BASIC RESEARCH INTO PERFORMANCE IMPROVEMENTS IN PLASTIC SCINTILLATOR MATERIALS FOR HOMELAND SECURITY

by

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ABSTRACT

Plastic scintillators are currently deployed around the world in first line radiation detectors for international borders, sensitive nuclear sites, national and academic lab settings. These scintillators are simple in their composition and their function, being composed of a common polymer matrix which has been doped with a small percentage of fluorescent molecules. This product fluoresces when radiation is present and incident on the plastic. This fluorescence is then detected by photodetectors which are coupled to the plastic. Currently, these detector systems are unable to provide any spectroscopic or particle identification information, and therefore can only be used for initial screening purposes. Further information about the radiation after a positive response is gleaned by using additional detector systems (e.g. sodium iodide crystals and then followed by HPGE detectors).

In this dissertation, two broad basic research approaches were explored to achieve a better understanding of these systems with the goal of enhancing them for better radiation detection capabilities. The first approach involved enhancing the plastic scintillators’ sensitivity to both fast and thermal neutrons, allowing for particle identification and a reduction in false positive detections of naturally occurring radioactive material (NORM). This was achieved via admixture of several different boron containing materials into the plastic scintillator’s basic formulation, allowing for both thermalization of a fast neutron spectrum via the (n,p) scattering reaction in the hydrogenous bulk matrix, and then a coincident signal of thermal neutron capture on the highly neutron sensitive $^{10}$B isotope. This effect was further enhanced by incorporating a recently identified method of inducing PSD capabilities into plastic scintillators, an analysis that has traditionally only been able to be performed with liquid organic scintillators or certain crystalline scintillators. Synthesized enriched $^{10}$B molecules compatible with common polymer matrices and liquid scintillator solvents were developed, a well studied, a commonly available and cheap boron containing chemical precursor
was identified which can be quickly and easily admixed into basic scintillator formulations, and finally, a family of aromatic, boron containing molecules which can be synthesized in both $^{10}$B enriched or natural boron variants has been identified and studied for effective use in plastic scintillators.

The second broad approach of research was aimed at furthering the understanding of the scintillation process and specifically testing the current theory of why pulse shape discrimination (PSD) capabilities occur. This was examined by altering several different families of fluorescent dopants, extensively cataloging both the dopant properties and the properties of the final scintillator plastic they produced. The results from these experiments will be useful to guide future research towards the ability of designing specific scintillator properties.
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<td>WMD</td>
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<tr>
<td>Colorado School of Mines</td>
<td>CSM</td>
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<tr>
<td>Special Nuclear Materials</td>
<td>SNM</td>
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<td>Naturally Occurring Radioactive Materials</td>
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<td>MINOS</td>
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<td>Polystyrene</td>
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<td>Light Yield</td>
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<td>2,5-diphenyloxazole</td>
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<tr>
<td>1,4-bis(5-phenyloxazol-2-yl) benzene</td>
<td>POPOP</td>
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</tr>
<tr>
<td>weight percent</td>
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</table>
tetraborylated benzene ........................................ TBB

tetraborylated pyrene ........................................ TBP

1,2,4-triborylated benzene .................................. 124TrBB

1,3,5-triborylated benzene .................................. 135TrBB

bis(pinacolato)diboron ....................................... B$_2$Pin$_2$

Monoborylated benzene ...................................... MBB

Pulse Shape Discrimination ................................. PSD

Figure of Merit ................................................ FoM

Förster resonance energy transfer ......................... FRET

Photomultiplier Tube ......................................... PMT

Triplet Triplet Annihilation ................................ TTA

9,10-diphenyl anthracene .................................. DPA

p-terphenyl ..................................................... PTP

Kilo Electronvolt (electron equivalent) .................... keV$_{ee}$

Organic Light Emitting Diode ............................... OLED

Phenyl Fluorene ............................................... PhF

2,4,5 triphenyloxazole ....................................... TPO

Photo Luminescent Quantum Yield ......................... PLQY

Divinyl Benzene .............................................. DVB

Polymethyl Methacrylate .................................. PMMA
ACKNOWLEDGMENTS

I hope to express my gratitude and thanks to everyone that has been involved in the completion of my higher education. Uwe Greife is personally responsible for my growth as a better physicist and a better person. As my graduate school adviser and mentor at The Colorado School of Mines for both of my graduate degree programs, he has given an incredible amount of his own time and resources to me, and I hope that going forward, I am able to show how much that has meant.

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Alan Sellinger has broadened my scientific interests and knowledge into the realm of organic chemistry. He has helped push my skills as a research scientist, and introduced me to the world of professional scientific publication. I have accomplished as much as I have during my time at Mines thanks to the continued opportunities he has provided, and his efforts in our group to produce research and results that are of interest to communities beyond my own.

Thank you to the members of my Ph.D. committee, Fred Sarazin, Fred Gray, and Lawrence Wiencke, for contributing their time and input to my degree. Your input to this research has made it more meaningful to me, and to the scientific community.

Thank you to all of the educators at Mines and throughout my life, that have been involved in providing me an education through classwork and research opportunities.
My close friends from all periods of my life have helped make me the person that I am today. Thank you, everyone.

My family is responsible for giving me the life that I have, and has provided the world that allowed me to start on the path that has led me to this point. I hope to continue living the life and being the person that they helped make.

Julia, my wife, has supported me from the beginning of my graduate school tenure. With her, I have started a new part of my life, and began a new family. Without her, I would not be who I am. Thank you for everything.
For my family.

Past, present, and future.
CHAPTER 1
GENERAL INTRODUCTION

In this dissertation, basic research into organic plastic scintillator systems for radiation detection and measurement will be discussed. A deeper understanding of how these systems work on a more detailed level will allow for improvements to existing technology as well as building a more guided framework for developing new technology that can be integrated either in whole or in part to existing radiation detection systems.

This research is deeply collaborative in nature, and could not be performed without a synergistic partnership with colleagues from within the field of organic chemistry. Therefore, the thesis work has a significant overlap with that of Dr. Henok Yemam who in Spring 2017 successfully defended his Ph.D. in Applied Chemistry at Colorado School of Mines.

1.1 Dissertation Structure

The research performed in the past 6 years can be broadly broken down into two separate approaches, each of which is more specifically broken down into a few distinct subsections. This document will open with a discussion of the motivation for pursuing this research, detail the basic science and current knowledge base surrounding scintillators in general as well as each separate approach, and then give an executive overview of each chapter along with some examples of promising or published results. Several publications have come out of this research and will be utilized as chapters in the main body of this text. A breakdown of author contribution as well as any additional related information not detailed in the publication will be discussed in the executive summary of each chapters associated approach. The document will conclude with a general summary of all current results as well as any ongoing and future work that can be expected to be investigated.
1.2 Motivation & Background

The DNDO (Domestic Nuclear Detection Office) of the DHS (Department of Homeland Security) is the federal entity tasked with the stated mission of: “Prevent nuclear terrorism by continuously improving capabilities to deter, detect, respond to, and attribute attacks, in coordination with domestic and international partners” [1]. The DTRA (Defense Threat Reduction Agency) of the DoD (Department of Defense) has stated that its mission is to “Safeguard the United States and its allies from global WMD threats by integrating, synchronizing, and providing expertise, technologies, and capabilities.” [2]. Both groups have contributed funding to our research group at CSM to perform basic research on, and investigate possible alternatives to the world’s current detection systems in place as non-proliferation safeguards against illicit handling and movement of Special Nuclear Material.

Special Nuclear Materials (SNM), such as $^{233/235}$U and $^{239}$Pu, are radioactive isotopes 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 [3]. The widespread application of these combined detector systems is hindered 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, respectively [4].

The initial research was prompted by what became globally known as the $^3$He supply problem. The main radiation detection system in place to detect neutrons, specifically from SNM sources, consists of a gas proportional counter filled with $^3$He gas. Due to the kinematics of the neutron capture reaction (Equation 1.1b) and the way the gas detectors work, there are distinct signals from the reaction products and little to no sensitivity to the obfuscating gamma background radiation; thus $^3$He is the ideal isotope for unambiguous neutron detection. These detectors are an integral part of the Radiation Portal Monitor Program (RPMP) (developed by the U.S. Customs and Border Protection agency of the DHS), which are deployed at international borders globally. In addition, $^3$He has several other industrial and academic uses (i.e. cryogenics, condensed matter physics) [5]. Owing to the natural abundance of $^3$He being only 0.000137% of natural helium, the main source of the US $^3$He supply came from the decay of the tritium used in its nuclear weapons (Equation 1.1a) [6]. In the past 20 years, the increased demand by the US and global homeland security communities for $^3$He far outstripped the supply, and so alternatives needed to be investigated and developed.

\[
^3H \rightarrow \begin{cases} 
^3He + e^- + \bar{\nu}_e & Q = 18.6\text{ keV, } T_{1/2} = 12.32\text{y} \quad (a) \\
\end{cases}
\]

\[
^3He + n_{th} \rightarrow \begin{cases} 
^3H_{(573\text{keV})} + p_{(191\text{keV})} & Q = 764\text{ keV, } 100\% \quad (b) \\
\end{cases}
\]

Helium-3 Production & Thermal Neutron Capture Kinematics [7]

Alternative scintillator materials can broadly be categorized based on if they are made from organic or inorganic materials, with the main forms being gases, crystals, liquids, or plastics. Due to their relative low cost, current widespread deployment and integration into existing detector systems, and ease of manipulation and development of baseline controls, this research began and remains focused on investigating organic polymer based plastics (Figure 1.1).
Plastics are well-studied, durable, very low-cost, and importantly, can be formed, or machined into any shape or size. These qualities allow us to investigate several alternatives at once, as we can develop tests for several small scale alternative materials, before scaling up promising systems to confirm results and perform further material tests. The presumed simplicity of these systems was underestimated, but investigating the complexity of these systems is what has led to significant research findings, and further grant awards. This research has been or is funded through US DoD DTRA award number: HDTRA1-11-1-0025, as well as US DHS DNDO grants # DHS-14-DN-077-AR-NC7 and DHS-16-DNDO-077-001.

1.3 Organic Plastic Scintillator Basics

The simple purpose of a plastic scintillator is to produce detectable light in the presence of radiation. The working principle of how this occurs in plastic scintillators is that the absorption of the incoming radiation’s energy (Figure 1.2) by an inexpensive polymer matrix [e.g. poly(vinyltoluene) (PVT)] is followed by the subsequent cascade of energy transfers (Förster resonance energy transfer (FRET)) to a primary fluorescent dopant [e.g.
2,5-diphenyloxazole (PPO)] and an optional wavelength shifter [e.g. 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP)] [8, 9] (Figure 1.3). Finally, the emitted photons are collected by a photodetector such as a photomultiplier tube (PMT) or photodiode. A pulse is generated that is proportional to the deposited energy of the incident radiation, but might be quenched due to radiation type. The various pathways detailed in Figure 1.2 are important due to the scintillation light quenching nature of some of them. These pathways can also be taken advantage of in order to tune the scintillator’s response to allow for some particle identification properties as discussed in detail throughout this work.

Figure 1.2: Jablonski Energy Diagram [10]
Organic scintillators all produce scintillation light based on the presence of aromatic benzene rings in their molecular structure. This is due to the geometry of the ring structure which allows the $\pi$ electrons (electrons located in overlapping atomic orbitals between two atoms) to become de-localized above and below the plane of the benzene ring molecule. These de-localized electrons are easily excited to a singlet state (e.g. $S_0 \rightarrow S_1$) by incident radiation (green lines in Figure 1.2), and their subsequent de-excitation (red lines in Figure 1.2) is the source of luminescence in plastic scintillators, which is specifically known as fluorescence. The excitation can also put the electron into a triplet state (e.g. $S_0 \rightarrow T_1$), but this is less likely to occur as a result of direct excitation (due to forbidden spin transitions). Also as a result of the forbidden spin transitions, these triplet states orders of magnitude longer time to decay, which results in a longer wavelength of light known as phosphorescence.

Instead, the electrons populate triplet states via other mechanisms, such as intersystem crossing, which is more likely to occur when the vibrational substates of the singlet state, overlap with those in the triplet state (e.g. $S_{10} \rightarrow T_{14}$). This process becomes more probable with increasing nucleus size (high $Z$) and can be used to enhance scintillators’ radiation response (This is an avenue of future work discussed in 9.1.1). Another mechanism that is believed to contribute to the population of triplet states is ion recombination. Following significant ionization (bond breaking) from heavy charged particles traveling through the scintillator, instead of the electrons being excited into the triplet state, the electrons 'fall'
into the triplet state during the ion recombination. This is the current theory used to explain why heavy charged particles such as protons or alphas produce statistically more delayed fluorescence (which results from populated triplet states interacting with each other, and is discussed in detail in Chapter 6) than electrons and gammas, which in turn allows for PSD analysis.

All organic scintillators suffer in ion detection from a type of pulse height defect, known as quenching, that reduces the number of emitted scintillation photons to a small fraction of the quantity emitted in detection of gamma photons or fast electrons of the same energy. It has been observed that the addition of higher concentrations of additives (fluorescing or neutron sensitive) can lower the overall light output of a scintillator and/or worsen the quenching effect. This is known as concentration quenching. Additionally, a source of quenching can come from impurities in the system, most notably, molecular oxygen, which must be strictly controlled during polymerization. Leftover impurities from synthesis, even at the ppm level, can also drastically decrease light yield. Finally, another source of quenching is known as ionization quenching. This mechanism leads to the non-linear response and significantly decreased scintillation output from incident radiation that has higher charge or mass (i.e. dE/dx or stopping power), which is detailed with experimental results in Figure 1.4.

1.4 Radiation sources and scintillator interactions

Radiation can interact with matter in very different ways depending on the type and energy of the radiation, and the material it is incident upon. There are a few specific types of radiation and interactions that are important to this research.

1.4.1 Electromagnetic Radiation

Photons are the elementary quantum of the electromagnetic field, and are capable of interacting with matter in several different ways. Gamma rays, x-rays, and UV/visible/infrared light are all terms for photons of different energies. Gamma rays are generally associated
with high energy, and generated from nuclear processes, and what is of most relevance to this research. The three most common interactions are known as the photoelectric effect, Compton scattering, and pair production (which is not important to this discussion). Which interaction occurs can broadly depend on the energy of the incident photon and the Z (atomic number, or amount of protons) of the material the photon is interacting with (Figure 1.5).

As seen in Figure 1.5, the photoelectric effect is dominant at low photon energies and high Z materials. This interaction occurs when the photon interacts with a tightly bound electron, which absorbs all of the photon’s energy and is ejected from the atomic orbital (Figure 1.7, B). If all of this interaction were detected by a photodetector a feature known as a photopeak would result, which represents the specific energy of the incident gamma ray (the red line in Figure 1.6). Organic plastic scintillators are largely composed of hydrogen and carbon, with very few high Z atoms present. As such, the photoelectric effect does not occur in standard plastic scintillators to any significant degree (see 9.1.1 for discussion on
future work related to this effect). Instead, the Compton effect is the dominant interaction occurring when gamma radiation interacts with our plastic scintillators.

The Compton effect is a scattering process which occurs when the incoming photon interacts with a free (or loosely bound valence) electron by depositing some of its energy, and scattering off at a different angle, with the recoil electron scattering in another direction (Figure 1.7, D). Within the bulk matrix of plastic scintillators, which is very low $Z$ (being composed mostly of hydrogen and some carbon), all of the electrons are loosely bound, and this effect occurs frequently, and is the major source of interaction that is analyzed.

The angular distribution of the scattered electrons is what produces the Compton continuum and most importantly the Compton edge feature seen in blue in Figure 1.6. Since the photopeak is not produced in plastic scintillators, the Compton edge feature is what is used to calibrate the energy response of the individual plastic. This is due to the Compton edge occurring at a known energy, corresponding to when the incident gamma scatters the recoil electron at exactly $180^\circ$ (maximum energy transfer).
Figure 1.6: Example spectrum which details an idealized mono energetic photopeak and the resulting Compton continuum response to an incident gamma

Figure 1.7: Electromagnetic interactions [13]
Figure 1.8: Klein–Nishina angular distribution for photons scattering off of a free electron: ~0ev in orange, 661keV in blue, 12MeV in green
The angular distribution of the recoil electrons depend on the energy of the incident gamma. The cross section formula which describes the probability of this process is known as the Klein-Nishina formula (the equation is polar plotted in Figure 1.8 for three energies). This equation was derived in 1928 as one of the first verified results of quantum mechanics [14]. When this differential cross section is integrated and plotted against energy it can be used to visualize what an idealized Compton scattering spectrum looks like, as done for various energies in Figure 1.9.

![Figure 1.9: Theoretical idealized Compton edges for various energies](image)

It is useful to know what these theoretically could look like because in any real measurement, these features are never seen in this idealized form. There are several sources of smearing or broadening found in any detector system (electronic noise, scattering effects, background radiation, etc.), leading to spectra that look more like Figure 1.10. While there is no broadened photopeak in most plastic scintillator systems, the smeared Compton edge and continuum are specifically generated for each plastic scintillator sample tested, using a gamma source of a known energy. This spectrum is used for energy calibration and LY measurements (Section 1.6).

The gamma source used throughout this research was a $^{137}$Cs exempt button source with a strength of $\sim 1 \mu$Ci. The source was used because it emits a single gamma ray of 662keV.
The energy of the Compton Edge feature is 477 keV which was used to calibrate each sample individually and establish an individual sample energy scale, in keV$_{ee}$. The keV$_{ee}$ unit stands for kilo-electronVolt electron equivalent, and refers to the fact that different radiation types of the same energy will produce different signals due to ionization quenching (shown above in Figure 1.5). For example, a signal from a 2 MeV alpha particle that is detected with an energy of 100 keV$_{ee}$ means that a similar signal would be produced from an electron of 100 keV. The energy scale could be calibrated to a different source type but since gammas and electrons produce the least quenched signal they are used. 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.
1.4.2 Neutron Radiation

Neutrons are difficult to detect due to the neutrons lack of a net electric charge. They are considered indirectly ionizing radiation, since they do not interact via the electromagnetic force, and instead must physically collide with the nuclei of material in order to cause secondary interactions. They are approximately the same size and mass as a proton and as such the (n,p) scattering reaction is the most common form of interaction in the hydrogenous matrix of plastic scintillators. Once scattered, the recoil proton, which carries a charge, can then proceed to travel through the matrix either ionizing or exciting the electrons in its path and producing luminescence. Following the ionization (broken chemical bonds), the process of ion recombination populates more triplet states in the molecular orbitals, than occur from direct excitation from other forms of radiation (electrons and photons). This is a currently proposed mechanism for the source of delayed fluorescence from neutron radiation that allows for PSD.

With each scattering interaction, the neutron loses some of its energy (dependent on angle of scatter) and eventually becomes thermalized to an energy of ~25meV. At this energy the
neutron becomes more likely to be absorbed by certain materials, such as the 10B isotope. This is another method of detection which also forms the basis for a large portion of this research (Chapter 2).

To test the plastic scintillators response to neutron radiation, a $^{244}\text{Cm}/^\text{13}\text{C}$ based ($\alpha$,n) source with a strength of $\sim 60$ mCi (based on the $\alpha$ decay of $^{244}\text{Cm}$) was used. This source produces about half of its neutron fluence from $^{244}\text{Cm}$ undergoing spontaneous fission. The other source of the neutron fluence comes from the alpha decay of $^{244}\text{Cm}$ interacting with the $^{13}\text{C}$ isotope via Equation 1.2.

$$\alpha_{(5.8\text{MeV})} + ^{13}\text{C} \rightarrow n + ^{16}O^*$$

Equation 1.2

$^{244}\text{Cm}/^{13}\text{C}$ source ($\alpha$,n) reaction

In addition to the significant neutron flux produced by this source, the resulting $^{16}\text{O}$ nucleus is left in an excited state (2nd level) and emits a high energy gamma (6.13 MeV) upon de-excitation. This gamma then produces a significant Compton scattering background through the energy region of interest, and along with the gamma ray background resulting from the spontaneous fission decays, this source works effectively as mixed n/$\gamma$ field radiation source. This allows for PSD tests to be performed easily without the need of mixing multiple sources.

In order to better characterize the plastic scintillator samples’ (and the $^{244}\text{Cm}/^{13}\text{C}$ source itself) response, the neutron energy spectrum of the source was modeled (using the Sources 4C code [17]) in order to better know what energy neutrons the plastics were being exposed to. Figure 1.12b shows the resulting simulated neutron energy spectrum, which compares well to available experimental results [18]. With this source, the plastics are exposed to neutrons up to $\sim 8$ MeV, with a large amount of the neutrons having energies of $\sim 1$ MeV and $\sim 3.5-4$ MeV.
(a) Experimental neutron energy spectrum (gamma ray spectrum inset)[18]

(b) Sources-4C simulated neutron spectrum. The spontaneous fission neutron spectrum, ($\alpha$,n) spectrum and their sum are shown. (units of counts vs. MeV)

Figure 1.12: $^{244}$Cm/$^{13}$C neutron energy spectrum
1.4.3 Other sources for directly ionizing radiation

A few other sources were used in these experiments. A $^{241}$Am button source was used as a source of (roughly) mono energetic alpha particles. This was used to mimic a thermal neutron signal for testing mono energetic PSD (it would also give an idea of where the $^{10}$B capture signal will occur, which was useful when screening low LY samples). It was also used to quickly compare quenching effects between various samples, due to the high count rate of heavy charged particles when placed directly on (or submerged in) scintillators (Figure 1.13).

Figure 1.13: $^{241}$Am button source submerged in liquid scintillator mixture

A $^{90}$Sr and a $^{22}$Na source were also occasionally used in experiments to test responses to direct beta excitations and provide a higher energy gamma calibration for low LY samples.

1.5 Typical Equipment & Setup

There are several laboratories and different pieces of equipment required to synthesize and qualify the dopants, synthesize and qualify the finished plastic scintillators, and finally create and interpret the data produced from testing the plastic scintillator’s radiation response.

The dopant synthesis, purification and qualification procedures are gone over in the discussed publications, with even further detail on the involved chemistry being found in Dr. Henok Yemam’s PhD dissertation [19].
A basic plastic scintillator is a simple combination of a polymer matrix with some small amount of scintillating fluor doped into it. This recipe can be expanded upon greatly, and is the basis for much of the following chapters. The plastics are created by a bulk radical polymerization procedure, which involves taking a vial containing a measured amount of prepared monomer (on the order of 1-50 grams) and adding into it a small (≥1 wt%) amount of fluorescent dopants. This mixture is deoxygenated by running an inert gas (Argon or Nitrogen) through it, and then placed into a gas flooded vacuum oven (Figure 1.14a), and heated for several days during which the mixture polymerizes into a hard plastic puck (flat cylinder). These pucks are then broken out of the glass and one surface is machined, sanded, and polished to a high finish.

Once a plastic scintillator is finished, it is then wrapped in reflective tape, coupled to a photomultiplier tube with optical grease, and sealed in light tight material (aluminum foil and electrical tape). The sample’s radiation response is tested via exposure to several different radioactive sources. The two most utilized sources throughout this work are a $^{137}$Cs source (see 1.4.1 for specific source details), which is used to measure the samples’ response to mono energetic gamma rays and give a measure of light yield (as compared to a known control sample). The second is a $^{244}$Cm/$^{13}$C source (see 1.4.2 for specific source details) which is used to generate responses to a mixed field of high energy neutrons and gammas. The coupled plastic scintillator is normally tested in a heavily shielded lead castle, to better shield from background (and moderate the flux of the neutron source), however the energy spectra of the neutrons can be heavily moderated by testing the sample inside of a castle built out of high density polyethylene blocks (Figure 1.14b). This allows for a more rapid testing of the scintillator’s response to thermalized neutrons.

The scintillators’ fluorescence response to the incident radiation is captured by the PMT and sent to a DAQ system (Figure 1.15a) based on a 250 Msample/sec waveform digitizer (built in-house based on a design used by the MuCap collaboration [20]), which is controlled by a MIDAS software interface [21]. The ROOT data analysis framework was utilized to an-
Figure 1.14: Synthesis and Testing Equipment
alyze the collected data, and develop relevant output spectra [22]. A CAEN DT5720 desktop waveform digitizer (Figure 1.15b) was purchased and tested in some of the WNR experiments (2.2.1), and is currently being phased in to main DAQ system for future experiments in this work.

![Waveform Digitizers](image)

(a) DAQ electronics card  
(b) CAEN DT5720

Figure 1.15: Waveform Digitizers

The individual waveforms can be further analyzed for subtle differences in decay timing which allow for particle identification. The waveform pulse can be divided into 2 areas by selecting a specific amount of time following the peak; one comprising the prompt fluorescence in the peak of the pulse, and the other area making up the decay tail of the pulse which comes from delayed fluorescence (further explanation and examples are found in 1.6.2) . When interacting in the scintillator, incident radiation with a higher stopping power will produce more delayed fluorescence [9] (Figure 1.16), which allows us to compare the ratio of the waveforms’ areas in an analysis technique which is known as pulse shape discrimination (PSD). This property has been known for decades and utilized extensively in conjunction with liquid organic scintillators and in certain inorganic crystal scintillators, and while mentioned early on [9], it has not been further explored in solid plastic scintillators until recently. This is discussed in detail in Chapter 6.
Further material properties of the finished plastic are recorded, such as glass transition temperature and a basic measure of hardness by using a differential scanning calorimeter and a Shore-D testing apparatus respectively. Samples of interest are often repeated with measurements being retaken at later dates to test for aging effects of the plastic, such as yellowing, clouding or crazing, all of which negatively affect the measured radiation response via light quenching effects (1.3). Recently a solid state fluorescence spectrometer (QEPRO) has been purchased by our group and is being used to measure the fluorescence emission spectrum of the entire scintillator system (instead of the individual components in solution) in response to specific wavelengths of light, and possibly directly from ionizing radiation.

