness of the plastic over-doped with the dopants. PhF and TPO doped plastic scintillators are both a suitable alternative to PPO plastic with superior mechanical properties and good pulse shape discrimination.

The detection of thermal neutrons was approached through various methodologies using small molecules containing boron. Both traditional as well as microwave synthesis of borylation provided good yields with the conditions being suitable for a fast and reliable method for large scale synthesis. The $^{10}$B enrichment of those additives will be key in the future in order to replace the current state of the art m-carborane doped plastics. Triborylated benzene (124TrBB in particular) doped plastics showed minimal change in radiation performance (light output and FoM).

### 6.2. Outlook for the Future

There are multiple avenues that could be explored to better understand the superior discrimination performance of over-doped PSD plastic scintillators. The first step should be focused on altering the oxazole ring and replacing it with a closely related heteroatom ring such as thiazole that has sulfur instead of oxygen. To expand on this idea of exploring PPO-like small molecules, the following shown in Figure 6.1 are proposed as a starting point. The choices of these molecules were solely based on molecular resemblance to PPO in order to explore geometrical and electronic effects of substituting the oxazole and phenyl rings of PPO with a thiazole. The ground state geometry of these molecules is calculated and can be seen in appendix C. This is by no means limited to just thiazoles but could be expanded on by adding other heteroatom containing aromatic rings such as furan.

![Thiazole derivatives for PSD applications](image)

Fluorinated fluorene derivatives (Figure 6.2) were synthesized using simple Suzuki coupling chemistry (Scheme 6.1). From chapter 2, only solubilizing groups were attached to $p$-terphenyl core that essentially didn’t alter the optical properties of the synthesized derivatives. However, in this chapter both the optical and energy levels of $S_1/T_1$ of fluorene derivatives were changed and, their effects on the radiation
performance of the derivatives were thoroughly discussed. The new fluorinated derivatives are currently being investigated for their unique properties of identical optical property as PhF but with different electronic properties ($S_1/T_1$). In addition, we will investigate the addition of perfluoro effect with regards to spin-orbit coupling.  

Scheme 6.1 Synthesis of fluorinated fluorenes via Suzuki Coupling.

Figure 6.2 Synthesized fluorinated fluorenes
REFERENCES


64. Jankus, V.; Aydemir, M.; Dias, F. B.; Monkman, A. P., Generating Light from Upper Excited Triplet States: A Contribution to the Indirect Singlet Yield of a Polymer OLED, Helping to Exceed the 25% Singlet Exciton Limit. *Advanced Science* **2015**.


Figure A.1. Differential scanning calorimetry data for tBuPTP

Figure A.2. Differential scanning calorimetry data for nBuPTP
Figure A.3. Differential scanning calorimetry data for ehPTP

Figure A.4. Differential scanning calorimetry data for hepPTP
Figure A.5. Differential scanning calorimetry data for ditBuPTP

Figure A.6. Differential scanning calorimetry data for mtBuPTP
Figure A.7. Differential scanning calorimetry data for mditBuPTP

Figure A.8. Differential scanning calorimetry data for mopPTP
Figure A.9. Differential scanning calorimetry data for mehPTP
Figure B.1. Proton and Carbon NMR of tBuPTP precursor
Figure B.2. Proton and Carbon NMR of tBuPTP
Figure B.3. Proton and Carbon NMR of nBuPTP
Figure B.4. Proton and Carbon NMR of ditBuPTP
Figure B.5. Proton and Carbon NMR of ehPTP
Figure B.6. Proton and Carbon NMR of hepPTP
Figure B.7. Proton and Carbon NMR of mopPTP
Figure B.8. Proton and Carbon NMR of mtBuPTP
Figure B.9. Proton and Carbon NMR of mditBuPTP
Figure B.10. Proton and Carbon NMR of mehPTP
Figure B.11. Proton and Carbon NMR of PhF
Figure B.12. Proton and Carbon NMR of SF
Figure B.13. Proton and Carbon NMR of PFP
Figure B.14. Proton and Carbon NMR of SFS
Figure B.15. Proton and NMR of BrPPOMe
Figure B.16. Proton and Carbon NMR of BrPPOtBu
Figure B.17. Proton and Carbon NMR of TPO
Figure B.18. Proton and Carbon NMR of SPO
APPENDIX C

Figure C.1. Ground state geometry optimization of TPO, SPO and VPO (left to right)

Figure C.2. Ground state geometry optimization of various thiazole derivatives