5-2022

Development of Upconverting Films Containing Singlet Sink

Blake McKay

The University of Southern Mississippi

Recommended Citation

McKay, Blake, "Development of Upconverting Films Containing Singlet Sink" (2022). *Honors Theses*. 828.
https://aquila.usm.edu/honors_theses/828

Development of Upconverting Films Containing Singlet Sink

by

Blake McKay

A Thesis
Submitted to the Honors College of
The University of Southern Mississippi
in Partial Fulfillment
of Honors Requirements

May 2022

Approved by:

Yoan C. Simon, Ph.D., Thesis Advisor,
School of Polymer Science and Engineering

Derek L. Patton, Ph.D., Director,
School of Polymer Science and Engineering

Sabine Heinhorst, Ph.D., Dean
Honors College

ABSTRACT

Upconversion is the conversion of light from a longer wavelength to a shorter wavelength. This technique has a wide range of applications in solar technology, bioimaging, drug delivery, and many other fields.[1] In this study, a three-part upconverting system was developed including a component termed *singlet sink* in order to increase upconversion efficiency. The components of this system included Palladium (II) Octaethylporphrin (PdOEP), pyrenebutanol, and 9-phenyl-10-(*p*-tolylethynyl)-anthracene (PTEA). A procedure was developed in order to create and process films containing these three materials dispersed in a poly(methyl methacrylate) (PMMA) matrix. Upconversion was analyzed in both solution and the solid state through fluorimetry to determine the emission intensity of upconverting systems. It was found that while all systems exhibited a detectable amount of upconversion, systems containing singlet sink exhibited far greater upconversion than equivalent systems without a singlet sink. As a result, the optimal amount of sensitizer, annihilator, and singlet sink were determined to produce bright upconverted emission.

Keywords: upconversion, triplet-triplet annihilation, singlet sink

DEDICATION

Dedicated to my friends, family, and everyone who supported me through the thesis process.

ACKNOWLEDGMENTS

I would like to thank Dr. Yoan Simon for his help and advisement through the thesis process, as well as all the opportunity to pursue research in his group. Working in the Simon Research Group has deepened my knowledge of the research process and has been especially enjoyable because of the subject of material that I have researched during my time in the group. I would also like to thank Sonia Stanciu, my graduate mentor. Her assistance in this project and throughout my research experience helped my understanding and ability immensely.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF FIGURES

LIST OF ABBREVIATIONS

PTEA	9-phenyl-10-(*p*-tolylethynyl)anthracene
PUC	Photochemical Upconversion
ISC	Intersystem Crossing
TTET	Triplet-triplet Energy Transfer
TTA	Triplet-triplet Annihilation
FRET	Förster Resonance Energy Transfer
PdOEP	Palladium (II) Octaethylporphrin
THF	Tetrahydrofuran
DPA	9,10-Diphenylanthracene
PMMA	Polymethylmethacrylate
CuI	Copper (I) Iodide
FCC	Flash Column Chromatography
DSC	Differential Scanning Calorimetry
TGA	Thermogravimetric Analysis

CHAPTER I: INTRODUCTION

Upconversion is a process in which light of a longer wavelength is converted into light of a shorter wavelength. This results in a higher energy of light emitted than absorbed. Because of this, the process of upconversion has a myriad of applications in solar technology, bioimaging, and many other fields.[1] Currently, the efficiency of this process is limited to approximately 25% in solution and 3% in solid-state systems.[1,2] It is important to note, however, that the maximum upconversion quantum yield is 50%, as in a theoretically perfect system one photon of upconverted light is emitted per two photons of absorbed light. One proposed way to increase upconversion efficiency is through the use of a singlet sink, which would aid in the prevention of back-FRET.[3] This project aims to develop a three-part upconverting system containing a singlet sink as well as a processing procedure in which the system can be used.