1.6 Analysis Codes and Results

Analyzing the radiation response of a scintillator sample requires several different computer programs and codes to produce meaningful, easy to interpret results. Examples of results generated and seen throughout this body of work are introduced.
1.6.1 MIDAS and Resanalysis

A version of the MIDAS software[21], which was customized for use in the MuCap experiment[20], was used to interface with the waveform digitizer. This DAQ frontend is designed to be operational via a Web browser, and allows for customization of DAQ parameters. Several timing and threshold options can be adjusted to capture the pulses/waveforms of interest. Once optimized, the user can (via the MIDAS web interface) tell the digitizer (via a single or combination of chosen triggers) when to begin recording data and then save them to a MIDAS specific binary file.

Resanalysis is the name of a C++ program that was written to parse the binary file that MIDAS generates which contains the digitized waveform data. The code records peak pulse values and associated timing information, as well as integral counts contained within various pre-defined areas following the identified peak of the individual waveforms. This is performed on data which was recorded in each active channel of the digitizer. If multiple channels are used, coincidence information between the channels is also saved. As all this information is parsed, it is saved into a ROOT filetype to allow for further data manipulation and analysis with the ROOT framework.

1.6.2 ROOT and Data Manipulation

The ROOT platform is data analysis framework designed by and for the CERN collaboration [22]. The programming is written in C++ and through its use of program specific data containers and substructures, called “trees”, “branches”, and “leaves”, it is specialized to perform numerous types of analysis on large data sets, such as those generated in nuclear and particle physics experiments. Standard mathematical functions, histogramming, curve fitting, and various forms of graphical visualizations are some of the common uses. ROOT was used extensively in this work to parse the individual waveforms digitized from the scintillators radiation response. Once saved and extracted, the pulses were analyzed for peak height, integral counts through the entire waveform, as well as in a specific portion of the
pulse designated by the user at a certain bin following the peak (a delayed area).

Throughout this work results are commonly presented in plots similar to the ones in Figure 1.17. The plots on the left are often referred to as PSD figures and are produced by plotting the peak height of the pulse (x axis) against the \( \frac{Q_{DA}}{Q_{tot}} \) value, which is ratio of counts in the delayed area of the pulse to the integral counts in the total pulse (y axis). As more delayed fluorescence is produced by the incident radiation, this ratio increases, and causes the pulse shapes to change enough that they separate into discrete bands corresponding to photon radiation and in this case, fast neutron radiation. In common scintillators where delayed fluorescence (triplet state population) is not enhanced, pulses from mixed radiation types all have the same shape, and can not be discriminated, and appear plotted together in a single data band.

To quantify the ‘goodness’ of the PSD capabilities a cut is made at a specific energy, and a projection of all the signals is put onto the y axis, resulting in the corresponding plots seen on the right of Figure 1.17. From here a dimensionless Figure of Merit can be calculated by fitting a double Gaussian curve to the peaks, and extracting the fit parameters. This FoM metric and its meaning are discussed fully in Chapter 6.

1.6.3 Compton Edge Analysis

As discussed in 1.4, the Compton Edge feature found in the \(^{137}\text{Cs}\) spectra is never an ideal “edge” but a broadened or smeared slope due to detector effects and the individual response function of each plastic sample. In order to determine LYS and energy calibrations for our plastic scintillators, an approximation has to be made as to the location (bin) of the the Compton edge. In this research the Compton edge was assumed to be at \( \sim 50\% \) between the local maximum and minimum of the smeared edge. This allowed for quick and accurate visual identification of the bin, which allowed for more rapid analysis.

For published data a more rigorous method was used to determine the location of the edge bin. A Mathematica notebook was written that read in the histogrammed data from the ROOT file of a \(^{137}\text{Cs}\) spectrum. The data surrounding the local area of the edge feature
Figure 1.17: Example of plots generated based on comparing delayed energy over energy and y projection [24]
then had a curve fit applied to it. The curve of the smeared edge was modeled by convolving a Gaussian function with a step function as seen in Figure 1.18. There are 5 values of the fit equation which are allowed to vary, which correspond to the standard deviation of the Gaussian function, and the slope and intercept of the two sides of the step function.

Once the fit variables provide a smooth, continuous curve in the edge location, it is then analyzed to find where the second derivative minimum is, which represents the inflection point (50% mark) of the smeared (real data) Compton edge (Figure 1.19). This value has consistently been found at >1% difference of visual approximations, with larger differences only occurring in extremely low (>5% LY) quality samples where the edge is often smeared into the background noise of the spectrum.

Figure 1.18: Smeared edge modeled by convolution of Gaussian distribution with an arbitrary step function
Figure 1.19: Minimizing the second derivative for inflection point and assumed location of C.E.

1.7 References Cited


CHAPTER 2
APPROACH 1 - BORON 10

This chapter provides an introduction into the specific research thrust of utilizing boron 10 isotope to enhance the radiation response of plastic scintillators. There is also an executive summary of each of the following three chapters, which are journal publications covering this material in depth. Major results and any additional relevant details of research not covered in the published material are discussed.

2.1 Introduction

Detection of neutrons plays an important role in the identification of illicit trafficking of special nuclear materials. With increasing demand, the currently deployed state-of-the-art neutron detectors, which are based on $^3$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 [1, 2]. Recent advances in $^3$He alternatives have used plastic or liquid scintillator compounds that contain high neutron cross-section isotopes such as $^6$Li, $^{10}$B, and $^{155}$Gd/$^{157}$Gd isotopes [3, 4]. This first approach towards investigating avenues for improving plastic scintillators focused on the incorporation of boron containing organic compounds because of the significant natural abundance (~20%) of $^{10}$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 [5–7] and has been used in some commercial products (e.g. Eljen Technology EJ-254). However, the price of the neutron sensitive scintillator products is still dominated by carborane prices 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
$^3$He based detectors motivating further research on improving boron containing scintillator systems.

\[
^{10}B + n_{th} \rightarrow \begin{cases} 
^{7}Li_{(1.01 MeV)} + \alpha_{(1.78 MeV)} \\
Q = 2.790 MeV, \ 6.3\% \\
^{7}Li_{(0.84 MeV)}^* + \alpha_{(1.47 MeV)} \\
\rightarrow ^7Li^* \rightarrow ^7Li + \gamma_{(478 keV)} \\
Q = 2.310 MeV, \ 93.7\% 
\end{cases}
\]  

(2.1)

Boron-10 Thermal Neutron Capture Kinematics [8]

The neutron induced reaction on $^{10}$B has a thermal cross section of 3837 barns ($^{3}$He: 5333 barns) [9] and results in light charged ions (alpha and $^7$Li) as the products that carry significant kinetic energy to be easily detected in several different detector setups (Equation 2.1). Commercial plastic scintillators currently use a m-carborane (Figure 2.1) as a boron source due to its high boron content (75%), which allows for a lower loading. The solubility limit in plastic scintillators is ~5 wt%. Despite their current established use, m-carboranes are very expensive (current list price of $184 a gram from Sigma Aldrich), not easily enriched in $^{10}$B (no commercial source currently offers this for purchase), and recently there is difficulty in obtaining them from their current synthesis source, so prices of commercial plastics containing this material are rising and an alternative boron source is needed.

Figure 2.1: m-carborane[10]

It is worth noting that the lithium reaction is attractive due to its high Q Value (Equation 2.2), and there is active research into utilizing this as an additive for thermal neutron detection [11]. However, the organic chemistry involving lithium is more complicated and
expensive, the isotope of interest has a lower natural abundance (5%), and the cross section for the reaction is much lower (938 barns) \[9\], so it has significant drawbacks.

\[
^6\text{Li} + n_{th} \rightarrow \begin{cases} 
^3\text{H}_{(2.73\text{MeV})} + \alpha_{(2.05\text{MeV})} \\
Q = 4.78\text{MeV}, \ 100\%
\end{cases}
\]  

(2.2)

Lithium-6 Thermal Neutron Capture Kinematics \[8\]

Gadolinium has the highest cross section for thermal neutron capture of any of the elements. This is due to 2 naturally occurring isotopes, \(^{155}\text{Gd}\) (14.80% abundance) and \(^{157}\text{GD}\) (15.65% abundance) which have 60,900b and 254,000b cross-sections, respectively. Gadolinium hasn’t been as extensively studied for use in plastic scintillators as boron and lithium until recently \[12, 13\]. Due to the orders of magnitude higher cross section than other neutron sensitive candidate, gadolinium based additives could prove effective at extremely low loading concentrations. One of the large drawbacks to utilizing gadolinium additives is that both neutron capture reactions are radiative capture reaction, which do not produce a heavy ion as a reactant (Equation 2.3). Following de-excitation, there is significant nuclear and atomic rearrangement, which results in a large shower consisting of several gamma rays, x-rays, as well as internal conversion and auger electrons. 99.2% of the Q value is carried by the photons, while only 0.8% is carried with the electrons. These reactants do not allow for meaningful PSD, and create a large white background of radiation signals in scintillation detectors. Online gamma rejection, or tagging of high energy gammas would be required to glean important information related to quantifying neutron detection.

\[
^{155}\text{Gd} + n_{th} \rightarrow \begin{cases} 
^{156}\text{Gd}^* \rightarrow ^{156}\text{Gd} + X\gamma + Ye^- \\
Q = 8.536\text{MeV}, \ 100\%
\end{cases}
\]  

(2.3)

\[
^{157}\text{Gd} + n_{th} \rightarrow \begin{cases} 
^{158}\text{Gd}^* \rightarrow ^{158}\text{Gd} + X\gamma + Ye^- \\
Q = 7.937\text{MeV}, \ 100\%
\end{cases}
\]

Gadolinium-155/157 Thermal Neutron Capture Kinematics \[8\]
There are issues with introducing new compounds into the standard plastic scintillator formulations. As discussed in 1.3 the admixture of fluorescing or neutron sensitive dopants can produce quenching effects which lower the overall light output of a scintillator. In the case of boron additives, the reactants of a successful thermal neutron capture event are an alpha particle and lithium nucleus (Equation 2.1). The alpha particle is light enough to travel a distance (∼ O(10µm)) through the plastic and deposit its energy which produces detectable scintillation light. Due to the (relatively) high mass and charge of the α, there is a strongly quenched, non-linear response resulting in the signal being found at significantly lower energies than the alpha originally carried. The spectrum in Figure 2.2 shows an example of a peak corresponding to ~2000 thermal neutron capture events. Despite the fact that the alpha particles that produced that peak were born with ~1.5 MeV, the light signal produced in the scintillator material is only equivalent to a ~90 keV electron.

Figure 2.2: Experimental result affected by ionization quenching [10]
The combination of light output and quenching effects determines the overall performance of a scintillator in how well one can separate the neutron reaction signal from gamma backgrounds and electronic noise. This and other sources of quenching can be introduced with the addition of boron dopants, and must be considered.

This boron work is unique due to the close collaboration between Mines physics and chemistry groups, which allow for a feedback based approach towards synthesizing, altering, qualifying and testing the dopants, instead of only working with what is commercially available.

Based on this approach our group has pursued 3 different patents for our work with boron, 2 of which have been awarded [14, 15], and one which has been converted to a non-provisional. In addition, there are 3 papers published (and 1 in progress) by our group on these various subsection results [16–18].

2.2 Borate Esters / Extrusion / Liquids

The initial research project was funded by the Defense Threat Reduction Agency (DTRA) of the Department of Defense (DoD), with the stated goal of basic research towards $^3$He alternatives. The research began with a collaboration between our Nuclear Physics group and a Chemical Engineering group who had access to, and background experience in operating a large scale plastic extruder on campus. Pascale Meysing (née Chouinard-Dussault) defended a M.S. degree in Chemical Engineering in 2012 based on her collaboration with this research and was instrumental in the early stages of understanding these systems.

Seeking to reproduce success found in other large-scale extruded plastic scintillator experiments such as the MINOS detector[19], the initial steps in this research began with a large learning curve where the group learned how to first make basic plastic scintillators (Figure 2.3), and how to deal with all the associated difficulties and concerns of installing, and running a industry grade extrusion machine (Figure 2.4).

This initial work led to the establishment of 3 separate laboratories, (a chemical engineering lab for chemical analysis, the extruder lab in the GRL for plastics processing, and a
(a) Liquid scintillators
(b) Solid scintillators

Figure 2.3: Borate Ester Based Scintillators

Figure 2.4: A Berstorff ZSK-25 twin-screw extruder, with hopper, water cooled conveyor, and control panel. Installation shown at Mines based GRL lab.
nuclear physics lab at the Denver Federal Center for radiation response testing and analysis), the building of the detector systems and setup of the first testing procedures, writing of initial analysis codes, and finally the first successful plastic scintillators made at CSM. After more rigorous chemistry was pursued, several new boron containing molecules the group successfully developed and tested. The 3 different borate esters (Figure 2.5) that were studied are all compatible in liquid scintillator mixtures as well as both cast and extruded plastic scintillators of various matrices (PVT, PS, PC, PMMA).

![Chemical Structure 1](image1.png)

**Figure 2.5:** The molecules were referred to as CPA-10, CPA-16, and CPA-51 respectively for documentation and communication.

![Chemical Structure 2](image2.png)

![Chemical Structure 3](image3.png)
These liquid dopants are unique due to their ease of synthesis with enriched $^{10}\text{B}$ materials (a spectrum showing the scintillators response to thermal neutrons is shown in Figure 2.6), and they are all classified as non-flammable (or non-combustible) based on flash point testing. Further testing of these esters were performed at the WNR beamline at the LANSCE of LANL (See 2.2.1). This allowed for testing of scintillator response at a much higher fluence and energy of incident radiation. The non-flammability allowed for much easier transport and storage of liquid scintillators on the national lab campus.

![Figure 2.6: Poly carbonate based scintillator containing CPA51 with clear boron capture response and PSD](image)

Figure 2.6: Poly carbonate based scintillator containing CPA51 with clear boron capture response and PSD

Overall it was determined that the extruder did not effectively allow for basic research and would only become useful and applicable once a precise formulation has been established, as there are far too many variables in the machine (screw arrangement, various mixing elements, different temperature zones) and the organic plastic systems (matrix, and various dopants in multiple ratios) to optimize for each small variation or new idea that requires extensive repeatable testing. Significant experimentation moved to doing small scale bulk
polymerization.

The developed borate esters were put into an invention disclosure which has been awarded US Patent #9,796,921 [14]. This initial establishment of research methods and success led to the current and ongoing collaboration with Alan Sellinger’s Chemistry group at CSM.

2.2.1 WNR Tests at LANL LANSCE

To fully characterize these enriched borate esters and explore their utility as detectors in nuclear science laboratory settings, a new source of neutrons was sought, since the neutron energies and fluence with our laboratory source was relatively low as compared to other facilities. Based on recommendations from colleagues and collaborators who have (or had) setups (e.g. TPC [20], and SPIDER [21] experiments) located at the Weapons Neutron Research Facility (WNR) at LANSCE, it was determined that this facility would provide valuable data. This experiment would also allow us to test our scintillators timing sensitivities. We applied for, and were granted beamtime in a flight path containing the highest energy spectrum of neutron energies. This experiment was performed concurrently with experimental tests of a novel, filtered BaF$_2$ detector discussed to the author’s Nuclear Engineering M.S. research [22].

The Weapons Neutron Research facility, located at LANSCE in LANL, can be summarized as a large scale proton/neutron beam experiment setup. Experimental research in this facility includes basic, applied, industrial, and most relevantly, defense related research [23]. The facility provides an 800 MeV proton beam originating from the linear accelerator (LINAC) based at LANSCE. This beam (for WNR) impinges on an unmoderated tungsten spallation target, which generates a large (white) fluence of neutrons. These are collimated and directed into specific beamlines providing specific spectra of varying neutron “hardness” depending on angle in respect to the original proton beam. Figure 2.7 below details the facility and the different different flight paths (FP) (and alternative facilities) which are available. The FPs are named based on their angle off of the main proton beam (i.e. FP90L refers to the flight path which is 90 degrees to the left of the main beamline).
Our experiment was approved for testing in Flight Path 15 Right (FP15R), which is used as “a flexible general-purpose experimental area that can be used for a wide range of experiments” [24]. The 800 MeV protons are pulsed onto the tungsten target with a micropulse spacing of 1.8\(\mu s\). The charged particles resulting from the spallation are quickly steered off via magnets, while the gammas and neutrons are allowed to traverse the flight path. Figure 2.8 details the neutron spectrum which is measured at the different flight path angles. FP15R has neutron energies ranging from \(~100\text{keV}\) up to 600 MeV (the highest
available at the WNR).

![WNR Neutron Flux](image)

Figure 2.8: WNR Neutron Spectrum in various Flight Paths (vs relative flux) [24]

Our experimental setup was transported to the WNR and set up on site. The WNR provides the t0 signal which corresponds to the neutron pulse starting down the flight path which was fed into our digitizer. To reduce the chance of overloading and damaging our photodetectors, the gamma flash and neutrons were scattered off of a tantalum sheet into our detector setup which was located just outside of the beam path, approximately 20m from the tungsten target.

Although there was significant beam downtime, several tests were still completed and showed us that our plastic (and liquid) scintillators respond to and can produce meaningful data from very high energy, high fluence, mixed radiation fields. Adjustments had to be made to the digitizer electronic settings to allow for efficient data collection with such a significantly higher data rate than was produced with our laboratory $^{244}$Cm/$^{13}$C laboratory source. Figure 2.9 shows a PSD spectrum and y-projection of a PS sample irradiated by 15R. There is significant scattering background, and there a distinct third band of signals,
which most likely is produced from deuterons or breakup reactions of $^{12}$C in the matrix, due to the high energy neutrons incident on the plastic.

![Image](image1.png)

(a) a PSD spectrum from a 20% PPO sample containing 10% CPA16 exposed to 15R

(b) y-projection of the spectrum

Figure 2.9: Borate ester based scintillator response in the WNR beamline

With the provided T0 signal from the tungsten source, a short time of flight (tof) analysis code was written and for use with this data. Figure 2.10 shows the spectrum from the simple timing analysis, where a clear peak from the gamma flash is seen followed by a full response to the resulting neutron energy spectrum. Due to the micropulse timing, there is wraparound data in this timing snapshot. 1 MeV neutron signals arrive $\sim$1440ns after the gamma flash, which is also where $\sim$650keV neutrons and finally the $\sim$160keV neutron signals arrive. Deeper analysis into the plastic scintillator’s timing properties has not been pursued but would be an interesting property to begin characterizing in future experiments.

### 2.3 Boron Containing Dopants

The second round of research was funded by DHS / DNDO. Although the funding source changed, the research approach remained the same: Basic research into cost effective $^3$He replacements for neutron detection. In close collaboration with the Mines Chemistry de-
Figure 2.10: Plastic Scintillator time of flight response to 15R fluence, showing full energy sensitivity

Department (Sellinger group), we built upon our experience with adding boron compounds to plastic scintillator formulations and began by investigating any aromatic hydrocarbons that could be easily borylated. This led to the initial formation of TBB and TBP; Tetra borylated pyrene and tetra borylated benzene. These boron containing molecules both fluoresce on their own and produce samples that displayed thermal neutron capture with some measurable LY. However, the solubility of the molecules did not allow for testing higher boron content. We here began to investigate the effect of molecule size and symmetry and instead of tetra borylated benzene, two different tri-borylated benzene molecules were synthesized. One was very symmetrical like TBB (1,3,5 TrBB), the other an identical molecule but organized in an asymmetrical configuration (1,2,4 TrBB). These molecules, although being identical in composition, interacted very differently with our organic systems due to their geometry (Figure 2.11).

$^{135}$TrBB had a solubility limit of $<5$ wt% and $^{124}$TrBB could be added into the polymer matrices (polystyrene (PS) and polyvinyltolune (PVT)) up to 20 wt%. This was the first indication on how important molecular geometry of dopants would be in this research and in part led to the second major avenue of this research as discussed in 6.
Figure 2.11: Geometry comparison of triborylated benzene molecules

(a) Symmetrical 135TrBB
(b) Asymmetrical 124TrBB

Figure 2.12: 124TrBB Boron Capture
Figure 2.12 displays a spectrum of a plastic scintillator containing 15 wt% of 124TrBB as exposed to a neutron source that had its flux thermalized. The prominent spot feature corresponds to the mono energetic capture reaction of thermal neutrons by the $^{10}$B isotope.

It was also seen that high concentrations of 124TrBB began to induce the onset of PSD (Figure 2.13) in plastic scintillators with very low primary fluor concentrations (1 wt% PPO). This could be due to the aromatic nature of the 124TrBB molecule itself, or a triplet state populating method, similar to the intersystem crossing seen in heavy metal complexes (9.1.1), known as hyperfine coupling. This has recently been identified as a source of phosphorescence (where populated triplet states which are allowed to decay directly to singlet ground states without annihilation) in other phenylboronic acids [25].

To build on this successful dopant, new synthesis was proposed and developed to create a version of this dopant that would be enriched in the $^{10}$B isotope based on different precursors (see 2.5). The developed boron dopants were put into an invention disclosure which has been awarded US Patent #9,864,077 [15].

This work is detailed in Chapter 3 as a published journal article. Significant research contributions were made by the listed authors. Henok Yemam performed the synthesis, purification, and characterization of all the chemical dopants and made polymer samples; Adam Mahl made polymer samples, performed the machining/polishing and test preparation of the finished scintillators, and conducted the radiation testing and results analysis; Unsal Koldemir helped to set up the initial synthesis experiments and grow the analyzed TBP crystals, Sean Parkin performed the TBP crystallography analysis, Tyler Remedes assisted in sample preparation and providing sample photographs, Alan Sellinger and Uwe Greife were the P.I.s and research advisors who generated the initial ideas and provided funding and supervision for the work. Principal editing and review was performed by Henok Yemam, Adam Mahl, Uwe Greife, and Alan Sellinger.
Figure 2.13: 1%PPO, 17% 124TrBB displaying onset of PSD
2.4 $\text{B}_2\text{Pin}_2$

During our ongoing investigation and synthesis of our previously discussed dopants, a commercial molecule was purchased and heavily utilized in synthesis, known as bis(pinacolato)diboron; $\text{B}_2\text{Pin}_2$ (Figure 2.14).

$\text{B}_2\text{Pin}_2$ was first used in organic reactions by Miyaura et al. to create an intermediate for Suzuki coupling [26]. The conversion of arylhalides to arylboronates using an inexpensive and readily available borylating reagent such as $\text{B}_2\text{Pin}_2$ has been extensively used in the pharmaceutical and organic electronics industries [27, 28]. While the reactions were scaled up to synthesize the gram quantities necessary for tests with radiation of our previously discussed compounds, we ran the same tests utilizing the precursor $\text{B}_2\text{Pin}_2$ as a boron source. It was cheap ($0.5/g$) and readily available in a highly pure form.

$\text{B}_2\text{Pin}_2$ was able to be added to our scintillators up to 15 wt% with no significant quenching of LY until max loading, and produced a clear boron capture signal in all samples. This molecule was also compatible with plastic scintillators that had been overdoped with significant amounts (>20 wt%) of PPO (the details of this mechanism are discussed in Chapter 6) allowing the thermal neutron capture signal to be differentiated from the gamma ray background as detailed above in Figure 2.15. This result was directly comparable to scintillator formulations being developed by other groups [5] but at lower cost. With all constituents of this scintillator being easily obtained and mixed, this scintillator can be easily developed in-house by any research group without the need for significant chemistry capabilities or
Figure 2.15: $B_2pin_2$ containing scintillator displaying PSD + Boron Capture features

funds. Although the initial samples displayed visual aging effects over the course of a year of ambient exposure, the effects were not large and could be minimized with various methods and our now refined polymerization procedures.

$B_2pin_2$ was also tested and found to be compatible when admixed into various liquid scintillator cocktails. The dopant had a solubility of up to 14 wt% in EJ-309, which is a uniquely non-flammable liquid scintillator, and up to 31 wt% in BC-501/EJ-301, which is the more common, xylene based liquid scintillator cocktail. Very clear thermal neutron capture signals were seen along with the standard PSD found in liquid scintillators (Figure 2.16). LY was only slightly quenched (~90%) with concentrations at ~15 wt%, and was reduced to 80% LY in ~30 wt% loadings. With liquid scintillators being de-oxygenated and hermetically sealed, there has been no yellowing of the cocktail or dopant crashing out in over 5 years of storage.

This work is detailed in Chapter 4 as a published journal article [17]. Significant research contributions were made by the listed authors. Adam Mahl made polymer samples,
Figure 2.16: $\text{B}_2\text{pin}_2$ admixed into liquid scintillator cocktail BC501 displaying PSD + Boron Capture features.
performed the machining/polishing and test preparation of the finished scintillators, and conducted the radiation testing and results analysis; Henok Yemam performed the synthesis, purification, and characterization of all the chemical dopants and made polymer samples; John Stuntz and Tyler Remedes assisted with sample preparation, Alan Sellinger and Uwe Greife were the P.I.s and research advisors who generated the initial ideas and provided funding and supervision for the work. Principal editing and review was performed by Adam Mahl, Henok Yemam, Uwe Greife, and Alan Sellinger.

2.5 Enriched Boron

Since only the $^{10}$B isotope captures the thermal neutrons, 80% of the boron atoms in our dopants and subsequent samples do not contribute to the detection efficiency. In order to maximize the efficiency at low concentrations of dopant, it became important to develop new synthesis routes that begin with easily obtainable material already enriched in $^{10}$B. The established synthesis of B$_2$pin$_2$ does not lend itself to these changes, so the 124TrBB synthesis was altered to utilize enriched $^{10}$Boric Acid, a very cheap and readily available material created as a byproduct from the electronics industry. This altered synthesis resulted in a new molecule: Enriched Mono $^{10}$Borylated Benzene (MBB). Even though its total boron content per molecule was lower than our previous dopants, it was made with enriched boron so the $^{10}$B content was significantly higher (Figure 2.17).

![Figure 2.17: Borylated benzene possibilities with boron content (MBB, DBB, 124TrBB)]
Figure 2.18: Enriched $^{10}$B samples radiation responses
Figure 2.18 details the Compton edge response and thermal neutron capture peaks produced by samples containing varying amounts of MBB. As far as we know this is the first alternative enriched boron source compatible in organic polymer matrices reported in the literature. Currently, the only commercially available scintillators utilize m-carboranes as their boron source, which are too expensive for widespread deployment. After synthesis, a cost analysis was done to compare this dopant materials cost to the cost of purchasing m-carboranes for use, (which is not available in enriched $^{10}$B form). MBB costs approximately $111.26 per gram of $^{10}$B. From a list price of $174 a gram to a quoted price of $104.40 a gram for a bulk 20g purchase from Sigma Aldrich, m-carboranes cost approximately $696-1160 a gram of $^{10}$B (≈6-10x the cost of synthesizing MBB).

The MBB dopant is also compatible with the overdoping PPO method to allow for PSD. Samples containing MBB have suffered far less aging effects than those containing $^{124}$TrBB or $B_2pin_2$ and display no signs of yellowing, crazing or macroscopic aggregation in a year of storage in ambient conditions, and only minimal response losses. A drawback of MBB is its low melting point, which causes plastics with high loadings to become soft. This issue can likely be mitigated by combining this dopant with our developed cross-linked scintillator formulation discussed in 6.3 and Chapter 8. Our group has filed an invention disclosure for this molecule and its synthesis which has been converted to a non-provisional patent.

This work is further detailed in Chapter 5 as a published journal article [18]. Significant research contributions were made by the listed authors. Adam Mahl made polymer samples, performed the machining/polishing and test preparation of the finished scintillators, and conducted the radiation testing and results analysis; Henok Yemam performed the synthesis, purification, and characterization of all the chemicals and dopants and made polymer samples; Roshan Fernando outlined the initial proof of concept synthesis procedure of the MBB; Joshua Koubek assisted in scaling up the synthesis of MBB; Alan Sellinger and Uwe Greife were the P.I.s and research advisors who generated the initial ideas and provided funding and supervision for the work. Principal editing and review was performed by Adam
2.6 References Cited


CHAPTER 3
BORON-RICH BENZENE AND PYRENE DERIVATIVES FOR THE DETECTION OF THERMAL NEUTRONS


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3.1 Abstract

A synthetic methodology is developed to generate boron rich aromatic small molecules based on benzene and pyrene moieties for the detection of thermal neutrons. The prepared aromatic compounds have a relatively high boron content up to 7.4 wt%, which is important for application in neutron detection as $^{10}$B (20% of natural abundance boron) has a large neutron induced reaction cross-section. This is demonstrated by preparing blends of the synthesized molecules with fluorescent dopants in poly(vinyltoluene) matrices resulting in comparable scintillation light output and neutron capture as state-of-the art commercial scintillators, but with the advantage of much lower cost. The boron-rich benzene and pyrene derivatives are prepared by Suzuki conditions using both microwave and traditional heating, affording yields of 40-93%. This new procedure is simple and straightforward, and has the potential to be scaled up.

3.2 Introduction

Plastic scintillators are polymer-based detector materials for gamma radiation, fast neutrons and other charged particles[2–4]. Their low cost, fast-timing resolution and ease of
large-scale production make it a first-line detection method compared to inorganic crystal
scintillators[5, 6]. 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 $^3$He gas detectors at international borders and airports to detect illicit trafficking of
special nuclear materials (SNM)[7]. Due to $^3$He scarcity and increasing demand, alternative
isotopes such as $^{10}$B and $^6$Li with comparable thermal neutron capture cross sections and
higher natural abundances have been investigated[8, 9]. Current developments of neutron
sensitive plastic scintillators mainly rely on commercially available carboranes as a boron
source due to their high boron content[10]. Thermal neutrons are detected via the capture reaction on the nucleus of $^{10}$B and measuring the scintillation light produced by the
alpha particles ($^4$He) released by this reaction, shown in Equation 3.1[11]. Although carbo-
ranes have high boron content (≈75%wt.), they have limited solubility in plastic scintillator
formulations, are very expensive, and the cost is significantly higher in their $^{10}$B enriched form.

$$^{10}B + n_{th} \rightarrow \begin{cases} 
7Li + ^4He, & Q = 2.790 \text{ MeV}, \ 6.3\% \\
7Li + ^4He + \gamma_{(480\text{keV})}, & Q = 2.310 \text{ MeV}, \ 94\%
\end{cases} \quad (3.1)$$

Alternative methods of thermal neutron detection include boron containing semiconductor
ystals, enriched boron-10 fluoride ($^{10}$BF$_3$) gas filled proportional counters, and boron
lined tube counters along with liquid scintillators doped with boron compounds such as
trimethyl borate[12–14]. However, growing crystals in large quantities for significant area
coverage is difficult and $^{10}$BF$_3$ has severe limitations in deployment due to its toxicity[15, 16].
While boron lined tubes are physically similar to $^3$He tubes, they suffer from reduced effi-
ciencies due to the energy loss effects from having a solid boron wall coverage. Trimethyl
borate mixed into liquid scintillators of many varieties has a very low flash point and is
required to be very well sealed from oxygen in order to reduce quenching effects and main-
tain efficiency. Other isotopic candidates for scintillators such as $^6$Li or $^{155}$Gd/$^{157}$Gd are not
as attractive as $^{10}$B due to higher cost, lack of availability, and reduced compatibility with
inexpensive polymer matrices[17–20]. Furthermore, the price of $^{10}$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. Alternatives to carboranes need to be produced with efficient synthesis methods and inexpensive reagents.

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[21–26]. 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[27]. 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[28]. 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%[29, 30]. 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[31, 32].

We report here the borylation of multi-halo functionalized benzene and pyrene derivatives using the very efficient and mature Suzuki chemistry to afford soluble materials with boron content as high as 7.43wt%. 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.

3.3 Results and Discussion

3.3.1 Synthesis

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 (B₂Pin₂)[33]. In our efforts to complete these reactions within a reasonable time, we used slight excess equivalents of B₂Pin₂ to complete the multiple borylations. Increasing the heating to 90 °C was crucial for completing these reactions in less than 24 hours (Figure 3.1) and our microwave assisted conditions resulted in similar reaction yields in much shorter reaction times (40 min vs. 24 hr).

![Figure 3.1: Conventional heating condition (Trad.) and Microwave (µW) heating condition for generating tetra-borylated pyrene (TBP). These conditions were used for all the reactions.](image)

To show applicability of the aforementioned conditions to other aromatic molecules, related boron containing molecules (Figure 3.2) were synthesized using lower catalyst loading, shorter reaction times, simpler purification methods, and comparable synthesis yields as previous literature methods[34].

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 40–60min[35, 36]. Table 3.1 summa-
Figure 3.2: Boron containing pyrene and benzene derivatives.

Table 3.1: Comparison of multiple borylation by conventional heating vs microwave synthesis.

<table>
<thead>
<tr>
<th></th>
<th>B&lt;sub&gt;2&lt;/sub&gt;Pin&lt;sub&gt;2&lt;/sub&gt;[equiv]</th>
<th>KOAc[equiv]</th>
<th>Microwave</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>3.0</td>
<td>68</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
<td>6.0</td>
<td>63</td>
<td>79</td>
</tr>
<tr>
<td>3</td>
<td>6.0</td>
<td>10.0</td>
<td>85</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>4.5</td>
<td>7.5</td>
<td>61</td>
<td>69</td>
</tr>
<tr>
<td>5</td>
<td>4.5</td>
<td>7.5</td>
<td>83</td>
<td>97</td>
</tr>
<tr>
<td>6</td>
<td>6.0</td>
<td>10.0</td>
<td>41</td>
<td>36</td>
</tr>
</tbody>
</table>

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

The synthesis of 1 (Figure 3.2, 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 percent yield (Table 3.1)[37]. We believe we are the first to report...
the synthesis of this molecule by microwave-assisted borylation. Both $^1$H and $^{13}$C NMR for compound 1 are found in Figure A.1. 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 B$_2$Pin$_2$, and reaction time, however the microwave yield couldn’t be improved. Both NMR and MALDI TOF MS for this compound confirm the product purity and can be found in Figure A.2 and Figure A.6 respectively.

The synthesis of TBP (Figure 3.2, 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[38]. 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[25]. Despite this shortcoming, we turned our attention to analysing this molecule by MALDI TOF MS that confirmed the molecule as shown in Figure 3.3. By utilizing 1,8,9-trihydroxyanthracene as a matrix, all the possible fragments 707.4 (M$^+$), 581.1, 454.8 and 227.3 Da 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 3.4. The pyrene ring system is essentially flat, but the Bpin rings are non-planar and disordered over two distinct conformations[39–41]. 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. More information with regard to the TBP crystal structure can be found in the supplementary information.
Figure 3.3: MALDI-TOF-MS of TBP with 1,8,9-trihydroxyanthracene as a matrix.
The synthesis of $^{135}\text{TrBB}$ and $^{124}\text{TrBB}$ (Figure 3.2, 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 mass (7.11%). NMR for both of these molecules can be found in Figure A.3 and Figure A.4. As with the TBP molecule, $^{124}\text{TrBB}$ also provided $^1\text{H}$ NMR spectra with high integration ratios between the aliphatic and aromatic protons. We addressed this issue by running the NMR experiment in d$_6$-DMSO (rather than CDCl$_3$) at 80°C (rather than room temperature). Also GC/MS results confirmed the formation and purity of $^{124}\text{TrBB}$.

Generally, the yield for conventional heating was slightly improved (except for entry 6) over the microwave approach (Table 3.1). Entry 6 (Figure 3.2, TBB) was helpful in understanding the lack of accurate NMR spectra for TBP since its aliphatic to aromatic proton ratio is higher (48:2 to 48:6). However, both $^1\text{H}$ and $^{13}\text{C}$ NMR unambiguously confirmed the synthesis of this molecule (Figure A.5). The crystal structure and two-step reaction
synthesis of this molecule was published by Wagner et al.[28]. More detailed information on the synthesis and characterization of all the materials can be found in the supplementary information (Appendix A).

3.3.2 Discussion

Plastic scintillators are a composite of a matrix (PVT) that absorbs radiation energy and transfers this energy mainly to a primary dopant (PPO) via Förster resonance energy transfer (FRET)[42]. The PPO emission is then with nearly 100% efficiency absorbed by a wavelength shifter (POPOP) that has an efficient fluorescence peak matched to the photomultiplier tube (PMT) sensitivity[43, 44]. Table 3.2 shows the composition of plastic scintillators prepared incorporating the synthesized boron materials (entry 3–6, Figure 3.2) 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 3.2: Plastic scintillator formulations.

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

a – Total mass of each sample: 20.0 g.
b – TBP acting as boron source and primary dopant
The light output of these samples (4.7 cm diameter × 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 3.2, 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 3.3. 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 seen in column 5 (Table 3.3), the signal produced by the 1.48 MeV alpha and 0.48 MeV $^7$Li ion (products of thermal neutron reaction with $^{10}$B) is quenched to produce scintillation light equivalent in amplitude from an electron with an energy of 60–100 keV depending on sample composition.

Table 3.3: Light output, boron capture and polymer properties of plastic scintillator samples.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>95</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.37</td>
<td>3.52</td>
<td>2.57</td>
</tr>
<tr>
<td>ii</td>
<td>74</td>
<td>0.035</td>
<td>0.007</td>
<td>No capture</td>
<td>1.20</td>
<td>2.36</td>
<td>1.96</td>
</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>

Samples ii–iv (Figure A.15) contain increasing amounts of 135TrBB (Figure 3.2, 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 $^{10}$B (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.

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 3.2, entry 5) as the boron additive (Fig. 5) 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 3.3, entry v and vi).

Figure 3.5: Left to right: Sample v and vi incorporating 1 and 5% 124TrBB respectively.

Figure 3.6 shows a one minute collection of data using the $^{244}$Cm/$^{13}$C source for 5% 124TrBB (Table 3.2, entry vi), that already shows distinct neutron capture above the background noise. This sample resulted in a $^{10}$B thermal neutron capture signal at approximately 92 keV$_{ee}$ with 81% relative light output. To our knowledge, this is the highest thermal neu-
tron capture signal observed from a boron doped plastic scintillator.

![Graph showing thermal neutron capture using a 5% 124TrBB plastic scintillator, sample vi.](image)

Figure 3.6: Thermal neutron capture using a 5% 124TrBB plastic scintillator, sample vi.

Samples vii and viii both had TBB (Figure 3.2, 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 A.16). Despite its poor solubility, it showed a clearly visible boron capture signal even at 1% (Table 3.3, entry vii). Increasing the concentration to 5% wt decreased the optical clarity significantly as shown in Figure A.16. 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 3.2, entry 3) as both a boron source and primary dopant resulted in lower light output and neutron capture likely due to unoptimized energy transfer from the matrix to TBP and wavelength shifter (Figure A.8). 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 3.3, entry xi). This sample showed a dramatic increase in light output and the thermal neutron induced reaction signal became clearly visible (Table 3.3, entry xi). All of
the samples containing TBP (Figure 3.7) were slightly yellow due to its pale yellow color. Absorption and emission spectra for TBP can be found in Figure A.7.

Figure 3.7: Left to right: Sample ix, x and xi incorporating 1, 2 and 1% TBP respectively.

3.4 Conclusion

Both 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) 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 $^{10}$B neutron capture signal registered a stronger signal than state-of-the-art boron doped plastic scintillators. We are currently working on the synthesis of $^{10}$B enriched versions of our boron-rich additives in order to increase thermal neutron capture probability. Additionally, we will attempt to differentiate the thermal neutron capture and fast neutron
scattered signals from gamma radiation signals through pulse shape discrimination using the PPO (and newer dopants) over-doping method.

3.5 Methods

Both microwave and conventional syntheses are described in the Supporting Information (Appendix A).

3.5.1 Characterization

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 CuKα radiation. The structures were solved using SHELXT and refined using SHELXL programs[40]. 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[39], and by validation routines of the Platon program[41] 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 355nm 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 1.0mL/min (Viscotek GPC pump; PLgel 5um MIXED-C and MIXED-D columns: molecular weight range 200–2,000,000 and 200–400,000 g/mol (PS

68
equiv), respectively.

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[45]. Samples were subjected to gamma radiation from a $^{137}$Cs source to quantify general scintillation response. A $^{244}$Cm/$^{13}$C neutron-gamma source was tested in both a polyethylene cave to produce a high thermal neutron flux, as well as a lead cave, for fast neutron and gamma response.

### 3.5.2 Preparation of Samples

Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. The inhibitor in 4-vinyltoluene was removed by filtering through a 100mg 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 15–30min. The solution was then bulk polymerized in an oil bath or an argon-filled vacuum oven at 80 °C for 96hours, followed by 90 °C for 12hours. The sample was cooled to room temperature and the glass bottle was broken with a mallet, giving a clear polymer disk (Figure 3.5, Figure 3.7 and Figure A.15-Figure A.16) 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.
3.6 Acknowledgements

This research is supported by the US Department of Homeland Security-Domestic Nuclear Office (DHS- 14-DN-077-ARI-NC7). We thank Dr. Peter Menge and Dr. Mark Mayhugh at Saint Gobain Crystals for their useful discussion and continued support. We extend our appreciation to Dr. Yuan Yang for her NMR advice and support.

3.7 References Cited


CHAPTER 4

BIS(PINACOLATO)DIBORON AS AN ADDITIVE FOR THE DETECTION OF THERMAL NEUTRONS IN PLASTIC SCINTILLATORS

A paper published in *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*[1].

*Adam Mahl*1,*, Henok A. Yemam*2,*, John Stuntz2, Tyler Remedes1, Alan Sellinger2, Uwe Greife1,†

4.1 Abstract

A readily available and inexpensive boron compound was tested as an additive for the detection of thermal neutrons in plastic scintillators. Bis(pinacolato)diboron ($\text{B}_2\text{Pin}_2$) was determined to be a compatible boron source (8.51 wt% boron, 1.70 wt% $^{10}\text{B}$) in poly(vinyltoluene) based matrices. Plastic scintillator blends of 1-20 wt% 2,5-diphenyloxazole (PPO), 0.1 wt% 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP) and 1-15 wt% $\text{B}_2\text{Pin}_2$ were prepared that provided optical clarity, good mechanical properties, and the capability of thermal neutron detection. Independent of $\text{B}_2\text{Pin}_2$ concentration, strong $^{10}\text{B}$ neutron capture signals around 90 keV$_{ee}$ were observed at essentially constant light output. Increasing PPO concentration allowed for the use of pulse shape discrimination (PSD) in both fast and thermal neutron detection. High PPO concentrations appear to cause additional alpha quenching that affected the $^{10}\text{B}$ neutron capture signal. Aging effects after storage in air for several months were observed, which led to degradation of performance and in some samples of mechanical stability.

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*Authors Adam Mahl and Henok A. Yemam contributed equally to this publication and should be regarded as first authors.
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4.2 Introduction

Detection of neutrons 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 $^3$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 [2, 3]. Recent advances in $^3$He alternatives have used plastic or liquid scintillator compounds that contain high neutron cross-section isotopes such as $^6$Li, $^{10}$B, and $^{155}$Gd/$^{157}$Gd isotopes [4, 5]. Our group is focusing on the incorporation of boron containing organic compounds because of the significant natural abundance (˜20%) of $^{10}$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 [6–8] and has been used in some commercial products (e.g. Eljen Technology EJ-254). However, the price of the neutron sensitive scintillator product is still dominated by carborane prices 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 $^3$He based detectors motivating further research on boron containing scintillator systems.

The neutron induced reaction on $^{10}$B has a thermal cross section of 3837 barns ($^3$He is 5333 barns)[9] and results in light charged ions (alpha and $^7$Li) as the products that carry significant kinetic energy to be easily detected.

\[
^{10}\text{B} + n_{th} \rightarrow ^7\text{Li} (1.0\,\text{MeV}) + \alpha (1.8\,\text{MeV})
\]

\[
Q = 2.792\,\text{MeV}, \quad 7\%
\]

\[
^{10}\text{B} + n_{th} \rightarrow ^7\text{Li}^* (0.83\,\text{MeV}) + \alpha (1.47\,\text{MeV})
\]

\[
Q = 2.310\,\text{MeV}, \quad 93\%
\]

\[
^7\text{Li}^* \rightarrow ^7\text{Li} + \gamma (0.48\,\text{MeV})
\]
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 (fluorescing 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.

Figure 4.1: Molecular weight and elemental composition (%) of bis(pinacolato)diboron (B$_2$Pin$_2$).

Bis(pinacolato)diboron (B$_2$Pin$_2$) (Figure 4.1) was first used in organic reactions by Miyaura et al to create an intermediate for Suzuki coupling [10]. The conversion of arylhalides to arylboronates using an inexpensive and readily available borylating reagent such as B$_2$Pin$_2$ has been extensively used in the pharmaceutical and organic electronics industries [11, 12]. Our group uses B$_2$Pin$_2$ to create high boron content benzene and pyrene derivatives for use as scintillator additives [13]. Before we were able to synthesize the gram quantities necessary for tests with radiation of our new compounds, we ran the series of tests described here with the commercially available precurser B$_2$Pin$_2$ ($0.5/g$).

4.3 Preparation of Plastic Scintillator Samples

All chemicals used for this study were purchased from commercial vendors unless otherwise noted. Vinyl toluene (VT) was purified by removing the inhibitor 4-tert-butylcatechol (TBC) using a plug mixture of basic alumina with a small amount of potassium carbonate. The purified VT was stored in a freezer under nitrogen. Azobisisobutyronitrile (AIBN) rad-
ical initiator was recrystallized twice from methanol and stored in a freezer under nitrogen. B$_2$Pin$_2$ (Matrix Scientific cat. # 004889) was dried in a Buchi glass oven (model #B-585) at 40°C for 24 h and stored in a nitrogen filled glovebox. Each scintillator sample was prepared by adding the specific amounts of dopants, AIBN, and vinyl toluene (20 g total) to a 120 ml (51 mm dia. x 102 mm) glass bottle, followed by a gentle bubbling of argon gas to displace and remove oxygen. The presence of oxygen inhibits polymerization, causes significant light emission quenching, and sample discoloration. The glass bottles were tightly capped and put into a Fischer Scientific Isotemp vacuum oven (model #280A). The atmosphere inside the vacuum oven was exchanged from air to argon via a few cycles of evacuation followed by argon refill. The sample polymerization was performed in argon atmosphere over four days at 80°C and 12 hours at 90°C. After polymerization was complete, the glass bottles were broken to provide the raw scintillating polymer “puck”. As a first step rough edges were clipped and an even surface produced via machining or hand sanding with medium grid sand paper. Further sanding was performed using finer grit and polishing compounds until finally a buffing wheel achieved a polished surface sufficient for coupling to a photo-detector.

4.4 Experimental Procedure

To begin testing, the samples were wrapped tightly with white Teflon tape on all sides except the prepared polished face. This exposed face was then coupled to a photodetector (Hamamatsu PMT assembly, H2431-50) with a thin layer of optical grade silicone grease. The coupled assembly was wrapped in a layer of aluminum foil and sealed to a light-tight condition with black electrical tape. After an optimal voltage (-2.9 kV bias in all measurements) for viewing relevant features in the output spectra was determined, the PMT was connected to a data acquisition (DAQ) system and biased using standard NIM electronics. The DAQ system includes a 250 Msample/sec waveform digitizer built in-house, and is controlled by a MIDAS software interface [14]. In this approach the voltage pulse as it is recorded from the PMT anode is digitized and stored. 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.

Samples were first exposed to a $^{137}$Cs source ($1 \mu$Ci, 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 (160 mCi alpha activity; sealed with neutron and gamma emission) 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. 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. The Cd-shield background subtraction was not performed on the spectra from which we extracted a figure-of-merit (FOM) for pulse shape discrimination.

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 [15].

4.5 Results

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; $\text{B}_2\text{Pin}_2$ in this case. 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 4.1) was intended to test the solubility limit of $\text{B}_2\text{Pin}_2$ in PVT, holding the fluorescent dopant concentrations constant.

As $\text{B}_2\text{Pin}_2$ has a smaller boron content per molecule than carboranes, the achievable boron concentrations are lower than in 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%. 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 4.6, top). However, some slight nucleation could be seen in the 15 wt% sample and when increased to 20 wt% $\text{B}_2\text{Pin}_2$ (~1.7 wt% B), this sample showed significant nucleation which 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 Figure 4.2, Figure 4.3.

The $\text{B}_2\text{Pin}_2$ concentration appears to have little effect on light output when added at the 10 wt% level as shown in Figure 4.2; most samples produce a Compton Edge (numerically characterized as the halfway point between Compton edge maximum and zero) at 92-94%
Table 4.1: Plastic scintillator formulations.

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Matrix</th>
<th>Name</th>
<th>%wt</th>
<th>Primary dopant</th>
<th>%wt</th>
<th>Wavelength Shifter</th>
<th>%wt</th>
<th>B$_2$Pin$_2$ content</th>
<th>%wt</th>
<th>Nat-B content</th>
<th>%wt</th>
<th>$^{10}$B content</th>
<th>%wt</th>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>POPOP</td>
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<td></td>
<td></td>
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<td></td>
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</table>

* – Total mass of each sample: 20.0 g.

Figure 4.2: Number of counts vs uncalibrated pulse area in scintillating PVT based samples as measured through exposure to a $^{137}$Cs $\gamma$-source using the same PMT bias value.
that of a commercial control sample (Saint Gobain BC-408; 10,000 photons/1 MeV e\(^{-}\)). There is a more significant decrease at 15 wt% which is suspected to be due to the approaching solubility limit of B\(_2\)Pin\(_2\). It should be noted that in the few cases where we repeated samples of the same composition, our measured light yields varied of order ±2-3 %-points. Therefore, we would characterize sample variation in the range of 92-94% as essentially constant.

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

**Figure 4.3**: Number of counts versus calibrated pulse area (keV\(_{ee}\)) for \(^{10}\)B thermal neutron reaction spectra with gamma response subtracted via cadmium shielded measurement. The keV\(_{ee}\) sample scale adjusts all samples to the \(^{137}\)Cs Compton edge position of each sample (light yield adjustment) to make changes in alpha quenching apparent.

Thermal neutrons in the \(^{244}\)Cm/\(^{13}\)C “Poly Cave” setup were captured by the naturally occurring \(^{10}\)B isotope within B\(_2\)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 B\(_2\)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 4.3. The results here
reported on the position (keV\textsubscript{ee}) of the \(^{10}\text{B}\) neutron capture peak are similar to previously reported values on boron loaded plastic scintillators using carboranes \([6, 8]\). As mentioned above, raising the B\textsubscript{2}Pin\textsubscript{2} concentration appears to produce an essentially constant 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.

Table 4.2: Plastic scintillator formulations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Matrix</th>
<th>Primary dopant Name</th>
<th>%wt</th>
<th>Wavelength Shifter Name</th>
<th>%wt</th>
<th>(%\text{wt}^*)</th>
<th>DVB %wt</th>
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<tbody>
<tr>
<td>1</td>
<td>PVT</td>
<td>PPO</td>
<td>10</td>
<td>POPOP</td>
<td>0.1</td>
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<tr>
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<td>PVT</td>
<td>PPO</td>
<td>15</td>
<td>POPOP</td>
<td>0.1</td>
<td>11.75</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>
<td>11.75</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>
<td>11.75</td>
<td>0.1</td>
</tr>
</tbody>
</table>

* – 11.75\% B\textsubscript{2}Pin\textsubscript{2} is equivalent to 1\% boron content.