In order to achieve these objectives, several smaller tasks needed to be completed. Ongoing work has determined that the chromophore system of palladium octaethylporphyrin (PdOEP), 9,10-diphenylanthracene (DPA), and 9-phenyl-10-(*p*-tolylethynyl)anthracene (PTEA) is efficient at upconverting green light (543 nm) to blue light. First, we determined the viability of pyrenebutanol as an annihilator in solution through fluorimetry analysis. DPA was replaced with pyrenebutanol, and the optimal concentrations of sensitizer, annihilator, and singlet sink were determined for this modified system. Thermogravimetric analysis (TGA) was used to determine optimal melt-pressing conditions, and fluorimetry used to measure upconverted emission intensity.

CHAPTER II: BACKGROUND

2.1 Photophysical Process of Upconversion

The term "upconversion" is used to shorten the term photochemical upconversion (PUC) or sensitized triplet-triplet annihilation.[4] The process of upconversion includes three primary steps. These include intersystem crossing (ISC), triplet-triplet energy transfer (TTET), and triplet-triplet annihilation (TTA). All three of these steps are essential to the upconversion process and occur at various points in the energy reaction. In these mechanisms, two primary components are involved. These include the donor species (sensitizer) and the acceptor species (annihilator). Together, the sensitizer and annihilator (and later the sensitizer, annihilator, and singlet sink) can be referred to as a chromophore system. The requirements of each will be discussed below.

Upconversion occurs in a sensitizer-annihilator system in which the absorption of the sensitizer overlaps with the emission of the annihilator. Before any photophysical processes occur, light excites the donor species into its singlet excited state. From here, the first process in upconversion, ISC, occurs, whereby spin-orbit coupling facilitates the transition from an excited singlet state to an excited triplet state.[5] This change is considered a spin-forbidden transition, but the potential generated by the spin-orbit coupling allows transition to the excited triplet state.[6] The effectiveness of spin-orbit coupling in promoting intersystem crossing is proportional to the atomic number of the excited atom, which is why large atoms such as palladium are used.[7] The next process to occur is triplet-triplet energy transfer (TTET), a type of nonradiative energy transfer that can occur when the absorption of a donor species overlaps with the emission of an acceptor species.[8] This type of transition is considered a Dexter-type transfer. Dexter energy transfers allows the triplet exciton of the sensitizer to be transferred to the annihilator. The long lifespan of the triplet state in annihilators then allows accumulation of this species, which makes the eventual annihilation step possible.[10] As the amount of annihilator in the excited triplet state increases, triplet-triplet annihilation (TTA) occurs. In TTA, two excited triplets combine into an encounter complex. This results in one of the triplets entering its excited singlet excited state, and the other singlet relaxing into its natural ground state.[12,13] Delayed fluorescence of this excited singlet state results in emission of light at a lower wavelength than what was absorbed, i.e. upconversion.

Finding a donator-acceptor pair in which all of these steps can readily occur is paramount for an upconverting system. The Perrin-Jablonski diagram below can be used in order to visualize all of the energy transfer steps that occur.[14]