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. \([16]\) which in recent years inspired further work in several laboratories \([17–19]\). The compositions used in this sample set are provided in Table 4.2. The 11.75 \%wt\% B\textsubscript{2}Pin\textsubscript{2} concentration is equivalent to 1 \%wt\% natural boron content, and was chosen to be 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, acts as “impurities” in the polymerization process likely leading to lower polymer molecular weight and thus diminished mechanical properties. 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$_2$Pin$_2$ 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$_{ee}$. The resulting spectrum from the thermalized $^{244}$Cm/$^{13}$C neutron source is detailed in Figure 4.4 and various PSD figures of merit (FoM) numbers using the fast neutron spectrum are shown in Figure 4.5. The measured FoM at 100 keV$_{ee}$ of 1.04 compares well to the published value of 0.9 at 120 keV$_{ee}$ for the commercial Eljen Technology EJ-299-33, which presumably uses the PPO over-doping method [20].

![Figure 4.4: Full PSD (Full Pulse Area over Delayed Area Fraction) spectrum of PVT sample containing 11.75 wt% of B$_2$Pin$_2$, 20 wt% PPO, 0.1 wt% POPOP as measured in the $^{244}$Cm/$^{13}$C “poly cave” setup. In addition to the thermal neutron capture peak a band between the fast neutron and gamma bands becomes tentatively visible which contains also thermal neutron capture events, however, here the exited state of the $^7$Li reaction product is populated and both an alpha and a 480 keV gamma is recorded in coincidence.](image-url)
Figure 4.5: 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 Figure 4.4 in the “lead cave” setup and projecting the Full PSD Spectrum after the energy cut onto the y-axis.
In order 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 B\textsubscript{2}Pin\textsubscript{2} doped samples (e.g. Figure 4.6, bottom) with average decrease of approximately 20% in light yield. However, \textsuperscript{10}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/\gamma PSD, had turned opaque with negligible light output (~10% of BC-408). The physical change in our sample is likely due to oxidation of residual radicals left 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 4.6: Plastic scintillator sample containing 1 wt% PPO, 0.1% POPOP and 11.75% B\textsubscript{2}Pin\textsubscript{2} in PVT at the time of first testing (top) and after 9 months ambient storage (bottom).
4.6 Summary

The research described here demonstrates that \( \text{B}_2\text{Pin}_2 \) can be used as a low cost \( ^{10}\text{B} \) additive that is compatible with commonly used plastic scintillator formulations to achieve plastic scintillator detectors with thermal neutron sensitivity. \( \text{B}_2\text{Pin}_2 \) 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 \( ^{10}\text{B} \) neutron capture peak occurring at \( \sim 90 \text{ keV}_{\text{ee}} \) in the basic formulations, and at \( \sim 60-65 \text{ keV}_{\text{ee}} \) 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 \( \text{B}_2\text{Pin}_2 \) with natural boron isotopic distribution, but pathways of synthesizing boron containing organic additives from readily available \( ^{10}\text{B} \) enriched compounds are being investigated by our group.

4.7 Acknowledgements

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4.8 References Cited


CHAPTER 5

\(^{10}\text{B} \text{ ENRICHED PLASTIC SCINTILLATORS FOR APPLICATION IN THERMAL NEUTRON DETECTION}\)

A paper published in *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* [1].

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*Alan Sellinger*[^2], *Uwe Greife*[^1]

5.1 Abstract

We report here on the synthesis and characterization of a novel \(^{10}\text{B} \) enriched aromatic molecule that can be incorporated into common poly(vinyltoluene) (PVT) based plastic scintillators to achieve enhanced thermal neutron detection. Starting from relatively inexpensive \(^{10}\text{B} \) enriched boric acid, we have prepared 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (MBB) in three high yield steps. MBB is soluble and compatible with PVT based formulations and results in stable plastic scintillators. Chemical synthesis, solubility limit in PVT, and the physical properties of the dopant were explored. The relevant response properties of the resulting scintillators when exposed to neutron and gamma radiation, including light yield and pulse shape discrimination properties were measured and analyzed.

5.2 Introduction

Over the past decade, the rapid increase in deployment of radiation portal monitors to address domestic and international security concerns has produced a significant demand for \(^{3}\text{He} \) gas. \(^{3}\text{He} \) is a stable isotope of helium that is used in the detection of neutron radiation

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as a counting gas in proportional counters. These detectors are not only used for security purposes but also found in large scale neutron science experiments as well as in nuclear scattering and imaging research fields. With the demand for $^3$He gas far outweighing the production, the US federal government began rationing the store of $^3$He, only allocating it for certain groups or purposes [2]. Research aimed toward finding a viable alternative to be used for detection of neutrons is currently ongoing and motivated the research presented here.

Plastic scintillators are traditionally utilized as a first line detection method in radiation detection systems. Their large volume, relatively low cost, and fast response times allow for their efficient use as gross counters, but they provide very limited spectroscopic information about the incident radiation. Due to their large hydrogen content, plastic scintillators are sensitive to fast neutron radiation via proton collisions that in turn have a thermalizing effect on the incident neutrons, allowing them to be detected by the currently employed $^3$He based proportional counters. By incorporating material into the plastic that has a high thermal neutron interaction cross section, these detectors can directly measure the neutron radiation, that may reduce the need for $^3$He based technology [3].

Although there are several possible neutron sensitive isotopes to explore, each with their own pros and cons, we are focusing our efforts on incorporating the $^{10}$B isotope into plastic scintillators via organo-boron based molecules. The relatively high natural abundance of $^{10}$B (20%) in boron, established organic chemistry methods, and the nuclear properties of the capture reaction (Eq. 5.1) are attractive for the development of new detector materials [4–6].

$$10B + n_{th} \rightarrow \begin{cases} 7Li_{(1.01MeV)} + \alpha_{(1.78MeV)} \\ Q = 2.790 \, MeV, \ 6.3\% \\ 7Li^*_{(0.84MeV)} + \alpha_{(1.47MeV)} \\ \leftrightarrow 7Li^* \rightarrow 7Li + \gamma_{(478keV)} \\ Q = 2.310 \, MeV, \ 93.7\% \end{cases}$$ (5.1)
Reaction scheme for thermal neutron capture on $^{10}$B; at thermal neutron energies (25 meV), $^{10}$B has a neutron reaction cross section of 3837 barns (compared to $^3$He: 5333 barns) [7].

Carboranes have traditionally been used as additives to increase boron content in plastic scintillators however, they are very expensive. Searching for more cost effective alternatives, we first utilized the commercially available bis(pinacolato)diboron (Pin$_2$) as the boron additive in plastic scintillators and also as a chemical precursor for borylated benzenes explored for the same purpose [8, 9]. Although we achieved good neutron detection capabilities, we reached a solubility limit that corresponded to a $^{10}$B content of 0.2 wt%. To increase our $^{10}$B content, and therefore enhance neutron detection, we explored the use of $^{10}$B enriched precursors. This would lead to lower material loading into the plastic matrix while maintaining or increasing neutron sensitivity, and enhancing the mechanical integrity of the resultant plastic scintillators. We report here the synthesis of $^{10}$B enriched 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane, termed monoborylated benzene (MBB), in three high yield steps (Figure 5.1) and its incorporation into poly(vinyltoluene) (PVT) based scintillators for use in thermal neutron detection. MBB was admixed into PVT at loadings up to 20.0 wt% (1.06 wt% $^{10}$B) [10].

5.3 Preparation of Monoborylated Benzene (MBB)

Initially, the synthesis of $^{10}$B enriched Pin$_2$ was explored however, the toxicity and high price of the enriched starting material ($^{10}$BF$_3$) led us to look for safer synthetic routes and affordable alternatives [11]. From a synthetic standpoint the most readily available source of enriched $^{10}$B is boric acid, so we developed our chemistry starting from this material. Figure 5.1 shows the chemistry we designed and performed in order to prepare a PVT compatible and stable MBB from 1-bromobenzene. Initial attempts to prepare di- and tri-borylated $^{10}$B enriched aromatics starting from 1,3-dibromobenzene and 1,2,4-tribromobenzene and t-butyl lithium were unsuccessful.
Figure 5.1: Three step reaction to synthesize $^{10}$B enriched monoborylated benzene (MBB) (4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane) (Predicted elemental analysis shown in wt%).

The synthesis of MBB began with enriched boric acid (>96% $^{10}$B) as the precursor which was purchased from Ceradyne Inc. ($1.74/gram). Precursors 1 and 2 (Figure 5.1) were synthesized following literature procedures [12, 13]. For MBB preparation, a dry two-neck 250 mL round-bottom flask equipped with a stir bar and a dropping funnel was evacuated and refilled with argon four times. Tert-butyl lithium (tBuLi) (50mL of a 1.7M solution in pentane, 0.085 mol) was added to the flask using a cannula followed by 45.0 mL of anhydrous pentane. The solution was cooled to -78 °C and stirred for 30 min. To a dry 50.0 mL round bottom flask was added bromobenzene (8.45 mL, 0.079 mol) followed by vacuum/argon refill four times then by 10–15 min of bubbling argon through the solution followed by an additional vacuum/argon refills four times. Anhydrous THF (10 mL) was added to the bromobenzene and the resultant solution transferred to a dropping funnel that was then slowly added dropwise into the -78 °C tBuLi solution over a period of 30 min. The solution went from pale yellow to off-white after approximately 2 h of stirring. Then dry isoproopxy $^{10}$Bpin (2) (15.9 g, 0.085 mol) was added to the dropping funnel and slowly dripped into the reaction over 30 min. The reaction was stirred at -78 °C for a day. The reaction vessel was removed from the cold bath and allowed to warm to room temperature with stirring for 5 h. Isopropyl alcohol was slowly added to the completed reaction in order to quench any excess BuLi. The reaction was then extracted with diethyl ether, dried with magnesium sulfate, and concentrated to remove the majority of the solvents. The product was vacuum distilled to remove the remaining volatile materials and then collected as a white solid and stored in
the freezer until needed. (Yield 46%, 7.54 g) The final product was characterized by proton and carbon nuclear magnetic resonance ($^1$H and $^{13}$C NMR). $^1$H NMR (500.0 MHz, CDCl$_3$) \(\delta 1.34\) (s, 12 H), 7.34–7.38 (t, 2 H), 7.44–7.47 (t, 1 H), 7.80–7.81 (d, 2 H). $^{13}$C 1 NMR (125.8 MHz, CDCl$_3$): \(\delta 135.13\) (CH), \(\delta 131.65\) (CH), \(\delta 128.10\) (CH), \(\delta 84.15\) (CCH$_3$), \(\delta 25.24\) (CH$_3$), n.o. (C-B).

5.4 Preparation and testing of plastic scintillator samples

Details on the preparation and testing of plastic scintillators can be found in our previous publications [8, 9]. Briefly, purified vinyltoluene monomer (VT) (inhibitor removed by flowing through an alumina gel plug) and recrystallized azobisisobutyronitrile (AIBN) radical initiator were mixed with a specific wt% of dopants. After being sparged with argon to de-oxygenate the mixture, the samples were polymerized in glass jars (the surfaces are silanized to prevent sticking) in an inert atmosphere oven at 80 °C for four days then at 90 °C for one day. After reaching ambient temperature, the glass jars were broken to provide the 20 g plastic scintillators (4.7 cm diameter by 1.1–1.3 cm) that were then machined and polished on a single side. Each finished sample was wrapped in a reflective tape, coupled to a PMT (on the finished side), and exposed to fields of ionizing radiation. The samples response was measured with a DAQ system based on a 250 Msample/s waveform digitizer built in-house, controlled by a MIDAS software interface [14]. Pulse integration occurs over a 120 ns interval. In this study we used 2,5-diphenyloxazole (PPO) as the primary dopant and 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP) as a wavelength shifter.

Light yield (LY) of a sample was determined by comparing the positions of the Compton Edge (C.E.) feature resulting from exposure to a $^{137}$Cs source, to a Saint Gobain Crystals BC-408 commercial sample. The known energy of the C.E. allowed us to calibrate each sample individually and establish an individual sample energy scale (in keV$_{ee}$). Next, the samples were exposed to a $^{244}$Cm/$^{13}$C source in various shielding configurations, which produce different mixed neutron and gamma fields. The sample responses to fast and thermalized neutron fluences were recorded to identify and analyze the $^{10}$B neutron capture reaction as well as
any n/γ PSD capabilities. Gamma background spectra were taken with the use of a cadmium shield (˜1 mm) around the coupled sample. The ROOT data analysis framework was utilized to analyze the collected data, and develop relevant output spectra [15].

5.5 Results

We first explored the solubility limits of MBB in vinyltoluene to determine how much $^{10}\text{B}$ could be added (as indicated earlier, the detection of thermal neutrons is achieved via the $^{10}\text{B}$), as well as testing the compatibility of MBB with a plastic scintillator formulation (PVT overdoped with 20.0 wt% PPO) that allowed for PSD for further particle identification [16]. Table 5.1 details the various samples that were produced and tested for radiation response. MBB was still soluble in PVT at 20.0 wt%, however, polymerization of the final plastic was already significantly hindered at this level and an upper limit for the solubility was not determined. For comparison, we prepared m-carborane based samples in order to compare radiation response and physical properties such as dopant solubility and $^{10}\text{B}$ content, total light yield, energy of boron capture peak.

The measured $^{137}\text{Cs}$ response of samples containing MBB and m-carborane are shown in Table 5.1 (a 5% error is assumed in the LY measurements) and it is seen that the LY trends lower both with increasing MBB and m-carborane concentrations. The two samples containing MBB with the lowest LY (sample 4 and 6) were too soft to fully machine or polish, due to the amount of dopants (combined MBB and PPO) in the sample, leading to a practical limit of $<15$ wt% MBB for usable plastics. Likely, incomplete polymerization lowered the LY as well as poor optical coupling to the photodetector. The LY of the samples vary from $>50\%$ to $\sim 90\%$ of a commercial control sample (BC-408; app. 11,000 photons/1 MeV; 64% anthracene). The m-carborane containing samples all polymerized to clear, colorless samples, which were hard enough to machine and polish. However, the drop off in LY is more pronounced for m-carborane samples containing equivalent amounts of $^{10}\text{B}$ to MBB samples, likely due to the absence of aromatic groups in m-carborane compared to MBB.
Table 5.1: Sample list of $^{10}$B containing prepared scintillators.

<table>
<thead>
<tr>
<th>Sample$^a$</th>
<th>m-Carborane content</th>
<th>MBB content</th>
<th>$^{10}$B content$^c$</th>
<th>Light yield (LY)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
<td>%wt</td>
<td>%wt</td>
<td>% of BC-408</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>0.26</td>
<td>77</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>0.53</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>0.80</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>1.06</td>
<td>57</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>0.28</td>
<td>80</td>
</tr>
<tr>
<td>6$^b$</td>
<td></td>
<td>5.3</td>
<td>0.28</td>
<td>58</td>
</tr>
<tr>
<td>7$^b$</td>
<td></td>
<td>1</td>
<td>0.05</td>
<td>89</td>
</tr>
<tr>
<td>8$^b$</td>
<td>0.34</td>
<td></td>
<td>0.05</td>
<td>79</td>
</tr>
<tr>
<td>9$^a$</td>
<td>1.88</td>
<td></td>
<td>0.28</td>
<td>69</td>
</tr>
<tr>
<td>10$^b$</td>
<td>1</td>
<td></td>
<td>0.15</td>
<td>72</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td></td>
<td>0.75</td>
<td>59</td>
</tr>
<tr>
<td>13$^b$</td>
<td>5.3</td>
<td></td>
<td>0.79</td>
<td>42</td>
</tr>
</tbody>
</table>

a – Total mass of each sample is app. 20.0 g and contains 1% PPO/0.1% POPOP.

b – Total mass of each sample is app. 20.0 g and contain 20% PPO/0.1% POPOP.

c – Based on 100% enrichment for MBB samples, and natural enrichment for m-carborane.

Figure 5.2 shows the thermal neutron capture peaks resulting from exposing the samples to thermalized neutrons. Data was collected with an analogous gamma background run subtracted, where cadmium shielding surrounded the sample. The relative peak positions are similar between samples that contain 1 wt% PPO (85–90 keV$_{ee}$) as compared to the samples that contain 20.0 wt% PPO (64 keV$_{ee}$) regardless of MBB content. There is no additional quenching of the capture signal as the MBB content is increased, with the peak energy shifting only when significant quantities of the primary fluor (PPO) are included. The peak counts (captures) trend up with $^{10}$B content, until the capture rate slows markedly ($\sim$15% MBB, 0.8% $^{10}$B). This $^{10}$B content corresponds to a theoretical maximum in capture rate documented in literature [17]. The m-carborane samples displayed a boron capture peak in the same location with 1 wt% PPO samples having a peak at $\sim$80 keV$_{ee}$ and the over-doped PPO samples all occurring in the 63–69 keV$_{ee}$ range.

As MBB doping is compatible with PPO overdoping to achieve PSD, we can analyze the pulse shapes generated by the 20.0 wt% PPO containing samples through integration of pulse
Figure 5.2: Number of counts versus electron-equivalent, energy calibrated, integrated pulse area (keV\textsubscript{ee}) for \textsuperscript{10}B thermal neutron capture reaction spectra with gamma response subtracted via cadmium shielded measurement.
content over a prompt and a delayed time interval. The 2-D spectrum of samples 5 and 7 is shown in Figure 5.3, where the monoenergetic capture reaction from thermalized neutrons (Figure 5.2 is an x-projection of this feature from all samples) is seen along with the signal bands from fast neutrons and the gammas; In sample 5 these bands are overlaid and cannot be discriminated from each other, while in sample 7, (containing overdoped amounts of PPO) the signal bands are clearly separated, allowing for effective fast and thermal neutron/gamma discrimination. A y-projection of this spectrum from sample 7, made at an energy cut of 100 keV_{ee} and 500 keV_{ee} produces a FoM value of 1.04 and 1.67 respectively. These FoM values correspond well to previous work as well as analogous samples we produced that contain no MBB dopant, indicating no loss in PSD capabilities through the new dopant. FoM values are calculated via:

\[ FoM = \frac{Centroid_n - Centroid_g}{FWHM_n + FWHM_g} \]

The plastic scintillator samples containing MBB did not display significant aging over the course of one year. There is no indication of oxidative yellowing, and the dopant does not appear to migrate or precipitate from the plastic matrix. Our production method (radical bulk polymerization) can occasionally introduce some heterogeneous clouding during polymerization, however, the clouding does not grow or intensify with age; we have not identified what causes this to occur. The 5.3 wt% MBB (0.26 wt% 10B) (Figure 5.4) sample was tested after storage at ambient conditions for 11 months, and lost approximately 14% of the initially measured LY, with the boron capture peak shifting \( \sim 8 \) keV_{ee} down in energy.

5.6 Summary

The research described here details a novel boron containing molecule that is easily synthesized from relatively low cost \(^{10}\text{B}\) enriched boric acid resulting in a dopant that is compatible with common plastic scintillator formulations and allows for enhanced thermal neutron sensitivity. Testable plastic scintillators with up to \( \sim 1.0 \) wt% \(^{10}\text{B}\) contents were achieved and characterized for their thermal neutron detection efficiency. Samples do not
(a) Sample 5 (Energy calibration from LY measurement, with y-axis representing $Q_{\text{delayed}} / Q_{\text{total}}$ of pulse energy).

(b) Sample 7 (Energy calibration from LY measurement, with y-axis representing $Q_{\text{delayed}} / Q_{\text{total}}$ of pulse energy).

Figure 5.3: Full PSD (Full Pulse Area over Delayed Area Fraction of Pulse) spectrum of PVT samples containing varying amounts of PPO, when exposed to a mixed neutron/gamma field which has been heavily thermalized via high density polyethylene shielding.
Figure 5.4: Plastic scintillator sample containing 20 wt% PPO, 0.1% POPOP and 1% MBB in PVT under natural and UV light. Also shown is a 1 wt% PPO/5.3 wt% MBB one year after synthesis, with only slight clouding, no yellowing and minimal crazing occurring over time.
appear to have significant degradation after one year of storage in ambient conditions. However, the lack of full optical transparency and the developing softness with increasing dopant concentration does not yet make the final plastics suitable candidates for commercial applications. Further work on MBB derivatives and alternative polymerization methods are underway in our research group.

5.7 Acknowledgements

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5.8 References Cited


This chapter provides an introduction into the specific research thrust of better understanding and inducing the pulse shape discrimination mechanism into plastic scintillators. There is also an executive summary of both of the following two chapters which are journal publications which cover this material in depth. Major results and any additional relevant details of research not covered in the published material are discussed.

6.1 Introduction

In recent years, research groups have begun investigating and describing methods to enhance the sensitivity of plastic scintillators for distinguishing fast neutron signals from gamma radiation. A simple, reproducible method has emerged by introducing an increased amount of a highly soluble, fluorescent primary dopant (over-doping) into standard plastic scintillator formulations to induce interactions that allow for pulse shape discrimination (PSD) analysis [1]. PSD analysis makes use of the slight difference in decay signatures between signals induced by different types of incident radiation. Gamma radiation, once its energy is converted to fast electrons in the plastic, inherently deposits less energy over the same distance relative to neutron radiation that produces proton recoils [2]. As a result, neutrons scattering in the plastic will result in higher atomic excitation density distributed in singlet and triplet excited states [3]. The singlet state electrons decay promptly (relatively) 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 a 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 either a higher triplet state, or annihilate (referred to as triplet-triplet annihilation (TTA)) into singlet state populations [4]. The
resulting singlet states 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 normal (for current commercial plastic scintillator products) 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. 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 is that at higher primary dopant concentrations the migration and annihilation of first excited triplet states increases, which leads to increased delayed fluorescence (Figure 6.1) [5]. Until recently, only PPO, a diphenylantracene (DPA) derivative, and m-terphenyl have been reported in the literature to show PSD capabilities when doped at high concentrations in common polymer matrices [6, 7]. Furthermore, PPO is the only primary dopant capable of PSD used in a commercial plastic scintillator product at higher concentrations.

At higher concentrations of PPO, the mechanical properties of the final plastics soften, making it challenging to process into final shapes, as well as provide difficulties for transportation and field deployment. There is no definitive explanation as to why over-doping PPO leads to enhanced PSD capabilities. This is due to the lack of highly soluble fluorescent

\[ T_1 + T_1 \]

\[ \text{Delayed Fluorescence} \]

\[ 1/9 (S_1 + S_0) \]

\[ 1/3 (T_1 + S_0) \]

\[ 5/9 (T_5 + S_0) \]

\[ \text{Triplet Recycling} \]

Figure 6.1: Triplet-Triplet Annihilation (adapted from [4])

At higher concentrations of PPO, the mechanical properties of the final plastics soften, making it challenging to process into final shapes, as well as provide difficulties for transportation and field deployment. There is no definitive explanation as to why over-doping PPO leads to enhanced PSD capabilities. This is due to the lack of highly soluble fluorescent
dopants with which to systematically study the parameters that affect the PSD performance. If efficient TTA is the driving mechanism, then over-doping other highly emissive primary dopants should introduce similar PSD capabilities as well.

In this approach, alternative primary dopants were synthesized that could be admixed into common plastic matrices at high concentrations to: 1. find alternatives to PPO that lead to PSD without worsening of mechanical properties; and 2. help identify the PSD mechanism. Therefore, we have prepared highly luminescent alkylated p-terphenyl and fluorene derivatives with the intent of identifying the main parameters that affect the onset and magnitude of PSD. To systematically study these parameters, we took two approaches: First, 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 as well as thermomechanical properties of the final plastic. Second, fluorene derivatives with varied photoabsorption and photoemission were compared to PPO based on their general scintillation characteristics in PVT and PSD performance.

PSD performance is measured by a dimensionless Figure of Merit (FoM) metric which is calculated as detailed in Equation 6.1.

\[
FoM = \frac{Centroid_n - Centroid_g}{FWHM_n + FWHM_g}
\]

PSD Figure of Merit (FoM)

These values are obtained by examining the signals within an energy range of the neutron and gamma lines. A y-projection is performed and a double Gaussian fit is assigned to the peaks. The centroids and FWHM are extracted and a FoM is obtained (Figure 6.2). Currently >20 wt% PPO samples are achieving FoM of >1 at 100 keV_{ee} and >1.6 at 500 keV_{ee}. These values imply very strong separation between signals, thus a high confidence in signal discrimination. These are the values we are attempting to attain with our newly synthesized dopants. A FoM value of 1.27 is considered a benchmark in the community based on statistical analysis of 2 peaks with clear centroid separation value of 3, and a perfectly
Gaussian FWHM in both peaks of 2.36 [8]. While it is important to identify a benchmark for ease of comparison across research groups, it is important to be aware that the FoM values need to be looked at in conjunction with LY measurements as well as what energy the metric is being measured at. The counting statistics can often produce a numerical value, but there should still be an emphasis on visual inspection of the spectra. Despite there being a calculated FoM, there is often negligible separation between the different signal bands, and only a slight “spreading” of the original response band. This can be useful to qualitatively evaluate the potential of fluors which begin to show the onset of PSD at lower concentrations, and proceed with further testing. FoM values are also only informative when given in conjunction of the energy that they were measured at, as the numerical value changes rapidly between lower energies (≤100 keV$_{ee}$) and higher energies (500 keV$_{ee}$ - >1MeV$_{ee}$). This difference becomes important when interested in low energies where signals are more easily mixed, and secondary signals of interest (thermal neutron capture) occur.

![Figure 6.2: Visual representation of FoM calculation values][8]

Based on this approach our group has applied for 1 provisional patent which is in the process of disclosure and converted 1 non-provisional patent [9]. In addition, there 2 papers published (and 2 in progress) by our group on these various subsection results [10, 11].
6.2 Primary Dopant Variation

With an established method of producing scintillators, and altering soluble dopants, we began attempts to reproduce the effects seen with the PPO molecule via alternative dopants, to determine which properties lead to PSD properties.