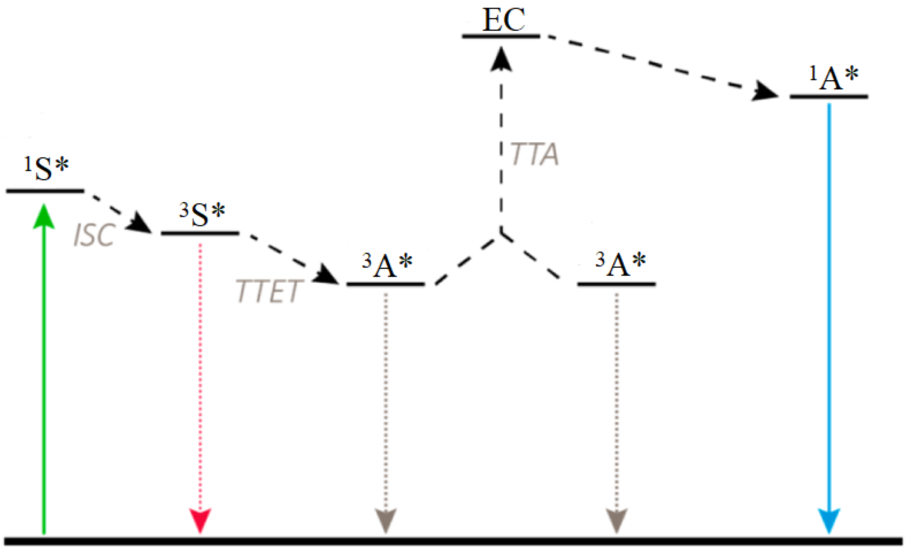


Figure 1. Summary of upconversion process. Modified from The Role of Triplet Exciton Diffusion in Light-Upconverting Polymer Glases.[2]

Figure 1 shows the general process of upconversion as well as the relative energy levels between each step. The height of each step represents its relative energy level $^1S^*$ and $^3S^*$ represent the singlet and triplet states of the sensitizer respectively, whereas $^3A^*$ and $^1A^*$ represent the triplet and singlet states of the annihilator. EC represents the encounter complex formed during TTA. While this process may seem straightforward, there are many complications that arise and considerations that must be accounted for when attempting to create an upconversion-capable sensitizer annihilator pair.

Sensitizer selection also must promote the production of triplet excitons, which occurs more readily in larger atoms. This results in materials such as heavy metal porphyrins to be widely used.[16] Annihilator selection is dependent on the sensitizer being utilized in the system, as even if an acceptable sensitizer being utilized, upconversion cannot occur if there is not sensitizer absorption/annihilator emission overlap.

2.2 Solid-State Upconversion with Polymers

Solid-state upconversion is associated with complications that must be addressed and accounted for. Arguably the most significant issue is caused by the restricted mobility afforded to chromophores in the solid state. The rigidity imposed by solid-state systems prevents the molecular diffusion of excitons from sensitizer to annihilator. This issue has been partially addressed in literature by attempting to extend the lifetime of triplet states of sensitizers and annihilators.[1] While extending the lifetimes of both triplet states would be ideal, annihilators typically have much longer lifetimes than sensitizers, so sensitizer design plays a much greater role in addressing the issue.[1]

Another important factor in solid state upconversion is matrix selection of the system. There is a wide range of potential matrices that could be used as well as ways to incorporate sensitizer and annihilator into them. The two most commonly used matrices are rubbery polymers and glassy polymers.[17] In addition, if no matrix is utilized, the system can be referred to as a molecular glass.[17] Polymer matrices allow for movement of sensitizer and annihilator above the glass transition temperature (T_g) of the matrix, facilitating TTET and TTA even at low concentrations, but can result in separation of components.[17] Below T_g, however, the matrix once again becomes rigid, restricting mobility and limiting upconversion. The reduction in upconversion can be somewhat addressed by increasing the concentration of sensitizer and annihilator.[17] The increase in the sensitizer concentration can lead to other issues however, such as sensitizer aggregation, which results in greater separation between sensitizer and annihilator as well as phase de-mixing.[17] The final way in which solid state upconversion is commonly accomplished is the use of molecular glasses. Molecular glasses forego the need for a polymer matrix and instead use only the sensitizer and annihilator.[17] This removes any potential interference from a polymer matrix but has extremely limited mechanical properties.[17]

One final process that plays a role in limiting upconversion is known as back-Förster Resonance Energy Transfer (FRET).[18] Standard FRET is the nonradiative transfer of energy between donator and acceptor, and only occurs of the donors emission overlaps with the acceptors absorption.[6] Back-FRET is the reverse process of this, which results in transfer from the acceptor back to the donor.[3] Back-FRET might not seem like a major threat to upconversion efficiency because of the absorption-emission overlap that must be present for it to occur, but many sensitizers have a very broad absorption range due to the duel Soret band/Q-band phenomena, meaning that most upconverting systems are susceptible to back-FRET. The amount of quenching due to back-FRET has been shown to increase with an increase in sensitizer concentration.[3] Due to the scale of which back-FRET can impact upconversion, measures must be taken in order to mitigate its effects.

2.3 Use of Singlet Exciton Sink

One proposed way to address the issue of back-transfer is through the use of a component called a singlet-trapping sink. Singlet sinks function by trapping the excited singlet produced by TTA in the annihilator before back-FRET can occur.[3] In order for a molecule to function as a singlet sink, however, it must meet several important criteria. Steponas Raišys describes these four conditions as: (i) must display a high fluorescence quantum yield. (ii) have a lower singlet energy than that of the emitter to ensure FRET will occur, (iii) have a shorter singlet lifetime than the emitter, and (iv) have a higher triplet energy than the emitter.[3] Between the initial requirements of the sensitizer annihilator pair and those of the singlet sink, the selection of components for an upconverting system can be difficult.

In order to demonstrate the effectiveness of a three-part upconverting system, the novel singlet sink PTEA was used in conjunction with the annihilator 1-pyrenebutanol and the sensitizer PdOEP. Selection of this pair was made based on a modification to an existing chromophore pair in the following table:[17]

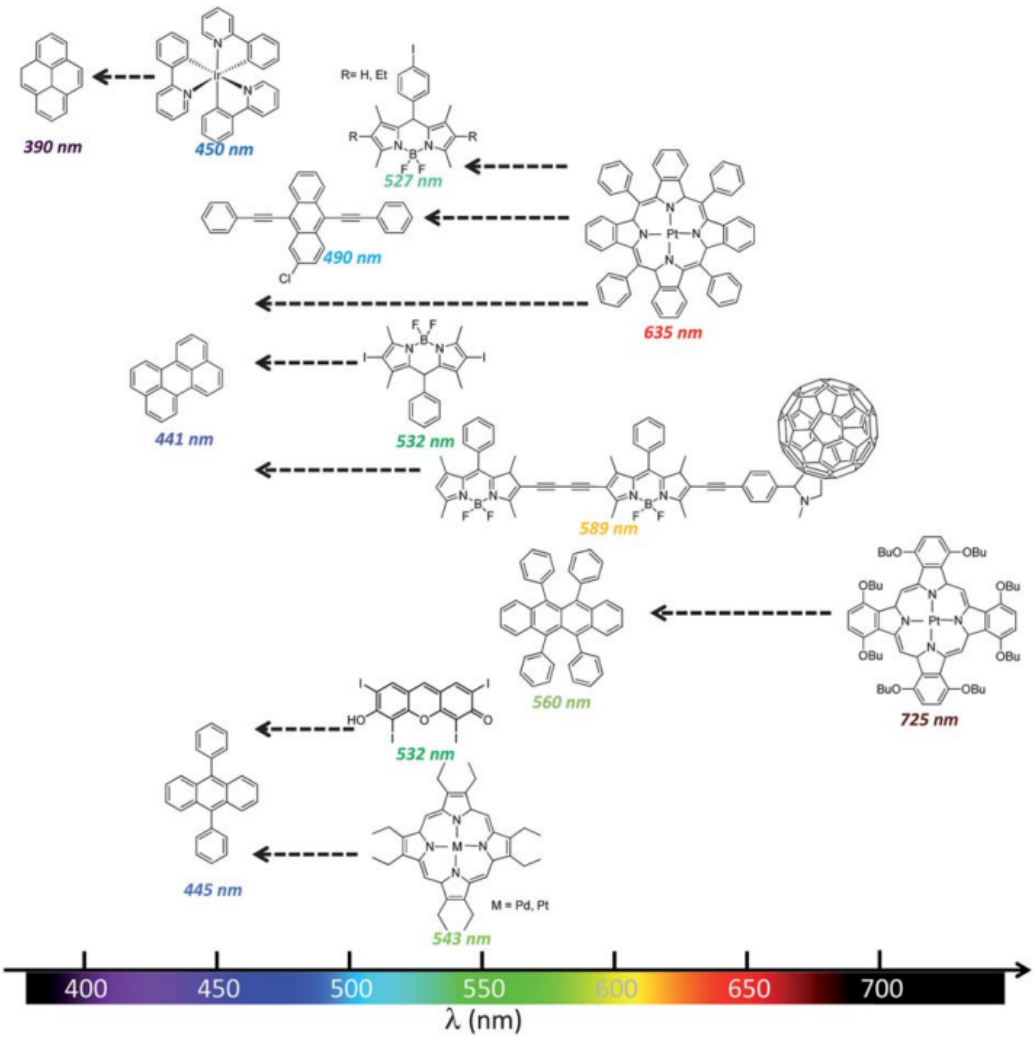


Figure 2. Image of sensitizer-annihilator pairs and their absorptions and emissions, respectively.[17]

The decision to use a pyrene derivative as the annihilator was made as an adjustment of the PdOEP/DPA pair in order to explore other lesser-used annihilators for PdOEP. Pyrene and its derivatives have frequently been used in previous literature, but never in combination with PdOEP as a sensitizer.[19-21] In order to determine if this chromophore system is capable of upconversion, fluorimetry can be utilized to observe the production of upconverted fluorescence upon excitation at the Q-band (543 nm) of PdOEP.

CHAPTER III: MATERIALS AND METHODS

3.1 Materials

The synthesis of the singlet sink utilized in this chromophore system required a moisture and oxygen free environment. The materials used in the synthesis were 9-bromo-10-phenyl anthracene (Sigma Aldrich), 4-Ethynyltoluene (Sigma Aldrich), Tetrakis(triphenylphosphine)palladium (Pd catalyst, Sigma Aldrich), copper iodide (Sigma Aldrich), tetrahydrofuran (THF), and triethylamine. All chemicals were used as received with no additional purification procedures employed.