6.2.1 p-Terphenyl Variants

p-Terphenyl (PTP, Figure 6.3) 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, e.g. Saint Gobain Crystals [12, 13]. 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 [14, 15]. 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 [16]. 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 very weak PSD [16]. In this approach, attempts were made to increase the solubility of PTP to further study this promising family of fluorescent dopants.

![p-terphenyl](image)

Figure 6.3: p-terphenyl molecule

In order to alter the base PTP molecule and its solubility in a polymer matrix, the chemistry employed changed the position and length of the alkyl substituents of PTP. Several different alkyl chains were proposed and tested, and can be broadly divided into two sub-
groups, those that are located on the para position, and those on the meta position.

Figure 6.4: 20 wt% mop-PTP sample spectrum

Figure 6.5: 10 wt% mop-PTP & PPO FoM comparison
Figure 6.4 details the PSD spectra taken from a successfully altered p-terphenyl variant. The alkyl chain is in the meta position and is the only variant which achieved 20% solubility, allowing the most meaningful comparison to PPO (Figure 6.5). To date, several alkylated p-terphenyl dopants have been synthesized and tested. The results of these tests show correlation between physical properties of the altered fluor and the final plastic produced with the new dopants.

6.2.2 Fluorene Variants

Fluorene (Figure 6.6) derivatives have been frequently used in Organic Light Emitting Diode (OLED) research due to the ease of chemical manipulation, efficient and predictable photophysical properties, thermal stability, efficient light output, and relatively low cost [17, 18]. Five fluorene derivatives that could potentially be used as emissive dopants have been synthesized in this research and tested to better understand the scintillation process as related to PPO.

These dopants differ from the p-terphenyl dopants due to a large variability in the absorbance and emission wavelengths of these dopants, while in the p-terphenyl dopants this property remained essentially constant. This class of dopant also allowed us to test the effect of extreme purification methods on commercially purchased dopants as well as fluors synthesized by our group.

Figure 6.7 shows the PSD spectra from a fluorene based dopant, which is our most successful comparison to PPO with an FoM of ~1.2 @ 500 keV_{ee}. Figure 6.8 details a FoM comparison between a lower loading of PhF and PPO. The sudden increase in FoM in PhF is not only due to loading increase, but an improved purification method involving recrys-
Figure 6.7: 20 wt% PhF sample spectrum

Figure 6.8: 15 wt% PhF & PPO FoM comparison
talization which removed extremely small (ppm) levels of contaminant. Another fluorene
based dopant (dimethyl fluorene, which was also studied as a possible candidate for co-
polymerization as discussed in 6.3) showed an even more drastic effect when cleaned after
purchase from a vendor (discussed in 7).

The results from this class of fluors led to several different questions and ideas for moving
forward with a more complete working theory of pulse shape discrimination. Contaminant
and isomeric purity, molecular ordering, computer modeling of energy state levels, and rigid-
ity of both the molecule and the host matrix are all areas that are discussed in Chapter 7 but
will also require further study. These ideas are being explored in combination with matrix
variants and a brand new PhF derivative as detailed below in 6.3

The work on both the p-terphenyl and fluorene dopant variants is detailed in Chapter 7
as a published journal article [10]. Significant research contributions were made by the listed
authors. Henok Yemam performed the synthesis, purification, and characterization of all
the chemicals and dopants, made polymer samples, and performed material characterization
of finished plastics; Adam Mahl made polymer samples, performed the machining/polishing
and test preparation of the finished scintillators, conducted the radiation testing and results
analysis, and performed material characterization of finished plastics; Jonathan Tinkham
performed computational calculations of the excited state energy levels; Joshua Koubek
generated the ground state geometries; Alan Sellinger and Uwe Greife were the P.I.s and
research advisors who generated the initial ideas and provided funding and supervision for
the work. Principal editing and review was performed by Adam Mahl, Henok Yemam, Uwe
Greife, and Alan Sellinger.

6.2.3 PPO Variants

Current work has moved towards investigating the inherent properties of the PPO molecule
itself. Based on our previous experience, we started synthesizing new alternative dopants
with different physical properties, to try to isolate what makes PPO uniquely useful as a
scintillator fluor. By attaching a third phenyl ring to the oxazole in the middle of the PPO
molecule, conjugated completely out of the plane of symmetry, we successfully synthesized TPO (2,4,5 triphenyloxazole) (Figure 6.9a). The photo-optical properties of TPO remain almost identical to PPO (Figure 6.9b,c) while the melting point was significantly increased (from 72°C for PPO to 115°C for TPO). The solubility of the molecule remained high enough (~25wt%) to produce overdoped samples to compare PSD signals.

![TPO Molecule](image)

(a) TPO Molecule

![Absorption](image)

(b) Absorption

![Emission](image)

(c) Emission

Figure 6.9: TPO Molecular properties

Figure 6.10 shows the PSD spectrum taken from the first large 20 wt% TPO sample produced. It has an FoM of 1.2 which is very comparable to PPO’s 1.6 @500 keV_{ee}. Although
the produced plastic is much more robust from a thermomechanical standpoint, the overall light yield from the sample is noticeably lower. This appears to be directly tied to the dopants lower relative PLQY (67%) as compared to PPO (100%). We now believe that this lowered property is the result of non-radiative losses via vibrational dissipation of the molecule’s new addition. Testing of this hypothesis is ongoing. Further modification of the molecule is under investigation as well, with 3 potential options being purified for initial tests. A communication on combining these PPO variations (as well as a new fluorene variation) with a PMMA matrix variation (discussed below) is currently being drafted (Henok Yemam, Adam Mahl, et. al, TBD, TBD, 2018).

### 6.3 Matrix Variation

Another (and current) thrust area in this research is aimed towards understanding how the morphology of a plastic scintillator affects the nuclear response. This area incorporates ideas and trends gleaned from the previous section’s results. Four major avenues are being
pursued all with the overarching goal of rigidizing the system, by altering how the matrix interacts with the fluor. Alternative matrix polymerization methods are also discussed.

6.3.1 Morphology Rigidization

There are four major thrust areas being pursued to change how the fluor and matrix are arranged in our organic systems. These re-arrangements produce different interactions resulting in radiation response and thermomechanical changes in the final scintillators.

6.3.1.1 Immobilization of primary fluor

The first attempt at this was to create fluorescent dopants that were physically much larger in size with a large stabilizing core surrounded by essentially a molecular “cage” of attached fluoros (Figure 6.11a). This would reduce the aggregation of the attached (planar) fluoros and decrease the effect of concentration quenching on the scintillators effective light yield. This first attempt had a higher Stokes shift (~70nm) as compared to the base PPO molecule (~50nm) and as such would not require a wavelength shifter. However, it proved extremely difficult to produce these molecules with any meaningful level of solubility in organic systems (Figure 6.11b), with the dopant turning the plastic a very dark color as polymerization completed. Although the dopant was visually very fluorescent, the plastics only barely produced light (~3% LY) when exposed to a more energetic $^{22}\text{Na}$ source (1.274 MeV $\gamma$). An alternate core for the basis of these molecules was proposed and produced a higher quality sample which resulted in more measurable fluorescence, indicating that this method can be investigated in future work.

6.3.1.2 Functionalization of primary fluor for co-polymerization

Secondly, we are investigating methods of creating fluorescent molecules that have vinyl groups attached to them, so that instead of being doped into the polymer matrix, they are physically incorporated into the backbone of the polymer chains. The goal being that when the physical distance is drastically decreased, the efficiency of the FRET process (which is
Figure 6.11: Immobilized PPO
related by $r^6$) should increase. The co-polymer system should also have an increased level of thermomechanical stability. Initial attempts included several acryl and vinyl variants of PPO (Figure 6.12). These dopants proved fluorescent at very low loadings (>90% LY), however at even 5 wt% they began to crash out, producing opaque white samples. This would seem to indicate that they were not being incorporated as a co-polymer, but merely acting as a low solubility fluorescent dopant.

![Figure 6.12: Vinyl and acrylate PPO variant molecules, Compton edge comparison, visible & UV light on co-polymerized samples](image)

Stilbene and one of our fluorene based dopants were also explored for vinylization. Stilbene is unique due to it being an very bright scintillator with significant PSD properties when grown as a large crystal (as discussed previously in 1.3). However it fails to incorporate into any polymer matrix to a significant degree, often crashing out of solution dramatically, and always producing very low fluorescence. While material characterization showed that it was
successfully vinylized, it too failed to incorporate (>1 wt%) into either PVT or PS (though it did produce more fluorescence). Figure 6.13 shows the first dopant that was successfully vinylized and incorporated into a polymer matrix, and showed a clear increase in fluorescence.

Figure 6.13: Compton edges of 20g samples containing 10 wt% of dimethyl fluorene and its vinylized analogue

Despite this result, the LY ceased to improve at higher loadings, and both dopants produced relatively low light yield (Chapter 7) compared to any of our other dopants. Still, this result was encouraging and the co-polymerizable dopants thrust continued to be researched.

Recently 2 successful co-polymerizable PPO variants have been identified, producing clear, hard samples at 40 wt% loadings, which display comparable PSD properties. These dopants are explored in depth as the subject of a recently defended Material Science M.S. thesis by Griselda Hernandez. Our group has filed a provisional invention disclosure for these PPO variants and a related publication is currently in draft.

6.3.1.3 Rigidization via use of non-aromatic matrices

In a third route, combined with the focus on over-doped primary fluor systems, we are studying the effect of changing our standard polymer matrix, PVT, to other matrices. One example is PMMA (poly(methyl methacrylate)) which is well known for being optically
clear, and much more physically robust than other polymers (i.e. Plexiglas), but only briefly explored in plastic scintillator applications as part of a mixed co-polymer system[19]. The downside from a scintillation standpoint is that it has no aromatic rings in it’s polymer chains, which greatly alters the energy transfer process. As discussed earlier, normally, the matrix is excited and transfers energy to the dopant. However, with our systems having >20 wt% dopant, we are much more likely to directly excite the dopant and can bypass the matrix-fluor transfer step. This lack of aromaticity provides an interesting control environment worth exploring. Our initial tests were very interesting, showing an expected decrease in LY and FoM (populated triplet and singlet states) with the standard PPO fluor based samples. However, when we tested one of our synthesized PTP dopants in PMMA in 20 wt% concentrations, we saw a similar decrease in LY (singlet state population) (Figure 6.14), but there was a more significant difference in FoM (triplet state energy population/transfer) as shown in Figure 6.19.

![137Cs Compton Edge Comparison](chart.png)

Figure 6.14: Compton Edge comparison of 20 wt% of dopants in PVT vs PMMA. PPO LY decreases from 97% to 71%. mopPTP LY decreases from 92% to 70%
Figure 6.15: PPO and mopPTP FoM y-projections in different matrices.
The change in matrix has affected the radiation response of the two systems in different ways depending on which fluor was overdoped. The fraction of delayed fluorescence did not decrease as drastically with the mopPTP fluor as it did with PPO, resulting in a similar FoM in PMMA based samples. To further explore this effect, PVT and PMMA samples were made with PhF and a new highly soluble (>20 wt%) PhF derivative that we have recently synthesized. This new fluor displays an even greater change in radiation response. While having a high (96%) LY, it shows insignificant PSD capabilities in standard PVT (Figure 6.16a). When tested in a PMMA matrix, the LY was unexpectedly reduced (in a more gradual manner than PPO), however, the sample now displays significant PSD (Figure 6.16b), indicating that the triplet state population is being altered radically. This is the first dopant tested that shows a completely opposite trend when switching from aromatic matrices to PMMA. Direct comparisons with PhF and tests between PPO and TPO are ongoing.

A possible explanation is that the rigidity of the PMMA matrix is helping to lock the dopant in place and lowering it’s ability to rotate and vibrate, thus decreasing the non-radiative losses discussed with our non-planar fluorescent molecules. Another possible effect could be the matrix altering the way dopants are able to aggregate into microcrystalline domains and form excimers. These excimers would effect the the electronic states and absorption/emission spectra. Density functional theory (DFT) calculations should be performed to determine the energy levels (singlets and triplets) of the dopants, and how they change based on matrix or packing arrangement. How these levels are arranged through the whole system (and how they differ) will help elucidate further detail into a complete PSD theory. A short communication on this idea detailing current results is being drafted for submission (Henok Yemam, Adam Mahl, et. al, TBD, TBD, 2018)

6.3.1.4 Cross-linking of polymer matrix

Finally, related to the idea of a co-polymer system, is the idea of cross-linking our existing polymer matrix. A cross-linking agent mixed in with the monomer will cause formed poly-
Figure 6.16: PSD spectra of PhF variant in different matrices.
mer chains to develop extra attachments (links) to each other. This will alter the amorphous matrix in several ways, including increases in rigidness, and glass transition temperature of the final plastic [20]. The issue with this route arises due to the organic system’s extreme sensitivity to small changes, and outright incompatibility in various mixtures. Our initial attempts to cross-linking our plastics failed with the addition of >0.01 wt% of divinylbenzene (DVB), a well studied cross-linker. In our established setup, the plastics polymerized far too rapidly in a heterogeneous matter, causing the plastics to turn opaque and break themselves apart. In other experiments, this cross-linker has been shown to improve thermomechanical stability of plastic scintillators but at the cost of degradation in radiation response [21]. Similar loss in LY and FoM are seen with other cross-linkers as well (e.g. Ethylene glycol dimethacrylate (EGDMA)). Recently however, we have identified a new and extremely promising system, that had not been used or studied in conjunction with plastic scintillators.

Bisphenol a dimethacrylate (BPA-DM) (Figure 6.17) is a cross-linker with a molecular structure that contains aromatic rings (which is important to help maintain radiation response due to the delocalized π-electrons), as well as methacrylate groups (which will provide the functionality to co-polymerize with polymer matrices).

![BPA-DM molecular structure](image)

Figure 6.17: BPA-DM molecular structure

BPA-DM has shown to be compatible with all of our current polymer matrices and dopants studied to date. The thermomechanical properties of samples prepared with BPA-DM are drastically altered, with samples ranging from too soft to polish (without melting) and are easily deformed by hand, to samples which can be aggressively beltsanded and finished to a high polish without softening, and a resistance to deformation similar to commercial scintillators. This property change is noticeable with as little as 3wt% of the crosslinker.
Current tests have shown it is soluble up to at least 10 wt%, with higher solubility possible, but not necessary at current dopant ratios, as this is where the rate of other thermomechanical improvements (glass transition temperature, and hardness) levels out. The cross-linking mechanism alters the kinematics of polymerization rates, so that higher concentrations (or lower dopant loadings) produce samples that polymerize heterogeneously and start to self-laminate in the oven, eventually breaking themselves apart Figure 6.18.

Figure 6.18: Cross-linked samples which have polymerized too rapidly

Figure 6.19 below shows samples that maintain essentially identical PSD scintillation response (LY remains constant or even shows slight increases) while altering the amount of BPA-DM in each plastic. Further results and discussion are found in 8 in addition to details of a synthesized fluorinated analogue, BPAF-DM, which was also tested as a possible additive to improve plastic scintillators surface resistance to weathering affects (e.g. water vapor absorption) which has been identified as a cause of clouding or fogging which degrades scintillator response [22].

Moving forward, it would be useful to identify a quantifiable metric that captures the “machinability” of these cross-linked plastics. The Shore-D test is a measure of bulk hardness, and is a commonly used value with commercial plastic scintillators, but the self-agglomeration that occurs with frictional heating during machining disappears quickly once the plastic is cross-linked, while further additional crosslinking continues to improve hardness.
Figure 6.19: PSD comparison of varying wt% of BPA-DM cross-linking agent measurements. Further characterization of how the cross-linking affects the surface properties and the way the plastic interacts with itself, will require a more in depth investigation into polymer tribology [23]. Our group has filed an invention disclosure for this system which has been converted to a non-provisional patent [9].

The work on cross-linking with BPA-DM is detailed in Chapter 8 as a published journal article [11]. Significant research contributions were made by the listed authors. Adam Mahl made the polymer samples, performed the machining/polishing and test preparation of the finished scintillators, conducted the radiation testing and results analysis, and helped perform material characterization of finished plastics; Allison Lim performed the synthesis, purification, and characterization of all the chemicals and dopants, made polymer samples, and helped perform material characterization of finished plastics; Henok Yemam made polymer samples, and helped perform material characterization of finished plastics; Joseph Latta assisted with the machining/polishing and radiation testing of the plastic scintillators; Alan Sellinger and Uwe Greife were the P.I.s and research advisors who generated the initial ideas and provided funding and supervision for the work. Principal editing and review was
6.3.2 Photopolymerization

After the initial years of establishing consistent production and testing procedures for our various new dopants and scintillator formulations, we began to investigate altering our polymerization method which had always been held constant (radical bulk polymerization). As discussed, our standard employed method took approximately a week from starting polymerization to final testable plastics. In addition to the long lead time on synthesis, there was always the chance that the samples would, for any multitude of reasons, not turn out as expected and test poorly, or not be able to be tested at all. While these failures occasionally provided valid data of some kind (such as leading towards our silanization procedure), often the reasons were unknown and just led to downtime. In an attempt to reduce the time required to produce samples we looked at research from the dental industry [24]. The now standard method for sealing teeth or filling caries has the dentist briefly shine bright LED lights of a specific wavelength on a mixture of monomer and photoinitiator in the tooth to induce a rapid photopolymerization leading to a new embedded filling. If the mixture used the correct monomer and also included some fluorescent dopants, this rapid photopolymerization method could be employed to produce testable plastic scintillators in a day instead of a week.

Figure 6.20 shows an example of our first attempt at photopolymerizing a plastic scintillator. Sample A contains no fluorescent dopant while Sample B contains a standard measure of scintillating fluor. The photoinitiator system initially chosen is a commonly used system consisting of a combination of camphorquinone (CQ), 4-dimethylamino benzonitrile (DMABN) [25]. This PI system works best with methacrylate based monomers, so the previously discussed crosslinker, BPA-DM (Figure 6.21) is also included to allow photopolymerization of our standard vinyltoluene based scintillators. This PI system reacts to photons in the visible blue range (~470nm) and samples produced in this method polymerize to a non-liquid state in a few hours. The samples are further cured in an oven to produce a sample hard enough
Figure 6.20: Initial photopolymerized samples under LED source and UV sunlight
to machine and test. Initial samples had LY in the ~50% range, and this was due to residual photoinitiator (which is very yellow and produces significant quenching effects) and incomplete polymerization. The ratio of the P.I. system to scintillator material is important, as is time under the LED and in the oven. With equipment upgrades including a more powerful LED lamp, and a mirrored chamber setup, we have now produced small 6g samples with ~90% LY and large 20g samples with ~90% LY within 24 hours which maintain comparable PSD FoMs as shown in Table 6.1.

Table 6.1: Comparison of radiation response between polymerization methods

<table>
<thead>
<tr>
<th>PPO (wt%)</th>
<th>FoM</th>
<th>LY</th>
<th>Shore D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Photo.</td>
<td>Thermal</td>
<td>Photo.</td>
</tr>
<tr>
<td>20</td>
<td>1.43</td>
<td>1.53</td>
<td>83</td>
</tr>
<tr>
<td>25</td>
<td>1.64</td>
<td>1.71</td>
<td>84</td>
</tr>
<tr>
<td>30</td>
<td>1.76</td>
<td>1.82</td>
<td>84</td>
</tr>
</tbody>
</table>

The photopolymerized samples are only slightly softer than normal samples and show signs of residual stress in the surface of the material (the surface cracks and spreads over the surface with light disturbance), however they are still easy to machine and polish for effective testing. This stress, and material differences may be a result of performing the photopolymerization in ambient conditions, where molecular oxygen is present and can have

Figure 6.21: Current PI system
a significant effect on the reaction kinematics. Identifying precisely what effect this has on
the process is being investigated.

These results can be further improved with timing optimization, better characterization
of the entire system (before, during, and after polymerization), as well as investigating differ-
ent photoinitiator systems, which may be better suited to this method. This novel method
of polymerization could also be employed for some more exotic dopant combinations which
would normally be too sensitive to temperature fluctuations to be included in a standard
scintillator synthesis (such as some of our recently investigated bismuth based dopants, dis-
ussed in 9.1.1). Our group has filed a provisional invention disclosure for this method,
and a publication on this method with current results and more discussion has been writ-
ten (Allison Lim, Adam Mahl, et. al, Plastic Scintillators with Efficient Light Output and
Pulse Shape Discrimination Produced via Photo-Initiated Polymerization, TBD, 2018), and
currently is in the submission process.

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CHAPTER 7
HIGHLY SOLUBLE P-TERPHENYL AND FLUORENE DERIVATIVES AS EFFICIENT DOPANTS IN PLASTIC SCINTILLATORS FOR SENSITIVE NUCLEAR MATERIAL DETECTION

A paper published in Chemistry A European Journal [1].

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7.1 Abstract

Plastic scintillators are commonly used as first-line detectors for special nuclear materials. Current state-of-the-art plastic scintillators based on poly(vinyltoluene) (PVT) matrices containing high loadings (>15.0 wt%) of 2,5-diphenyloxazole (PPO) offer neutron signal discrimination in gamma radiation background (termed pulse shape discrimination, PSD), however they suffer from poor mechanical properties. In this work, a series of p-terphenyl and fluorene derivatives were synthesized and used as dopants in PVT based plastic scintillators as possible alternatives to PPO to address the mechanical property issue and to study the PSD mechanism. The 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. A direct correlation was found between the melting point of the dopants and the subsequent mechanical properties of the PVT based plastic scintillators. Select fluorene derivatives produced scintillator samples whose mechanical properties exceeded those of the commercial

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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.

7.2 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 [2]. 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 [3].

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 [4, 5]. 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 [6]. 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 elastic scattering (also referred to as proton recoils) [7]. As a result, neutrons scattering through the plastic will result in higher atomic excitation density distributed in singlet and triplet excited states [8]. 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)) [9]. 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$_2$) [10]. 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 (Figure 7.1) [11]. To our knowledge, only PPO, a diphenylanthracene (DPA) derivative, and m-terphenyl have been reported in literature to show PSD capabilities when doped at high concentrations in common polymer matrices [12, 13]. Furthermore, PPO is the only primary dopant capable of PSD used in a commercial plastic scintillator product.

\[
\begin{align*}
T_1 + T_1 & \rightarrow 1/9 (S_1 + S_0) \rightarrow \text{Delayed Fluorescence} \\
& \rightarrow 1/3 (T_1 + S_0) \rightarrow \text{Triplet Recycling} \\
& \rightarrow 5/9 (T_5 + S_0)
\end{align*}
\]

Figure 7.1: Collision of first triplet excited states and the products of their annihilation \([T_1=\text{first triplet excited state}, S_1=\text{First singlet excited state}, S_0=\text{Singlet ground state}, T_5=\text{Higher Triplet excited state}]\).

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 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 work, alternative primary dopants were synthesized that could be admixed into common plastic matrices at high concentrations to: 1) find alternatives to PPO that lead to PSD with enhanced mechanical properties; and 2) help identify the PSD mechanism. Therefore, we have prepared highly luminescent alkylated p-terphenyl and fluorene derivat-
atives with the intent of identifying the main parameters that affect the onset and efficiency of PSD. To systematically study these parameters, we took two approaches: First, 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. Second, fluorene derivatives with varied photoabsorption and photoemission were compared to PPO based on their general scintillation characteristics in PVT and PSD performance.

7.3 Results and Discussion

7.3.1 Synthesis and physical characteristics of PTP derivatives

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 [14, 15]. 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 [16, 17]. 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 [18]. 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 [18]. We here attempt to increase the solubility of PTP to further study this promising family of fluorescent dopants.

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 absorption and emission properties (see Figure 7.2 & Figure 7.3 and Figure B.33 & Figure B.34), and yielded a more useful form of the dopant for possible PSD properties in plastic scintillators via over-doping. 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 (Figure 7.4, Figure 7.5, Figure 7.6) [19–21]. Synthetic procedures for precursors of PTP derivatives, and their corresponding $^1$H and $^{13}$C NMR can be found in the Supplementary Information. 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.

![Photoabsorption of p-alkylated PTP](image)

**Figure 7.2:** Photoabsorption of p-alkylated PTP.

The relative photoluminescent quantum yields (PLQY) of these compounds are also very similar (>90%), as shown in Table 1, and these deviations are within the systematic error of the relative quantum yield measurement [22]. The thermal properties of PTP derivatives were studied using differential scanning calorimetry (DSC) and results shown in Figure B.83-84. The $T_m$ 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 7.1), suggesting liquid crystalline (LC) phases (that has been previously reported for terphenyl molecules) [23, 24], but we found no correlation between the existence of the LC-phases and

138
Figure 7.3: Photoemission of m-alkylated PTP.

Figure 7.4: Synthesis of para-alkylated p-terphenyl derivatives.

Figure 7.5: Synthesis of meta-alkylated p-terphenyl derivatives.
Figure 7.6: PTP derivatives and their reaction yields (ditBuPTP is not shown on Figure 7.4 and Figure 7.5 for the sake of clarity).
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 7.1: p-Terphenyl derivatives and their physical properties.\(^a\)

<table>
<thead>
<tr>
<th>Primary</th>
<th>(T_m) [^\circ C]</th>
<th>LC-phase [^\circ C]</th>
<th>(\text{UV}_{\text{max}}) [^\text{nm}]</th>
<th>(\text{PL}_{\text{max}}) [^\text{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>ehPTP</td>
<td>17</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>di-tBuPTP</td>
<td>255</td>
<td>245-255</td>
<td>280</td>
<td>349</td>
<td>-</td>
</tr>
<tr>
<td>m-tBuPTP</td>
<td>94</td>
<td>N/A</td>
<td>274</td>
<td>342</td>
<td>90</td>
</tr>
<tr>
<td>m-tBu2PTP</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>

\(^a\) Melting point \((T_m)\) 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 [22]. N/A = not applicable (for these cases multiple thermal transitions were not observed and therefore liquid crystal properties do not exist).

### 7.3.2 Plastic Scintillator Sample Preparation

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 literature procedure [25]. 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 7.7 and Figure 7.14).

![Image of plastic scintillators](image)

Figure 7.7: Plastic scintillators doped with the new terphenyl derivatives (each small square is 1 cm x 1 cm).

### 7.3.3 Solubility Test and Radiation Characterization

The solubility limit of PTP in PVT was determined to be 2.0-3.0 wt% in agreement with literature[4]. The p-alkylated derivatives (Figure 7.3) solubility in PVT were determined to be between 5.0-7.0 wt% with the exception of tBuPTP (Figure 7.3) and ditBuPTP (Fig-
The higher melting points of PTP, tBuPTP and ditBuPTP when compared to the rest of the p-alkylated derivatives correlate to the lower solubility limit. 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 7.1, Figure 7.5).

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 7.3) has a melting point lower than room temperature and thus was not explored further for overdoping due to extreme softening (gel-like) of the final plastic at concentrations of 10.0 wt%.

To test their radiation response, each sample was polished (Figure 7.7), 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. Light yield is a general property of plastic scintillators that describe their scintillation or energy transfer efficiency. As in previous publications, light yields are presented by comparing with signals from commercial scintillators such as Saint Gobain Crystals (BC-408) and Eljen Technology. In this study, the light outputs of the samples (in Table 7.2) are compared to a similarly sized sample of BC 408 acquired from Saint Gobain Crystals. The $^{137}$Cs response spectra of all the samples are shown in the Supplementary Information (Appendix B).

In comparison of 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 ±5.0% (Table 7.2). 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 stacking of the derivatives [26]. 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 7.3) showing the lowest light yield as shown in Table 7.2. The steric hindrance affects the 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.

Table 7.2: 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></td>
<td>LY %</td>
<td>LY %</td>
<td>FOM</td>
<td>LY %</td>
<td>FOM</td>
</tr>
<tr>
<td>PTP</td>
<td>97.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>tBuPTP</td>
<td>85.4</td>
<td>71.0</td>
<td>0.58</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>nBuPTP</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>m-tBuPTP</td>
<td>86.0</td>
<td>94.0</td>
<td>0.79</td>
<td>90.0</td>
<td>0.81</td>
</tr>
<tr>
<td>m-tBu2PTP</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>

Next, a $^{244}$Cm/$^{13}$C source was used to generate a mixed neutron and gamma radiation field. The individual samples response was energy calibrated using the $^{137}$Cs spectrum, and then analyzed for any indication of n/$\gamma$ PSD. The PSD analysis was performed using the charge integration method. By integrating the digitized waveforms of the response for the total charge in each given pulse (total fluorescence), and comparing it to the charge in the tail of that pulse (delayed fluorescence), a ratio is calculated (delayed energy fraction) which is different due to the slight difference in decay signal between incident gammas and neutrons. The efficiency of PSD is then quantified by a figure-of-merit (FoM) measuring the separation of the two types of signals at a given energy. PSD performance is measured by a
dimensionless Figure-of-Merit (FoM) metric which is calculated as detailed in Equation 7.1.

These values are obtained by examining the signals within an energy range of the neutron and gamma lines. A y-projection is performed and a double Gaussian fit is assigned to the peaks. The centroids and FWHM are extracted and a FoM is obtained.

\[
FoM = \frac{\text{Centroid}_n - \text{Centroid}_g}{\text{FWHM}_n + \text{FWHM}_g}
\]  

(7.1)

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 7.2). 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 7.2). The results of PPO are shown as the last entry in Table 7.2 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 mtBu2PTP 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 [27]. 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 7.8 and Figure 7.9 show the n/\gamma 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 [6]. 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. PSD spectra for 10.0 wt% and 15.0 wt% mopPTP samples can be found in the Supplementary Information (Appendix B).

Figure 7.8: Onset of pulse shape discrimination (PSD) of 5.0 wt % mopPTP and 0.1 wt % POPOP in PVT.

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 (hardness as a function of % wt dopant concentration can be found in Figure B.82) shows hardness dropping off with increasing dopant concentration. This could be a result of fluorescent dopants retarding polymerization that creates softer plastic scintillators [28–30]. 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.
Figure 7.9: Pulse shape discrimination (PSD) of 20.0 wt % mopPTP and 0.1 wt % POPOP in PVT.

7.3.4 Fluorene Derivatives

Fluorene derivatives have been frequently used in Organic Light Emitting Diode (OLED) research due to their ease of chemical manipulation, efficient and predictable photophysical properties, thermal stability, efficient light output, and relatively low cost [31, 32]. 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 (Me2F) and PPO were directly purchased from Sigma-Aldrich. Me2F 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 synthesis procedure, as well as $^1$H and $^{13}$C NMR spectra can be found in the Supplementary Information (Appendix B). The fluorene derivatives (Figure 7.10) were designed to evaluate the effect of both blue-
and red-shifting of photo-absorption and emission spectra as compared to PPO as shown in Figure 7.11 and Figure 7.12. Scintillation samples for this study were prepared and tested in the same manner as the PTP derivative based samples.

![Figure 7.10: Fluorene derivatives for use as dopants in plastic scintillators in this study.](image)

![Figure 7.11: Absorption of fluorene derivatives.](image)

Melting points and optical properties of the fluorene derivatives and PPO are outlined in Table 7.3. 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 again used for light yield comparison.

Table 7.3: Photophysical properties and melting points of fluorene derivatives and PPO.\(^a\)

<table>
<thead>
<tr>
<th>Primary dopants</th>
<th>(T_m) [°C]</th>
<th>(\text{UV}_{\text{max}}) [nm]</th>
<th>(\text{PL}_{\text{max}}) [nm]</th>
<th>Relative PLQY [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO</td>
<td>72</td>
<td>304</td>
<td>367</td>
<td>100</td>
</tr>
<tr>
<td>Me2F</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>

\(^a\) – p-Terphenyl was used as a reference dye for PLQY measurement of Me2F and PhF, excitation wavelength at 270 nm whereas PPO was used as a reference dye for PFP and SF PLQY measurement, excitation wavelength at 320 nm. 9,10-Diphenylanthracene was used as a reference dye for SFS, excitation wavelength at 350 nm. 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 derivatives.

The photoemission of Me2F (Figure 7.12) 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% Me2F shows lower light output compared to the same PPO sample (Table 7.4). The purified
1.0 wt% Me2F showed a drastic increase in light output, nearly 1.5-fold compared to as received Me2F. 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 [33]. SFS absorbs and emits within the same region as POPOP so as expected, showed a high light output as a stand-alone dopant (Table 7.4). 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 measured PLQY of the fluorene based dopants.

Table 7.4: Radiation responses of fluorene derivatives plastic scintillators and PPO.

<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>
<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>

a – As-received Me2F was purified by passing through a silica column with 10% activated carbon.
b – 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 7.4). Despite increased purity, the PSD for all over-doped Me2F was negligible (Table 7.4). It shows that not all soluble fluorescent dopants could produce PSD when
exposed to a mixed radiation environment. 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 7.4, Figure 7.13) [34]. Radiation response data for PhF based samples can be found in the Supplementary Information (Appendix B). PFP precipitated out at 10%, and was 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. SF 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. All PSD data for SF can be found in the Supplementary Information (Appendix B). The reason for the low PSD at high SF concentrations is proposed to be attributed to a small percentage of cis-isomer present in the synthesized SF as shown in GC/MS data (Figure B.32). The first excited triplet state for cis-SF (1.93eV) was found to be lower than that of trans-SF (2.21eV) in our computational modeling results (Supplementary Information (Appendix B)). 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 [35]. In addition to the negligible increase in FoM, samples with a higher concentration of SF developed a yellow color during polymerization that is attributed to aggregation effects at higher concentrations (Figure 7.14). We are exploring the synthesis of pure trans-SF to test this theory.

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. Hardness measurements were done using the Shore-D durometer following the same procedures as with the PTP derivatives. As shown in Figure 7.15, as the concentration of PPO is increased, the hardness of the final plastic scintillator decreases dramatically. The same was true for purchased Me2F and
purified Me2F*. PhF and SF both displayed a significantly lower drop off in hardness as concentration increased.

Generally, fluorene derivatives and PPO had higher solubility in PVT than PTP derivatives regardless of melting point or photophysical properties. For instance, SF had a higher melting point than mtBuPTP but it also had 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) [36]. The models (Figure B.66-Figure B.81) 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°. Going forward we believe that computation can play an important role in
Figure 7.14: Plastic scintillators doped with fluorene derivatives and PPO (each small square is 1 cm×1 cm).
understanding how dopants work so that we can predict and design more efficient dopants.

It’s important to note that both PTP and fluorene-based samples have shown no noticeable physical change or degradation for over nine 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 [37].

7.4 Conclusion

The softening of plastics when over-doped with high concentrations 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 when doped into PVT resulted in encouraging PSD capabilities with
enhanced plastic mechanical properties compared to the analogous samples using PPO as dopants.

We were successful in preparing derivatives with enhanced solubility, and were able to show that over-doping of fluorescent material does not lead to a significant PSD in all cases. While we successfully achieved comparable PSD with mopPTP, the similar mtBuPTP showed decreased PSD, implying triplet exciton migration has a preferred morphological pathway to achieve efficient TTA as a plausible mechanism for PSD in over-doped samples. We also prepared fluorene derivatives with varied optical properties and did not find a direct correlation between spectral overlap of dopants, and final scintillating light output. Over-doped samples also 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 significantly harder (Shore-D of 81 vs 69) resulting in a final plastic that could be easily handled and polished. It is also important to investigate the effect of isomers on PSD performance as shown by the proposed detrimental effect of cis-SF on trans-SF.

The exact physics responsible for efficient PSD is still elusive, however we believe that planar molecules heavily influence how triplet states migrate, collide and annihilate each other. Our future work will focus on these investigations using computational modeling of excited states as well as the effect of plastic mechanical properties on PSD performance.

7.5 Acknowledgements

This research was funded through US DHS DNDO grants # DHS-14-DN-077-AR-NC7 and DHS-16-DNDO-077-001. The authors would like to thank Captain Brett McNichols for his help in the analysis of proton NMR spectra.
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CHAPTER 8
METHACRYLATE BASED CROSS-LINKERS FOR IMPROVED THERMOMECHANICAL PROPERTIES AND RETENTION OF RADIATION DETECTION RESPONSE IN PLASTIC SCINTILLATORS

A paper published in *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* [1].

Adam Mahl¹*, Allison Lim²*, Joseph Latta¹, Henok A. Yemam², Uwe Greife¹, Alan Sellinger²†

8.1 Abstract

Pulse shape discrimination (PSD) is an important method that can efficiently identify and separate neutron and gamma radiation signals. PSD is currently achieved in plastic scintillators by over-doping poly(vinyl toluene) (PVT) matrices with fluorescent molecules. Meaningful separation of the signals requires addition of >20 wt% 2,5-diphenyloxazole (PPO) fluor in PVT. At these concentrations PPO acts as a plasticizer, negatively affecting the physical properties of the final plastic such as hardness, machinability, and thermal stability. This work addresses these issues by implementing a cost-effective solution using cross-linking chemistry via commercially available bisphenol A dimethacrylate (BPA-DM), and a synthesized fluorinated analogue. Both improve the physical properties of over-doped PPO based plastic scintillators without degrading the measured light yield or PSD and Figure of Merit (FoM). In addition, the fluorinated analogue enhances the hydrophobicity of the surface of the plastic scintillators, which may improve the scintillators’ resistance to water diffusion.

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and subsequent radiation response degradation. The new formulations improve the feasibility of widely deploying long lifetime PSD capable plastic scintillators in large area coverage assemblies.

8.2 Introduction

Plastic scintillators are currently utilized as first line radiation detectors for special nuclear materials (SNM), due to their low cost, ease of manufacture and fast response time. Research is currently being performed on these detector materials and systems with various goals; such as making the plastic scintillators sensitive to thermal neutrons through neutron sensitive additives (e.g. $^{10}$B, $^6$Li), improving the photoelectric effect response of plastic scintillators through incorporation of high Z elements (e.g. Bi, Pb), and improving the radiation type classification capabilities (neutron/gamma discrimination) of different polymer/fluor formulations [2–8]. The most common technique used to address the latter is pulse shape discrimination (PSD). One current method of introducing PSD capabilities into plastic scintillators is based on incorporating >20 wt% fluorescent dopants, such as 2,5-diphenyloxazole (PPO) into poly(vinyl toluene) (PVT) matrices [9]. Although this formulation has been commercialized, the high concentrations of PPO required for meaningful PSD induce a plasticizing effect in the scintillators [10]. The resultant plastic scintillators are softer, difficult to machine and polish, and lack the thermal and structural integrity required for larger detector systems [11, 12]. In addition to these issues, when deployed in certain environments, current plastic scintillators are susceptible to degradation due to weathering from ambient humidity and temperature fluctuations which can lead to fogging [12, 13].

Research into improving the physical properties of PSD capable plastics includes developing new fluorescent dopants and using cross-linkers or alternative polymer matrices [4, 6, 14]. Common commercially available cross-linkers such as divinylbenzene (DVB) and ethylene glycol dimethacrylate (EGDMA) used with polystyrene (PS) or PVT, have been

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1At the time when this manuscript was submitted, Eljen Technology is starting to introduce a new variant of its PSD capable plastic (EJ-299-33M), which tests very similarly to the scintillators prepared in this work.
shown to enhance the thermomechanical properties of plastic scintillators to varying degrees, but these improvements appear to come at a cost of degrading the radiation response of the scintillator [15–17].

We report here on the use of cross-linkers that combine the aromaticity of DVB with the methacrylate functional groups of EGDMA. Retaining aromaticity was broadly expected to maintain radiation response due to the delocalized π-electrons, while the methacrylate groups provide the functionality to be co-polymerized into vinyl toluene matrices. A combination of these two properties was achieved with a commercially available cross-linker, bisphenol A dimethacrylate (BPA-DM) and its analogue, bisphenol AF dimethacrylate (BPAF-DM) (Figure 8.1). BPAF-DM was designed to improve the hydrophobicity of the scintillator surface and bulk in an attempt to reduce water permeability, as previously observed in fluorinated polymers [18–21]. We have prepared BPAF-DM in minimal step and high yield reactions using inexpensive and benign starting materials thus demonstrating its scalable production (Pages S1–S4 of Supplemental Information (Appendix C)). Both BPA-DM and BPAF-DM proved effective at maintaining or even improving light yield and PSD capabilities while simultaneously enhancing the thermomechanical properties of the plastic scintillators.

![Molecular structure of BPA-DM (left) and BPAF-DM (right).](image)

8.3 Experimental Methods

8.3.1 Preparation of Plastic Scintillators

Additional details on the preparation and testing of plastic scintillators can be found in our previous publications [4, 5]. Glass vials were silanized according to literature [22]
with dichlorodimethylsilane (DCDM) (Sigma-Aldrich) and used as scintillator molds. The inhibitor was removed from vinyltoluene monomer (VT) (TCI America) via an alumina (basic) column plug with dry potassium carbonate (Sigma-Aldrich). Azobisisobutyronitrile (AIBN) (Sigma-Aldrich) was used as a radical initiator (after purification from two recrystallizations in methanol) and dissolved in VT monomer to prepare a 0.01 wt% (0.014 mol%) AIBN/VT stock solutions. BPA-DM (Sigma-Aldrich), PPO (Sigma-Aldrich), and 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP) (Sigma-Aldrich) were used as received. Varying amounts of PPO (20–30 wt%), cross-linkers (0–10 wt%), and 0.1 wt% of POPOP (used as a wavelength shifter in each prepared sample detailed in this work) were added to AIBN/VT stock solutions in silanized glass vials to produce 20 g samples which were then gently sparged with argon for ∼30 min to displace oxygen. In our standard procedure, the vials were capped and placed in an argon filled vacuum oven (Fisher Scientific Isotemp 280 A) under a slight vacuum, and cured for four days at 80 °C, then 24 h at 90 °C before being allowed to slowly cool to room temperature. This polymerization period needed to be altered for samples modified with BPAF-DM as discussed later in Section 8.4.1. The glass vials were broken to extract the plastic pucks that were ∼4.7 cm in diameter and ∼1.25 cm thick. Samples were finished to a flat surface by machine and hand sanding before a final polishing on a buffer wheel.

8.3.2 Radiation and Hardness Characterization

Each finished sample was wrapped in PTFE tape, coupled to a Hamamatsu PMT (H2431-50) with light-tight covering, and exposed to different fields of ionizing radiation. The samples’ response was measured with a DAQ system based on an in-house built, 250 Msample/s waveform digitizer, which was controlled by a MIDAS software interface [23]. The individual waveforms were saved and the ROOT data analysis framework [24] was utilized to analyze the collected data, and develop relevant output spectra.

The gamma response of each sample was measured using a $^{137}$Cs (1 µCi) source. The collected, integrated PMT anode pulse content spectra produced a visible Compton edge
for each sample, which was used to calculate a sample specific light yield by comparing the position of the edge to one produced from a commercial scintillator (BC-408) machined to the same size as our samples. Samples were also exposed to a mixed neutron and gamma radiation field emanating from a $^{244}$Cm$/^{13}$C ($\sim$60 mCi) source. Each samples’ response was measured on a keV$_{ee}$ (kilo-electron Volt, electron equivalent) scale, calibrated using the $^{137}$Cs response spectrum. The quality of the PSD in each sample was quantified by a dimensionless Figure of Merit (FoM),

$$FoM = \frac{Centroid_n - Centroid_g}{FWHM_n + FWHM_g}$$ (8.1)

through analysis of a delayed pulse content interval compared to total pulse content in the analyzed waveforms. With typical decay times of order $\sim$8–10 ns, a delayed integration time window from 32–120 ns is compared to the total integrated pulse content in order to display PSD. The FoM metric was calculated for both 100–200 keV$_{ee}$ and 400–600 keV$_{ee}$ energy cut intervals.

Sample hardness was subjectively observed for machinability on a belt sander and polishing wheel during sample preparation by noting how each sample melted with the added friction. A Shore-D durometer (GxPro model# 560-10D) was used to quantify the hardness. The Shore-D values were obtained with the ASTM standards (ASTM D-2440) testing procedure, where 6 equidistant points were sampled on the face of the sample for $\sim$1 s and then averaged.

8.3.3 Thermal Characterization

Thermal stability was quantified via thermal gravimetric analysis (TGA) using a Q200 TA Instrument. To determine the decomposition temperature ($T_d$) of the plastics, portions were typically cut from the top edge of the plastic scintillator samples and ramped at 15 °C/min to 600 °C under an inert nitrogen atmosphere. Similar portions were cut from samples to use for differential scanning calorimetry (DSC) measurements to determine glass transition temperatures ($T_g$). DSC was performed on the Q2000 TA Instrument by heating
from -5 °C to 150 °C at 10 °C/min. TGA and DSC analysis used Universal Thermal Analysis software. Portions were also taken from the interior of the scintillators, but no difference was observed.

8.3.4 Contact Angle

Contact angle measurements were made on a Ramé-Hart Instrument Co. Standard Goniometer (Model No. 200-00) using 10 µl deionized water droplets. Analysis was performed on DropImage software.

8.3.5 Kinetics of Polymerization

Admixing the different cross-linkers into the monomer significantly affected the rate of polymerization. These effects were quantified as compared to pure monomer via gravimetric measurements adapted from established methods in literature [24, 25]. A stock solution of 0.01 wt% AIBN in VT monomer was used to dissolve 2 wt% of cross-linker. Solutions were degassed with argon for 10 min in glass vials before being heated at 80 °C in an oil bath. Aliquots of the polymerizing solution were removed via micropipette at designated times and cooled to 0 °C in an ice bath. The aliquot was dissolved in toluene then precipitated in cold methanol while stirring. The precipitate was filtered off, dried in ambient conditions, and weighed. The rate of change of the ratio of polymer to remaining monomer in time is indicative of the reactivity of the different cross-linkers.

8.4 Results and Discussion

8.4.1 Effect of Cross-Linking on Rate of Polymerization

When polymerized under the conventional conditions as described above, BPAF-DM samples appeared to polymerize more rapidly, leading to clouding and poor-quality samples. To verify this, the rates of polymerization were compared (Figure 8.2) as previously detailed in Section 8.3.5. Based on this increased reactivity, BPAF-DM based samples were produced.
by heating for 24 h at 60°C, 24 h at 70°C, 48 h at 80°C, and 24 h at 90°C. This slower heating profile led to clear and colorless samples allowing further testing and characterization (Figure C.8 in Supplemental Information (Appendix C)).

![Graph](image.png)

Figure 8.2: Relative comparison of rate of polymerization at 80°C between pure VT, VT with BPA-DM, and VT with BPAF-DM

### 8.4.2 Effects of Cross-Linking on Hardness and Measured Radiation Response

The first set of experiments focused on improving hardness and machinability in overdoped PPO plastic scintillators. For comparison, the commercial BC-408 sample, which has low primary dopant concentration and does not display PSD, has a Shore-D value of 85. Varying amounts of BPA-DM were used with 20, 25, and 30 wt% PPO. Increasing BPA-DM content led to an increase in Shore-D hardness (Figure 8.3) as well as a significant improvement in machinability. For example, at ≥3 wt% BPA-DM the samples could be belt sanded and machine polished without melting. Samples containing ≥5 wt% BPA-DM could withstand aggressive sanding and wheel polishing without exhibiting induced friction.
melting or self-agglomeration. The same trend was observed for BPAF-DM modified samples (Table C.1 in Supplemental Information (Appendix C)).

![Graph showing the relationship between hardness and concentration of BPA-DM](image)

**Figure 8.3: Relationship between hardness and concentration of BPA-DM**

Cross-linking had the most pronounced effect in the 30 wt% PPO samples. Without cross-linkers, the over-doped samples were very soft, bendable and could not be fully machined and polished. In all the unmodified over-doped plastics, the PPO quickly crystallized (within hours to under a week depending on the dopant concentration), leading to opaque scintillators (Figure C.8-Figure C.11 of Supplemental Information (Appendix C)). By cross-linking the scintillators, significant increases in hardness were observed together with a complete suppression of dopant crystallization. The cross-linked scintillators remain clear, colorless, and hard after >8 months of ambient storage (Figure 8.4, Figure C.9-Figure C.11 in Supplemental Information (Appendix C)). The cross-linked polymer matrix is proposed to inhibit diffusion of PPO, preventing the formation of aggregates that lead to opaque scintillators.
In addition to successfully enhancing the hardness and machinability of plastic scintillators, BPA-DM did not degrade the measured radiation response of the scintillators. As observed in Figure 8.5, Figure 8.6 and fully detailed in Table 8.1, over-doped samples with varying amount of cross-linker (all samples detailed contain 0.1 wt% POPOP as a wavelength shifter) show excellent and consistent PSD. Furthermore, there is no light output reduction observed in any of the cross-linked samples, with high concentrations of BPA-DM producing slightly enhanced light yields.

In the over-doped plastic scintillators cross-linked with BPAF-DM (Figure C.8 in Supplemental Information (Appendix C)), light yield and PSD capabilities remain comparable to unmodified scintillators. Overall, these samples are harder than uncross-linked over-doped plastics, but not as robust as BPA-DM based samples (see Shore-D and glass transition temperature ($T_g$) values detailed in Table C.1-Table C.3 of Supplemental Information (Appendix C)). Further examples of radiation response spectra for cross-linked samples can be found in Figure C.13-Figure C.15 of Supplemental Information (Appendix C).
Figure 8.5: Energy-calibrated signal plot for a 30 wt% PPO over-doped sample with 10 wt% BPA-DM displaying PSD.

Table 8.1: Radiation Detection Properties of BPA-DM Cross-Linked Samples

<table>
<thead>
<tr>
<th>BPA-DM (wt%)</th>
<th>Light Yield (% of BC-408)</th>
<th>FoM @ 100-200 keV&lt;sub&gt;ee&lt;/sub&gt;</th>
<th>FoM @ 400-600 keV&lt;sub&gt;ee&lt;/sub&gt;</th>
<th>Hardness (Shore-D)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I  II  III</td>
<td>I  II  III</td>
<td>I  II  III</td>
<td>I  II  III</td>
</tr>
<tr>
<td>0</td>
<td>87  81  89</td>
<td>1.03 1.16 1.38</td>
<td>1.47 1.71 1.88</td>
<td>66  65  6</td>
</tr>
<tr>
<td>0.5</td>
<td>91  86  92</td>
<td>1.11 1.20 1.37</td>
<td>1.54 1.67 1.85</td>
<td>70  68  29</td>
</tr>
<tr>
<td>1</td>
<td>89  86  91</td>
<td>1.08 1.24 1.41</td>
<td>1.58 1.75 1.94</td>
<td>74  68  43</td>
</tr>
<tr>
<td>2</td>
<td>86  89  100</td>
<td>1.07 1.25 1.44</td>
<td>1.48 1.66 1.90</td>
<td>75  70  37</td>
</tr>
<tr>
<td>3</td>
<td>92  86  97</td>
<td>1.11 1.17 1.43</td>
<td>1.55 1.70 1.93</td>
<td>75  71  39</td>
</tr>
<tr>
<td>4</td>
<td>89  92  99</td>
<td>1.08 1.23 1.34</td>
<td>1.57 1.71 2.00</td>
<td>75  71  56</td>
</tr>
<tr>
<td>5</td>
<td>93  86  95</td>
<td>1.12 1.16 1.32</td>
<td>1.55 1.70 1.95</td>
<td>77  73  60</td>
</tr>
<tr>
<td>6</td>
<td>91  89  97</td>
<td>1.05 1.23 1.39</td>
<td>1.52 1.68 1.90</td>
<td>79  73  59</td>
</tr>
<tr>
<td>8</td>
<td>90  92  92</td>
<td>1.09 1.25 1.35</td>
<td>1.54 1.66 2.05</td>
<td>74  74  66</td>
</tr>
<tr>
<td>10</td>
<td>88  94  93</td>
<td>1.08 1.16 1.35</td>
<td>1.53 1.71 1.82</td>
<td>77  75  73</td>
</tr>
</tbody>
</table>

I – Samples contain 20 wt% PPO

II – Samples contain 25 wt% PPO

III – Samples contain 30 wt% PPO
(a) For a deposited energy slice between 100-200 keV_{ee}.

(b) For a deposited energy slice between 400-600 keV_{ee}.

Figure 8.6: PSD FoM for 30 wt% PPO over-doped samples with varying degrees of crosslinking.
8.4.3 Effects of Cross-Linking on Thermal Stability of Plastic Scintillators

The thermal properties of over-doped plastic scintillators cross-linked with BPA-DM were compared to the analogous unmodified samples using DSC and TGA analysis. All BPA-DM cross-linked samples have a higher glass transition temperatures \( T_g \) than the unmodified PPO samples, indicating cross-linking enhances the thermal stability of the plastics Table 8.2 on page 171. As the concentration of PPO increased, the \( T_g \) decreased, which is expected and most likely due to PPO acting as a plasticizer within these scintillators [25]. The same thermal stability effects were observed for BPAF-DM modified samples leading to machinable scintillators, but less pronounced as compared to the BPA-DM samples. TGA revealed decomposition temperatures \( T_d \) of >350 °C for samples without PPO. For scintillators containing 30 wt% PPO, weight loss begins at 170 °C and stabilizes at 70% weight at ~260 °C (Fig. S11 in Supplemental Information). This is likely due to the sublimation of PPO as the \( T_d \) of PPO is much higher than this (a stated boiling point at 360 °C under ambient pressure). The decomposition of the remaining cross-linked polymer matrix then begins over 350 °C like the non-PPO containing samples. Cross-linked samples exhibit a slower maximum decomposition rate, attributed to cross-linkers impeding decomposition of the polymer matrix [26].

Table 8.2: Thermal Properties of BPA-DM and BPAF-DM Cross-Linked Samples

<table>
<thead>
<tr>
<th>Cross-Linker</th>
<th>( T_g ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>0 wt%</td>
<td>36.3 ± 0.5</td>
</tr>
<tr>
<td>5 wt% BPA-DM</td>
<td>57.9 ± 2.8</td>
</tr>
<tr>
<td>8 wt% BPA-DM</td>
<td>49.6 ± 0.5</td>
</tr>
<tr>
<td>5 wt% BPAF-DM</td>
<td>43.2 ± 1.3</td>
</tr>
<tr>
<td>8 wt% BPAF-DM</td>
<td>45.0 ± 1.0</td>
</tr>
</tbody>
</table>

I – Samples contain 20 wt% PPO  
II – Samples contain 25 wt% PPO  
III – Samples contain 30 wt% PPO
8.4.4 Enhancing the Hydrophobicity of Plastic Scintillators

When plastic scintillators are exposed to humid conditions and fluctuating temperatures, water vapor is absorbed by the matrix and can cause a fogging effect which leads to degradation of the radiation response signals [12, 13]. It may be possible to mitigate this issue by increasing the hydrophobicity of the plastics’ exposed surfaces. Fluorinated polymers tend to be more hydrophobic, so the contact angles of BPA-DM and BPAF-DM samples were measured to quantify the hydrophobicity of the prepared plastic scintillator surfaces (detailed in Section 8.3.5). As shown in Table 8.3 on page 172, varying the amount of BPA-DM did not induce a significant change in the hydrophobicity of the plastics. For reference a pure PVT sample containing no dopant was prepared and shows a contact angle of 95 ± 3. Samples cross-linked with BPAF-DM displayed on average, a measurable increase in contact angle, which is attributed to the increased fluorine content as shown in other cases in the literature [18–21]. The larger contact angle indicates the surfaces of BPAF-DM cross-linked samples are more hydrophobic, which may help stabilize scintillators in humid conditions. Further experiments using controlled humidity chambers are necessary to further explore this approach.

<table>
<thead>
<tr>
<th>PPO (wt%)</th>
<th>0 wt%</th>
<th>5 wt%</th>
<th>8 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BPA-DM</td>
<td>BPAF-DM</td>
<td>BPA-DM</td>
</tr>
<tr>
<td>20</td>
<td>97 ± 1</td>
<td>98 ± 3</td>
<td>94 ± 6</td>
</tr>
<tr>
<td>25</td>
<td>97 ± 1</td>
<td>89 ± 7</td>
<td>106 ± 2</td>
</tr>
<tr>
<td>30</td>
<td>92 ± 6</td>
<td>93 ± 3</td>
<td>102 ± 1</td>
</tr>
<tr>
<td>Averages*</td>
<td>96 ± 4</td>
<td>92 ± 4</td>
<td>101 ± 6</td>
</tr>
</tbody>
</table>

* – Including all samples prepared, independent of PPO content.

8.5 Conclusions

Large volume production and wide-scale deployment of PSD capable plastic scintillators need to balance enhanced radiation discrimination, thermomechanical properties, stability,
and light yield. We report in this work on a system that can achieve excellent PSD, high light yield, hard machinable plastics, and stability under ambient conditions. We achieve this by formulating PVT based scintillators, using both commercially available BPA-DM, and in-house synthesized fluorinated BPAF-DM methacrylate based cross-linkers. The BPAF-DM was designed to improve the hydrophobicity of the plastic scintillators, which may improve the scintillators’ resistance to water diffusion and subsequent radiation response degradation. These new plastic scintillators can be prepared from inexpensive starting materials, and known processing conditions leading to scalable systems.

8.6 Acknowledgements

This research was funded through US DHS DNDO grants # DHS-14-DN-077-AR-NC7 and DHS-16-DNDO-077-001.

8.7 References Cited


**Keywords:** Plastic Scintillators; Pulse Shape Discrimination; Cross-linking; Fluorination; Hydrophobicity;
CHAPTER 9
GENERAL CONCLUSIONS

9.1 Summary / Future Work

The collaborative work with the chemistry department has allowed us to develop several boron compounds that are compatible in many different liquid and plastic scintillator formulations, and allow for rapid and unambiguous detection of thermal neutrons. Furthermore, our collaboration has allowed for a more guided, rigorous investigation into how to develop, purify, and study the properties of new fluorescent dopants (or alter established dopants) for use in scintillation based radiation detector systems. This has been, and will continue to be an integral aspect in further development of the current (incomplete) theory of PSD in organic scintillators. Both approaches still have many avenues forward that need to be investigated.

9.1.1 High Z materials for gamma spectroscopy and spin orbit coupling induction

The research is currently being expanded upon by investigating how to develop polymer soluble, high Z (atomic number), organometallic compounds (such as iridium or bismuth containing complexes) and study how they will affect the scintillators nuclear response to incident radiation. In addition to altering plastic scintillators to better detect thermal neutrons, and provide some particle identification capabilities via PSD, the community is also interested in research aimed at producing plastic scintillators that can provide spectroscopic information via increasing the response of the photoelectric effect. Since the cross section for the photoelectric effect scales drastically with the increasing effective Z of the material, photons do not (statistically) interact with plastic scintillators (which are composed mainly
with low-$Z$ hydrogen and carbon) in this way. By introducing some high $Z$ material (such as tin, lead, or bismuth compounds), the cross section for the photoelectric effect can be enhanced to compete with the Compton effect shown in Figure 9.1 (and previously discussed in 1.4). Via this method, some historical and commercial scintillators have been able to provide plastics with slight photopoint resolution of >15%, which additionally comes at a significant decrease in light yield due to quenching effects of the organometallic compounds [1–3].

![Enhancing Photoelectric Interaction Cross Section](image)

Figure 9.1: Cross section comparison of scintillators which contain high $Z$ dopant materials

We have begun investigation into organometallic compounds based on bismuth due to the ease of the chemistry required to functionalize the element (make it more soluble and stable), and the unique lack of biological toxicity normally found in heavy metals [4]. Initial samples made with compounds reported in literature are being produced, however, these samples also reportedly suffer from reduced LY [5, 6], so new dopants based on our experience with manipulating molecular geometry and symmetry are being developed, to better counteract this quenching effect. Our initial results have also shown that these dopants are very sensitive to both ambient conditions and the thermal heating profiles normally used in our established polymerization methods. This makes photopolymerization an attractive option for producing
plastics containing these organometallic dopant varieties.

Inducing spin-orbit coupling (in addition to the discussed inducing of the photoelectric effect) by including Ir based organometallic dopants (Figure 9.2) is of interest to further enhance PSD, by allowing for more control over the triplet-state population and migration.

![Diagram of FIrPic molecule and Spin-Orbit coupling Jablonski](image)

(a) FIrPic molecule  
(b) Spin-Orbit coupling Jablonski [7]

**Figure 9.2: Iridium based Spin Orbit Coupling**

These molecules could produce reactions allowing for an alternative to PSD analysis for particle identification (e.g. spectral shape discrimination or SSD). Current research is ongoing to find compatible host matrices and primary dopants [7, 8].

It will also be important see this research investigate methods of scaling up both the dopant synthesis and plastic production. Often material properties will change with scale, and better testing of larger size plastics will yield more accurate results for real world deployment feasibility research being performed by other groups in the community.
9.2 Conclusion

This basic research has made progress in several directions towards developing new, alternative plastic scintillator formulations. A basis for synthesis and development of both organoboron compounds used for the detection of thermal neutrons in compatible polymer matrices as well as novel scintillating fluors has been developed and can be expanded upon. Throughout this research, 3 metrics were identified and measured as important, quantifiable properties of a plastic scintillator’s efficacy: LY, FoM, and machinability (hardness). These properties are important in the final plastic, but with the work presented here, they can be predicted and designed towards based on properties of the constituent parts (dopants and matrix). Through the PhF and TPO dopants, this research has produced the first reported dopant (to our knowledge at this time), other than PPO, capable of being overdoped in a PVT matrix and producing a FoM of >1.2 (@400 keV\textsubscript{ee}). Other highly soluble dopants were identified however, they did not produce a high FoM and often resulted in a decreased LY and/or measurable hardness. With the admixture of the BPA-DM crosslinking agent, a new standard of plastic scintillator composition has been identified, which is based on an overdoping of the primary fluor PPO (to \textasciitilde30 wt\%) into crosslinked PVT matrix, which produces a final plastic with PSD properties producing a FoM @ 100 keV\textsubscript{ee} of 1.3 and a LY matching (or slightly higher) than the current industry standard control plastic scintillator which displays no PSD capabilities. This final plastic retains significant thermomechanical properties, is easily machined and polished to a high finish without melting, and is stable under ambient conditions for several years. Finally several novel fluors were synthesized that produced plastic scintillators with LYS which were higher than both commercial controls and PPO based plastics. These fluors were studied in alternative matrices and revealed a new trend in the relationship between all 3 measured metrics.

A PhD dissertation in Chemistry covering the collaborative material for this project has been defended in April 2017 by Dr. Henok Yemam. A M.S. thesis in Materials Science covering polymerizable PPO derivatives was successfully defended by Griselda Hernandez in
July 2018. A Ph.D. dissertation in Materials Science by Allison Lim, and a Ph.D. dissertation in Nuclear Engineering by Joseph Latta further covering this material are expected to follow. Though the exact physics responsible for efficient PSD is still elusive, the 2 broad approaches have helped elucidate several properties related to the various components of plastic scintillators that can be altered and studied to help future development and understanding.

9.3 References Cited


APPENDIX A
CHAPTER 3 SUPPLEMENTARY INFORMATION

Supplementary information to a paper published in Nature: Scientific Reports[9].

Henok A. Yemam¹, Adam Mahl², Unsal Koldemir¹, Tyler Remedes², Sean Parkin³,
Uwe Greife², Alan Sel linger¹,

A.1 Experimental Section

A.1.1 Experimental Conditions (conventional heating)

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

In a flame-dried Schlenk tube under argon atmosphere, 1-bromopyrene (200mg, 0.71mmol) and B₂Pin₂ (270mg, 1.07mmol) were dissolved in 20ml 1,4-dioxane. Flame dried KOAc (210 mg, 2.13mmol) was added quickly to the mixture followed by PdCl₂(dppf) (17mg, 0.021mmol). The mixture was heated at 90°C overnight. Once the reaction was complete, the mixture was cooled to room temperature and 20-30ml 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 (175mg, 75%). ¹H NMR (300.0 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 (75.5 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 (2)

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In a flame-dried Schlenk tube under argon atmosphere, 1,6-dibrompyrene (200mg, 0.56 mmol) and B_2Pin_2 (420mg, 1.67mmol) were dissolved in 20ml 1,4-dioxane. Flame dried KOAc (327mg, 3.32mmol) was added quickly to the mixture followed by PdCl_2(dppf) (13.6mg, 0.017mmol). The mixture was heated at 90°C overnight. A scoop of catalyst (5mg) was added to complete the reaction. Once the reaction was complete, the mixture was cooled to room temperature and 20-30ml 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_4 and filtered. After concentrating down the filtrate, silica column chromatography with hexanes:dichloromethane (1:1) mixture as eluent gave a yellow powder (200mg, 79%).

\[ ^1H \text{NMR (300.0 MHz, CDCl}_3\] : \[ \delta 9.12 (d, 2H; CH), \delta 8.56 (d, 2H; CH), \delta 8.21 (d, 2H; CH), \delta 8.15 (d, 2H; CH), \delta 1.51 (s, 24H; CH}_3\].

\[ ^{13}C \{^1H\} \text{NMR (75.5 MHz, CDCl}_3\] : \[ \delta 133.77 (CH), \delta 133.20 (CH), \delta 129.22 (CH), \delta 127.99, \delta 124.55 (CH), \delta 83.96 (CCH}_3\), \delta 25.12 (CH}_3\), n.o. (CB). MALDI TOF MS: m/z 455 (M^+), 353, 326 (M-Bpin)^+.

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

In a flame-dried Schlenk tube under argon atmosphere, 1,3,6,8-tetrabromopyrene (500mg, 0.97mmol) and B_2Pin_2 (1.47g, 5.79mmol) were dissolved in 20ml 1,4-dioxane. Flame dried KOAc (952mg, 9.7mmol) was added quickly to the mixture followed by PdCl_2(dppf) (24mg, 0.029mmol). The mixture was heated at 90°C overnight. At the 16hr mark, 10mg catalyst was added to complete the reaction. Once complete, the mixture was cooled to room temperature and 20-30ml 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_4 and filtered. After concentrating down the filtrate, silica column chromatography with hexanes:ethyl acetate (8:2) mixture as eluent gave a yellow powder (592mg, 87%). MALDI TOF MS: m/z 707 (M^+), 581 (M-Bpin)^+, 454(M-2Bpin)^+, 227 (M-3Bpin)^+.

1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (4) (135TrBB)
In a flame-dried Schlenk tube under argon atmosphere, 1,3,5-tribromobenzene (200mg, 0.64mmol) and B$_2$Pin$_2$ (731.3mg, 2.88mmol) were dissolved in 20ml 1,4-dioxane. Flame dried KOAc (471.1mg, 4.8mmol) was added quickly to the mixture followed by PdCl$_2$(dppf) (15.5mg, 0.029mmol). 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. 20-30ml 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 MgSO$_4$ 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%, 200mg]. $^1$H NMR (300.0 MHz, CDCl$_3$): δ 8.36 (s,3H; CH), δ 1.32 (s, 36H; CH$_3$). $^{13}$C $^1$H NMR (75.5 MHz, CDCl$_3$): δ 144.14 (CH), δ 83.79 (CCH$_3$), δ 24.96 (CH$_3$), n.o. (CB).

2,2’,2”-(benzene-1,2,4-triyl) tris (4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5)

In a flame-dried Schlenk tube under argon atmosphere, 1,2,4-tribromobenzene (200mg, 0.64mmol) and B$_2$Pin$_2$ (731.3mg, 2.88mmol) were dissolved in 20ml 1,4-dioxane. Flame dried KOAc (471.1mg, 4.8mmol) was added quickly to the mixture followed by PdCl$_2$(dppf) (15.5mg, 0.029mmol). 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. 20-30ml 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$_4$ and filtered. After concentrating down the filtrate, hexanes:ethyl acetate (9:1) mixture was used to elute Rf 0.2 by silica column chromatography to yield a white powder (280mg, 96%). $^1$H NMR at 80°C (300.0 MHz, DMSO-d): δ 7.91 (s,1H; CH), δ 7.70 (d,1H; CH) , δ 7.52 (d,1H; CH), δ 1.34 (s, 12H;
$\delta$ 1.33 (s, 12H; CH$_3$), $\delta$ 1.19 (s, 12H; CH$_3$). $^{13}$C {$^1$H} NMR (75.5 MHz, CDCl$_3$): $\delta$ 139.48 (CH), $\delta$ 135.47 (CH), $\delta$ 132.41 (CH), $\delta$ 83.44 (CCH$_3$), $\delta$ 83.69 (CCH$_3$), $\delta$ 83.480 (CCH$_3$), $\delta$ 25.02 (CH$_3$), n.o. (CB).

$^{1,2,4,5}$-tetraakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (6) (TBB)

In a flame-dried Schlenk tube under argon atmosphere, 1,2,4,5-tetrabromobenzene (380mg, 0.97mmol) and B$_2$Pin$_2$ (1.48g, 5.82mmol) were dissolved in 20ml 1,4-dioxane. Flame dried KOAc (952.1mg, 9.70mmol) was added quickly to the mixture followed by PdCl$_2$(dppf) (23.6mg, 0.030mmol). 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. 20-30ml 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$_4$ 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 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%). $^1$H NMR (300.0 MHz, CDCl$_3$): $\delta$ 7.89 (s,2H; CH), $\delta$ 1.36 (s, 36H; CH$_3$). $^{13}$C {$^1$H} NMR (75.5 MHz, CDCl$_3$): $\delta$ 137.90 (CH), $\delta$ 83.84 (CCH$_3$), $\delta$ 24.99 (CH$_3$), n.o. (CB).

A.1.2 Experimental Conditions (microwave synthesis)

$^{4,4,5,5}$-tetramethyl-2-(pyren-1-yl)-1,3,2-dioxaborolane (1)

1-bromopyrene (500mg, 1.78mmol) and B$_2$Pin$_2$ (678.0mg, 2.67mmol) were added to a 20ml microwave flask. Flame dried KOAc (524mg, 5.33mmol) and PdCl$_2$(dppf) (58mg, 0.071mmol) were added quickly to the flask. After adding 12ml 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 15ml 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 MgSO$_4$ 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 (2)

1,6-dibromopyrene (500mg, 1.39mmol) and B$_2$Pin$_2$ (1.06g, 4.17mmol) were added to a 20ml microwave flask. Flame dried KOAc (818mg, 8.33mmol) and PdCl$_2$(dppf) (45.4mg, 0.056mmol) were added quickly to the flask. After adding 12ml 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 15ml 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 MgSO$_4$ and filtered. After concentrating down the filtrate, silica column chromatography with hexanes as eluent yielded a yellow powder (400mg, 63%).

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

1,3,6,8-tetrabromopyrene (500mg, 0.97mmol) and B$_2$Pin$_2$ (1.48g, 5.82mmol) were added to a 20ml microwave flask. Flame dried KOAc (952.0mg, 9.70mmol) and PdCl$_2$(dppf) (31.5mg, 0.039mmol) were added quickly to the flask. After adding 12ml 1,4-dioxane, the flask was capped tightly and run at 130°C for 1hr. Once the reaction was complete, the mixture was cooled to room temperature and 15ml 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 MgSO$_4$ 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 (579mg, 85%).

1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene(4) (135TrBB)
1,3,5-tribromobenzene (500mg, 1.59mmol) and B$_2$Pin$_2$ (1.82g, 7.15mmol) were added to a 20ml microwave flask. Flame dried KOAc (1.17g, 11.9mmol) and PdCl$_2$(dppf) (52mg, 0.064mmol) were added quickly to the flask. After adding 12ml 1,4-dioxane, the flask was capped tightly and run at 130°C for 1hr. 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 30ml 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$_4$ 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 (440mg, 61%).

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

1,3,5-tribromobenzene (500mg, 1.59mmol) and B$_2$Pin$_2$ (1.82g, 7.15mmol) were added to a 20ml microwave flask. Flame dried KOAc (1.17g, 11.9mmol) and PdCl$_2$(dppf) (51.9mg, 0.064mmol) were added quickly to the flask. After adding 12ml 1,4-dioxane, the flask was capped tightly and run at 130°C for 1hr. 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 30ml 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 MgSO$_4$ 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 a white powder (600mg, 83%).

1,2,4,5-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (6) (TBB)

1,2,4,5-tetrabromobenzene (500mg, 1.27mmol) and B$_2$Pin$_2$ (1.94g, 7.63mmol) were added to a 20ml microwave flask. Flame dried KOAc (1.25g, 12.7mmol) and PdCl$_2$(dppf) (41.6mg, 0.051mmol) were added quickly to the flask. After adding 12ml 1,4-dioxane, the flask was capped tightly and run at 130°C for 1hr. 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 30ml 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 a 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 (250mg, 41%).

A.2 ¹H and ¹³C NMR Spectra

Figure A.1, Figure A.2, Figure A.3, Figure A.4, Figure A.5

A.3 MALDI-TOF-MS

Figure A.6

A.4 Absorption and Fluorescence Spectra

Absorption spectrometry was performed using a Varian spectrophotometer. Steady-state fluorescence measurements were conducted using HORIBA Jobin Yvon fluorolog, FL-1057. Stock solutions of TBP were made in ACS grade n-hexanes. Figure A.7, Figure A.8

A.5 Scintillation and Neutron Capture Efficiency

Figure A.9, Figure A.10, Figure A.11, Figure A.12, Figure A.13, Figure A.14

A.6 Sample Images

Figure A.15, Figure A.16

A.7 Crystallographic data for C₄₆H₇₆B₄O₈

- Formula weight 792.24
Figure A.1: $^1$H and $^{13}$C NMR for monoborylatedpyrene.
Figure A.2: $^1$H and $^{13}$C NMR for 1,6-diborylatedpyrene.
Figure A.3: $^1$H and $^{13}$C NMR for 135TrBB.
- Temperature 210(2) K
- Wavelength 1.54178 Å
- Crystal system, space group Monoclinic, I2
- Unit cell dimensions $a = 16.4584(4) \, \text{Å}$, $\alpha = 90^\circ$, $b = 7.3229(2) \, \text{Å}$, $\beta = 96.2680(11)^\circ$, $c = 18.8669(7) \, \text{Å}$, $\gamma = 90^\circ$.
- Volume $2260.31(12) \, \text{Å}^3$
- $Z$, Calculated density 2, 1.164 Mg/m3
- Absorption coefficient 0.600 mm$^{-1}$
- $F(000)$ 856
- Crystal size 0.25 x 0.20 x 0.02 mm
Figure A.4: $^1$H and $^{13}$C NMR for 124TrBB.
Figure A.5: $^1$H and $^{13}$C NMR for TBB.
Figure A.6: MALDI-TOF-MS spectra for 1,6-diborylatedpyrene.

Figure A.7: Optical absorption and emission measurement of TBP.
Figure A.8: Unoptimized optical spectral overlap between emission of TBP and absorption of POPOP.

Figure A.9: Light output comparison of plastic scintillator (i-xi) vs EJ-204.
Figure A.10: Response of plastic scintillator (1% 135TrBB) to gamma and neutron source.

Figure A.11: Response of plastic scintillator (1% 135 TrBB) with gamma shielding lead.

$\chi^2$/ndf $= 130.7/42$

- Constant: $105.1 \pm 2.2$
- Mean: $78.85 \pm 0.81$
- Sigma: $18.99 \pm 0.82$
Figure A.12: Response of plastic scintillator (5% 135TrBB) to gamma and neutron source.

Figure A.13: Response of plastic scintillator (5% 124TrBB) to gamma and neutron source.
Figure A.14: Response of plastic scintillator (5% 124 TrBB) with gamma shielding lead.

\[
\begin{array}{|c|c|}
\hline
\chi^2 & 103 / 47 \\
\text{Constant} & 207.7 \pm 3.4 \\
\text{Mean} & 91.92 \pm 0.21 \\
\text{Sigma} & 14.06 \pm 0.23 \\
\hline
\end{array}
\]

Figure A.15: Left to right: Sample ii, iii and iv incorporating 0.5, 1.0 and 5% 135TrBB respectively.
Figure A.16: Left to right: Sample vii and viii incorporating 1 and 5% TBB respectively.

- Theta range for data collection 3.39 to 68.24°.
- Limiting indices -19≤h≤14, -8≤k≤8, -22≤l≤21
- Reflections collected / unique 15591 / 3702 [R(int) = 0.0431]
- Completeness to theta = 67.68° 99.7 %
- Absorption correction Semi-empirical from equivalents
- Max. and min. transmission 0.984 and 0.873
- Refinement method Full-matrix least-squares on F2
- Data / restraints / parameters 3702 / 349 / 316
- Goodness-of-fit on F^2 1.059
- Final R indices [I>2sigma(I)] R1 = 0.0637, wR2 = 0.1997
- R indices (all data) R1 = 0.0709, wR2 = 0.2093
• Absolute structure parameter 0.5

• Largest diff. peak and hole 0.348 and -0.491 e.Å-3

A.8 Crystallographic Information File (CIF) for C_{46}H_{68}B_{4}O_{8}

See [9].
APPENDIX B

CHAPTER 7 SUPPLEMENTARY INFORMATION

Supplementary Information to a paper published in Chemistry A European Journal [10].

*Henok A. Yemam*, Adam Mahl, Jonathan Tinkham, Joshua T. Koubek, Uwe Greife, Alan Sellinger

B.1 Experimental Procedures

B.1.1 Synthesis of p-alkylated PTP derivatives

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

![Figure B.1: Skeletal Formula](image)

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 MgSO$_4$ and filtered.

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After concentrating down the filtrate, silica column chromatography with hexanes as eluent gave 5.57 g white powder (76%). $^1$H NMR (500.0 MHz, CDCl$_3$): $\delta$ 7.81 (s, 2H), 7.42 (s, 2H), 1.34 (s, 21H). $^{13}$C $\{^1$H$\}$ NMR (125.8 MHz, CDCl$_3$): $\delta$ 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) (Figure B.2)

![Figure B.2: Skeletal Formula](image)

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%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.69 (m, 6H), 7.60 (d, 2H), 7.55 – 7.44 (m, 4H), 7.38 (t, 1H), 1.40 (s, 9H). $^{13}$C $\{^1$H$\}$ NMR (125.8 MHz, CDCl$_3$): $\delta$ 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 (Figure B.3)

![Figure B.3: Skeletal Formula](image)
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.

**4-butyl-1,1’:4’,1”-terphenyl (nBuPTP) (Figure B.4)**

![Figure B.4: Skeletal Formula](image)

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) (888mg, 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). $^{13}$C $\{$H$\}$ NMR (125.8 MHz, CDCl$_3$): $\delta$ 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.

$\text{4,4''-di-tert-butyl-1,1':4',1''-terphenyl (ditBuPTP) (Figure B.5)}$

![Figure B.5: Skeletal Formula](image)

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 $\mu$mol) was added and the mixture was heated to 90°C for 24hr. 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%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.66 (s, 4H), 7.59 (d, 4H), 7.49 (d, 4H), 1.38 (s, 18H). $^{13}$C $\{$H$\}$ NMR (125.8 MHz, CDCl$_3$): $\delta$ 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.

$\text{4-bromo-4'-(2-ethylhexyl)oxy)-1,1'-biphenyl (Figure B.6)}$

![Figure B.6: Skeletal Formula](image)

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 36hr 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, 11H), 1.02 (s, 8H). $^{13}$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) (Figure B.7)

Figure B.7: Skeletal Formula

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 µmol) was added and the mixture was heated to 90°C for 24hr. 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). $^{13}$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) (Figure B.8)

![Skeletal Formula](image)

Figure B.8: Skeletal Formula

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 µmol) 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 (88.4%).

\[ ^1H \text{NMR } (500 \text{ MHz, CDCl}_3) \delta 7.73 \text{ (m, 6H), 7.65 \text{ (d, 2H), 7.53 \text{ (t, 2H), 7.44 \text{ (t, 1H), 7.36 \text{ (d, 2H), 2.74 \text{ (d, 2H), 1.75 \text{ (t, 2H), 1.42 \text{ (m, 9H), 1.00 \text{ (t, 3H).}}}})}} \]

\[ ^{13}C \{^1H\} \text{NMR } (125.8 \text{ MHz, CDCl}_3): \delta 142.67, 141.12, 140.54, 140.15, 138.35, 129.92, 128.33, 127.89, 127.08, 36.04, 31.99, 29.66, 28.67, 23.07, 15.04, 14.11. \]

B.1.2 Synthesis of m-alkylated PTP derivatives

1-bromo-3-(pentyloxy)benzene (Figure B.9)

![Skeletal Formula](image)

Figure B.9: Skeletal Formula

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$_3$): $\delta$ 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$_3$): $\delta$ 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) (Figure B.10)

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, 0862 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$_3$) $\delta$ 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$_3$): $\delta$ 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.

3-(tert-butyl)-1,1':4',1”-terphenyl (m-tBuPTP) (Figure B.11)
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%). $^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ 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).

$^{13}$C $\{^1$H$\}$ NMR (125.8 MHz, CDCl$_3$): $\delta$ 151.79, 140.88, 140.59, 140.06, 129.61, 129.31, 128.29, 128.04, 127.81, 127.17, 126.94, 126.79, 126.56, 125.16, 123.77, 99.97, 37.55, 31.04.

**3,5-di-tert-butyl-1,1':4',1”-terphenyl (m-ditBuPTP)** (Figure B.12)

In oven-dried 150mL Schlenk flask under argon atmosphere, 1-bromo-3,5-di-tert-butyl benzene (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 415mg 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%). ¹H NMR (500 MHz, CDCl₃) δ 7.65-7.70 (m, 6H), 7.48 (m, 5H), 7.38 (t, 1H), 1.42 (s, 18H). ¹³C {¹H} NMR (125.8 MHz, CDCl₃): δ 150.59, 140.14, 129.37, 128.39, 128.04, 127.77, 127.57, 127.13, 126.70, 126.31, 122.16, 120.93, 34.92, 20.93.

1-bromo-3-((2-ethylhexyl)oxy)benzene (Figure B.13)

![Skeletal Formula]

Figure B.13: Skeletal Formula

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 36hr 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%). ¹H NMR (500 MHz, CDCl₃) 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). ¹³C {¹H} NMR (125.8 MHz, CDCl₃): 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) (Figure B.14)

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-biphenyl
boronic 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.

### B.1.3 Synthesis of fluorene derivatives

9,9-dimethyl-2-phenyl-9H-fluorene (PhF) (Figure B.15)

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-butylanmonium 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-D6) \(\delta\) 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\(_3\)): \(\delta\) 154.58, 141.87, 140.66, 139.16, 138.72, 129.77, 128.44, 128.21, 127.22, 126.90, 125.90, 123.58, 122.26, 121.30, 121.02, 120.03, 119.76, 47.18, 28.07.

**9,9-dimethyl-2,7-diphenyl-9H-fluorene (PFP) (Figure B.16)**

![Figure B.16: Skeletal Formula](image)

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-butylanmonium 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) (Figure B.17)**

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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-dimehtylfluorene (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.

**9,9-dimethyl-2,7-di((E)-styryl)-9H-fluorene (SFS)** (Figure B.18)

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-dimehtylfluorene (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, Chloroform-d) $\delta$ 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$_2$): 
$\delta$ 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.

### B.2 $^1$H and $^{13}$C NMR

Figure B.19 Figure B.20 Figure B.21 Figure B.22 Figure B.23 Figure B.24 Figure B.25 Figure B.26 Figure B.27 Figure B.28 Figure B.29 Figure B.30 Figure B.31

### B.3 GC-MS/MS of SF isomers

Figure B.32

### B.4 UV-VIS and PL spectra for m-substituted PTP

Figure B.33 Figure B.34

### B.5 Scintillation Efficiency (Compton Edge comparison)

Figure B.35 Figure B.36 Figure B.37

### B.6 Pulse Shape Discrimination data

Figure B.38 Figure B.39 Figure B.40 Figure B.41 Figure B.42 Figure B.43 Figure B.44 Figure B.45 Figure B.46 Figure B.47 Figure B.48 Figure B.49 Figure B.50 Figure B.51 Figure B.52 Figure B.53 Figure B.54 Figure B.55 Figure B.56 Figure B.57 Figure B.58 Figure B.59 Figure B.60 Figure B.61 Figure B.62 Figure B.63 Figure B.64 Figure B.65

### B.7 Computational set-up

NWchem 6.5 [11] was used to perform DFT computations on single molecules, and Avogadro [12, 13] 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
Figure B.19: $^1$H and $^{13}$C NMR of tBuPTP
Figure B.20: $^1$H and $^{13}$C NMR of nBuPTP
Figure B.21: $^1$H and $^{13}$C NMR of ehPTP
Figure B.22: $^1$H and $^{13}$C NMR of heptylPTP
Figure B.23: $^1$H and $^{13}$C NMR of ditBuPTP
Figure B.24: $^1$H and $^{13}$C NMR of mtBuPTP
Figure B.25: $^1$H and $^{13}$C NMR of mopPTP
Figure B.26: $^1$H and $^{13}$C NMR of mditBuPTP
Figure B.27: $^1$H and $^{13}$C NMR of mehPTP

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Figure B.28: $^1$H and $^{13}$C NMR of PhF
Figure B.29: $^1$H and $^{13}$C NMR of PFP
Figure B.30: $^1$H and $^{13}$C NMR of SF
Figure B.31: $^1$H and $^{13}$C NMR of SFS
Figure B.32: Chromatogram and Mass Spectra of Cis/Trans-SF
Figure B.33: Photoabsorption of m-alkylated p-terphenyl derivatives

Figure B.34: Photoemission of m-alkylated p-terphenyl derivatives
Figure B.35: Compton Edge comparison of commercial scintillator and p-alkylated PTP derivatives

Figure B.36: Compton Edge comparison of commercial scintillator and m-alkylated PTP derivatives
Figure B.37: Compton Edge comparison of commercial scintillator, PPO and fluorene derivatives
Figure B.38: Pulse Shape Discrimination of 5.0% tBuPTP and 0.1% POPOP in PVT

Figure B.39: Pulse Shape Discrimination of 5.0% nBuPTP and 0.1% POPOP in PVT
Figure B.40: Pulse Shape Discrimination of 5.0% ehPTP and 0.1% POPOP in PVT

Figure B.41: Pulse Shape Discrimination of 5.0% hepPTP and 0.1% POPOP in PVT
Figure B.42: Pulse Shape Discrimination of 10.0% mopPTP and 0.1% POPOP in PVT

Figure B.43: Pulse Shape Discrimination of 15.0% mopPTP and 0.1% POPOP in PVT
Figure B.44: Pulse Shape Discrimination of 5.0% mtBuPTP and 0.1% POPOP in PVT

Figure B.45: Pulse Shape Discrimination of 10.0% mtBuPTP and 0.1% POPOP in PVT
Figure B.46: Pulse Shape Discrimination of 15.0% mtBuPTP and 0.1% POPOP in PVT

Figure B.47: Pulse Shape Discrimination of 5.0% mtBu$_2$PTP and 0.1% POPOP in PVT
Figure B.48: Pulse Shape Discrimination of 10.0% mtBu$_2$PTP and 0.1% POPOP in PVT

Figure B.49: Pulse Shape Discrimination of 15.0% mtBu$_2$PTP and 0.1% POPOP in PVT
Figure B.50: Pulse Shape Discrimination of 5.0% Me\textsubscript{2}F and 0.1% POPOP in PVT

Figure B.51: Pulse Shape Discrimination of 10.0% Me\textsubscript{2}F and 0.1% POPOP in PVT
Figure B.52: Pulse Shape Discrimination of 15.0% Me$_2$F and 0.1% POPOP in PVT

Figure B.53: Pulse Shape Discrimination of 20.0% Me$_2$F and 0.1% POPOP in PVT
Figure B.54: Pulse Shape Discrimination of 5.0% purified $\text{Me}_2\text{F}$ and 0.1% POPOP in PVT

Figure B.55: Pulse Shape Discrimination of 10.0% purified $\text{Me}_2\text{F}$ and 0.1% POPOP in PVT
Figure B.56: Pulse Shape Discrimination of 15.0% purified Me$_2$F and 0.1% POPOP in PVT

Figure B.57: Pulse Shape Discrimination of 20.0% purified Me$_2$F and 0.1% POPOP in PVT
Figure B.58: Pulse Shape Discrimination of 5.0% PhF and 0.1% POPOP in PVT

Figure B.59: Pulse Shape Discrimination of 15.0% PhF and 0.1% POPOP in PVT
Figure B.60: Pulse Shape Discrimination of 5.0% PFP and 0.1% POPOP in PVT

Figure B.61: Pulse Shape Discrimination of 5.0% SF and 0.1% POPOP in PVT
Figure B.62: Pulse Shape Discrimination of 10.0% SF and 0.1% POPOP in PVT

Figure B.63: Pulse Shape Discrimination of 15.0% SF and 0.1% POPOP in PVT
Figure B.64: Pulse Shape Discrimination of 20.0% SF and 0.1% POPOP in PVT

Figure B.65: Pulse Shape Discrimination of 25.0% SF and 0.1% POPOP in PVT
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 [14].

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 [15] where large changes in electron density can occur. 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 [15–17].

B.8 Computational data for ground state geometrical optimization

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.

Figure B.66 Figure B.67 Figure B.68 Figure B.69 Figure B.70 Figure B.71 Figure B.72 Figure B.73 Figure B.74 Figure B.75 Figure B.76 Figure B.77 Figure B.78 Figure B.79 Figure B.80 Figure B.81

Figure B.66: Ground state geometrical optimization of PTP

Figure B.67: Ground state geometrical optimization of tBu-PTP

Figure B.68: Ground state geometrical optimization of nBu-PTP

B.9 Hardness measurement of m-alkylated PTP plastics

Figure B.82

B.10 Differential Scanning Calorimetry

Figure B.83 Figure B.84 Figure B.85 Figure B.86 Figure B.87 Figure B.88 Figure B.89 Figure B.90 Figure B.91
Figure B.69: Ground state geometrical optimization of ehPTP

Figure B.70: Ground state geometrical optimization of hep-PTP

Figure B.71: Ground state geometrical optimization of ditBu-PTP

Figure B.72: Ground state geometrical optimization of mtBu-PTP
Figure B.73: Ground state geometrical optimization of mditBuPTP

Figure B.74: Ground state geometrical optimization of mop-PTP

Figure B.75: Ground state geometrical optimization of meh-PTP
Figure B.76: Ground state geometrical optimization of Me₂F

Figure B.77: Ground state geometrical optimization of PPO

Figure B.78: Ground state geometrical optimization of PhF
Figure B.79: Ground state geometrical optimization of PFP

Figure B.80: Ground state geometrical optimization of trans-SF

Figure B.81: Ground state geometrical optimization of trans-SFS
Figure B.82: Hardness of final m-alkylated PTP plastic scintillators as a function of dopant concentration

Figure B.83: Differential scanning calorimetry data for tBuPTP
Figure B.84: Differential scanning calorimetry data for nBuPTP

Figure B.85: Differential scanning calorimetry data for ehPTP
Figure B.86: Differential scanning calorimetry data for hepPTP

Figure B.87: Differential scanning calorimetry data for ditBuPTP
Figure B.88: Differential scanning calorimetry data for mtBuPTP

Figure B.89: Differential scanning calorimetry data for mditBuPTP
Figure B.90: Differential scanning calorimetry data for mopPTP

Figure B.91: Differential scanning calorimetry data for mehPTP
APPENDIX C
CHAPTER 8 SUPPLEMENTARY INFORMATION

Supplementary information to a paper published in *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* [18].

*Adam Mahl*¹,* Allison Lim*²,* Joseph Latta¹,* Henok A. Yemam²,* Uwe Greife¹,* Alan Sel linger²†

C.1 Chemical Characterization

NMR was performed on a JEOL 500 MHz liquid state NMR and spectra were analyzed using the MestReNova software. GC-MS was performed on Varian CP-3800 GC coupled to a 1200 L Quadrupole MS/MS with a Restek Rsi column.

C.2 Synthesis of BPAF-DM

4,4’-(Hexafluoroisopropylidene)diphenol (Sigma-Aldrich) (7.11 g, 0.021 mol, 1 eq.) was dissolved in anhydrous THF (Sigma-Aldrich) under argon and cooled to 0°C. Methacrylic acid (TCI America) (4.56 g, 0.053 mol, 2.5 eq.), N,N’-diisopropylcarbodiimide (DIC) (Sigma-Aldrich) (6.67 g, 0.053 mol, 2.5 eq.), and 4-N,N-dimethylaminopyridine (DMAP) (Sigma-Aldrich) (3.88 g, 0.032 mol, 1.5 eq.) were used as received and slowly added sequentially. The reaction was allowed to come to room temperature and checked for completion via TLC (5:1 hexanes:ethyl acetate). Liquid-liquid extraction was performed with 5% HCl (x2), saturated sodium bicarbonate (x2), DI-water (x1), and brine (x1) and the resulting organic layer was

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dried with anhydrous magnesium sulfate (Sigma-Aldrich) before concentrating on a rotary evaporator using room temperature water bath temperature. The crude white powder was purified via flash chromatography and recrystallized in hexanes to afford a white solid (78% yield). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 7.38 (d, \(J = 8.7\) Hz, 2H), 7.31 (d, \(J = 8.8\) Hz, 2H), 6.26 (s, \(^1\)H), 5.89 (s, \(^1\)H), 1.97 (s, 3H). \(^{13}\)C NMR (126 MHz, DMSO-\(D_6\)) \(\delta\) 165.28, 151.73, 135.56, 131.47, 130.10, 128.49, 124.39 (q, \(J = 286.4\) Hz), 122.61, 63.97 (p, \(J = 25.2, 24.5\) Hz), 18.42. \(^{19}\)F NMR (471 MHz, DMSO-\(d_6\)) \(\delta\) -63.24. GC/MS expected \(m/z\) 472.38. Actual \(m/z\) 472.3. Melting Point 108°C. Decomposition temperature 220°C. Figure C.1

Figure C.1: Synthesis of BPAF-DM via Steglich esterification.

C.3 Dopant Characterization

Figure C.2, Figure C.3, Figure C.4, Figure C.5, Figure C.6, Figure C.7

C.4 Sample Photographs

Figure C.8, Figure C.9, Figure C.10, Figure C.11

C.5 Plastics Characterization

Figure C.12, Table C.1, Table C.2, Table C.3, Figure C.13, Figure C.14, Figure C.15
Figure C.2: $^1$H NMR of BPAF-DM.

Figure C.3: $^{13}$C NMR of BPAF-DM.
Figure C.4: $^{19}$F NMR of BPAF-DM.

Figure C.5: GC-MS chromatogram (inset) and mass spectrum of pure BPAF-DM.
Figure C.6: DSC curve for BPAF-DM displaying melting point and polymerization peaks.

Figure C.7: TGA decomposition profile for BPAF-DM.
Figure C.8: Photos of BPAF-DM samples. Each square is 1 cm by 1 cm.
Figure C.9: Photos of BPA-DM samples with 20 wt% PPO. Each square is 1 cm by 1 cm.
Figure C.10: Photos of BPA-DM samples with 25 wt% PPO. Each square is 1 cm by 1 cm.
Figure C.11: Photos of BPA-DM samples with 30 wt% PPO. Each square is 1 cm by 1 cm.
Figure C.12: Thermal decomposition curves for cross-linked and uncross-linked samples.

Table C.1: LY, FoM and Hardness Properties of BPAF-DM samples

<table>
<thead>
<tr>
<th>BPAF-DM (wt%)</th>
<th>Light Yield (% of BC-408)</th>
<th>FoM @ 100-200 keV&lt;sub&gt;ee&lt;/sub&gt;</th>
<th>FoM @ 400-600 keV&lt;sub&gt;ee&lt;/sub&gt;</th>
<th>Hardness (Shore-D)</th>
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<td>II</td>
<td>III</td>
<td>I</td>
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<td>81</td>
<td>89</td>
<td>1.03</td>
</tr>
<tr>
<td>5</td>
<td>89</td>
<td>92</td>
<td>93</td>
<td>1.10</td>
</tr>
<tr>
<td>8</td>
<td>89</td>
<td>90</td>
<td>93</td>
<td>1.09</td>
</tr>
</tbody>
</table>

I – Samples contain 20 wt% PPO
II – Samples contain 25 wt% PPO
III – Samples contain 30 wt% PPO
Table C.2: Thermal Decomposition of BPA-DM. Onset 1 is likely PPO sublimation from the plastic sample.

<table>
<thead>
<tr>
<th>PPO (wt%)</th>
<th>BPA-DM (wt%)</th>
<th>Onset 1 (°C)</th>
<th>Onset 2 (°C)</th>
<th>( \text{T}_{\text{max}} ) Slope (°C)</th>
<th>Max Slope (wt%/°C)</th>
<th>( T_g ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0</td>
<td>165.1 ± 4.8</td>
<td>368.8 ± 2.6</td>
<td>399.3 ± 1.8</td>
<td>1.40 ± 0.05</td>
<td>36.3 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>179.0 ± 4.5</td>
<td>355.6 ± 14.4</td>
<td>400.0 ± 2.3</td>
<td>1.20 ± 0.17</td>
<td>57.9 ± 2.8</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>154.4 ± 2.6</td>
<td>345.4 ± 3.2</td>
<td>393.1 ± 4.1</td>
<td>1.04 ± 0.04</td>
<td>49.6 ± 0.5</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>181.9 ± 4.7</td>
<td>362.4 ± 2.1</td>
<td>397.2 ± 1.0</td>
<td>1.21 ± 0.04</td>
<td>30.1 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>181.4 ± 0.5</td>
<td>367.9 ± 3.6</td>
<td>402.7 ± 0.9</td>
<td>1.16 ± 0.13</td>
<td>42.5 ± 2.0</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>176.5 ± 5.1</td>
<td>357.1 ± 6.3</td>
<td>401.9 ± 2.8</td>
<td>1.03 ± 0.02</td>
<td>48.8 ± 4.7</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>183.3 ± 2.1</td>
<td>375.4 ± 1.1</td>
<td>403.5 ± 1.1</td>
<td>1.21 ± 0.02</td>
<td>20.7 ± 2.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>167.0 ± 1.7</td>
<td>361.9 ± 7.9</td>
<td>396.5 ± 1.2</td>
<td>1.11 ± 0.09</td>
<td>31.2 ± 2.4</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>182.9 ± 1.9</td>
<td>369.0 ± 3.2</td>
<td>402.4 ± 2.3</td>
<td>1.02 ± 0.01</td>
<td>34.8 ± 0.4</td>
</tr>
</tbody>
</table>

Table C.3: Thermal decomposition of BPAF-DM modified scintillators. Onset 1 is likely PPO sublimation from the plastic sample.

<table>
<thead>
<tr>
<th>PPO (wt%)</th>
<th>BPA-DM (wt%)</th>
<th>Onset 1 (°C)</th>
<th>Onset 2 (°C)</th>
<th>( \text{T}_{\text{max}} ) Slope (°C)</th>
<th>Max Slope (wt%/°C)</th>
<th>( T_g ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0</td>
<td>165.1 ± 4.8</td>
<td>368.8 ± 2.6</td>
<td>399.3 ± 1.8</td>
<td>1.4 ± 0.05</td>
<td>36.3 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>164.9 ± 0.6</td>
<td>357.7 ± 5.9</td>
<td>393.5 ± 2.7</td>
<td>1.3 ± 0.14</td>
<td>43.2 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>166.7 ± 2.3</td>
<td>362.7 ± 9.2</td>
<td>396.5 ± 0.3</td>
<td>1.2 ± 0.11</td>
<td>45.0 ± 1.0</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>181.9 ± 4.7</td>
<td>362.4 ± 2.1</td>
<td>397.2 ± 1.0</td>
<td>1.2 ± 0.04</td>
<td>30.1 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>175.2 ± 1.7</td>
<td>361.9 ± 4.8</td>
<td>394.4 ± 2.2</td>
<td>1.1 ± 0.09</td>
<td>24.1 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>164.4 ± 1.4</td>
<td>359.7 ± 2.8</td>
<td>398.1 ± 1.9</td>
<td>1.1 ± 0.03</td>
<td>32.0 ± 0.7</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>183.3 ± 2.1</td>
<td>375.4 ± 1.1</td>
<td>403.5 ± 1.1</td>
<td>1.2 ± 0.02</td>
<td>20.7 ± 2.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>173.0 ± 3.0</td>
<td>363.7 ± 5.2</td>
<td>396.5 ± 0.3</td>
<td>1.2 ± 0.12</td>
<td>27.5 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>164.1 ± 4.1</td>
<td>380.5 ± 11.5</td>
<td>399.7 ± 3.2</td>
<td>1.2 ± 0.03</td>
<td>22.6 ± 2.8</td>
</tr>
</tbody>
</table>
Figure C.13: $^{137}$Cs Compton edge features of plastic scintillators with varying concentrations (0-10 wt%) of BPA-DM and 20 wt% PPO.

Figure C.14: $^{137}$Cs Compton edge features of BPAF-DM linked samples (detailed in Table Table C.1 on page 268)
Figure C.15: Energy-calibrated signal plot for a 30 wt% PPO over-doped samples with 8 wt% BPAF-DM displaying PSD.
APPENDIX D
PATENT MATERIAL

Figure D.1 is the front matter of the patent awarded for the work detailed in Chapter 3. Figure D.2 is the front matter of the patent awarded for the work detailed in Chapter 4. In addition, this body of research has produced 2 invention disclosures which have progressed to the non-provisional patent stage (the work detailed in Chapters 5 & 8), and 2 invention disclosures submitted which are in the provisional patent stage (the work mentioned in Section 6.3.1.2 and discussed in Section 6.3.2).
United States Patent

BORON COMPOUNDS FOR USE IN SCINTILLATORS AND ADMIXTURE TO SCINTILLATORS

Applicant: Colorado School of Mines, Golden, CO (US)
Inventors: Cory Pecinovski, Longmont, CO (US); Pascale Meyssing, Golden, CO (US); Adam Mahl, Denver, CO (US); John Dorgin, Golden, CO (US); Ewe Greif, Golden, CO (US); Tyler Remedes, Colorado Springs, CO (US)
Assignee: Colorado School of Mines, Golden, CO (US)

Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 6 days.

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CPC CO9K 11/06 (2013.01); C09F 5/04 (2013.01); G01T 1/2042 (2013.01); G01T 3/06 (2013.01); G21K 4/00 (2013.01)

Field of Classification Search
CPC G01T 1/1642; G01T 3/00; C09K 11/06

References Cited
U.S. PATENT DOCUMENTS
2,880,326 A* 3/1995 Muscant

OTHER PUBLICATIONS
(Continued)

Abstract
The present disclosure is directed to liquid boron compounds for use in scintillators. The present disclosure further relates to liquid boron compounds for admixture to plastic and liquid scintillators.

Primary Examiner — David Porta
Assistant Examiner — Hugh H Maupin
Patent Examiner — Philip J. Ector
Attorney, Agent, or Firm — Sheridan Ross P.C.

17 Claims, 18 Drawing Sheets

Figure D.1: Boron Compounds for Use in Scintillators and Admixture to Scintillators, US Patent #9,796,921 [19].
Figure D.2: Boron Containing Organic/Hybrid Scintillation Materials for Gamma and Neutron Detection, US Patent # 9,864,077 [20].