After synthesis and purification of singlet sink (PTEA) was performed, it was used in the creation of upconverting films. In addition to PTEA, the following materials were also used: 9,10-diphenylanthracene (Sigma Aldrich), 1-Pyrenebutanol (Sigma Aldrich), palladium (II) octaethylporphyrin (Frontier Scientific), poly(methyl methacrylate) with M_n = 10,000 g/mol, and chlorobenzene. All chemicals were used as received with no additional purification procedures employed.

3.2 Preparation of Singlet Sink

The synthesis of the singlet sink was performed via air-free palladium-catalyzed copper-assisted Sonogashira cross-coupling reaction. A stock solution of tetrakis(triphenylphosphine)palladium (0) ($Pd(PPh_3)_4$ and deuterated tetrahydrofuran (THF) was prepared in a nitrogen (N_2) glovebox at a concentration of 6 μmol/mL and stirred at room temperature for 1 hour. An additional solution containing 64 μmol (12.18 mg) of copper (I) iodide (CuI) cocatalyst was weighed in the glovebox to prevent exposure to oxygen. Then, outside of the glovebox, the reaction flask containing 0.80 mmol (266 mg) of 9-bromo-10-phenylanthracene and 0.96 mmol (122 μL) of 1-

ethynyltoluene was solvated by 12 mL of dried tetrahydrofuran (THF), stirred, and degassed via argon for 45 minutes at room temperature. Separately, 16 mL of pure triethylamine was degassed at room temperature for 45 minutes at room temperature.

The vial of CuI was removed from the glovebox and 16 mL of degassed triethylamine was added to the via vacuum-tight syringe. The CuI/triethylamine solution was stirred for 15 minutes, after which its entire contents were rapidly added to the reaction with care to prevent the incorporation of oxygen into the systems. After 1 hour of stirring the $Pd(PPh_3)_4$ solution was removed from the glovebox and 32 μmol of catalyst were added to the reaction flask. The contents of the reaction flask were then stirred at 70^o C for 3 hours, results in a dark yellow/brown solution with faint blue fluorescence under ambient light. The reaction was quenched by removing the flask from the heat source and opening its contents to oxygen.

The final contents were isolated by rotary evaporation, leaving behind a dark yellow powder. Thin-layer chromatography demonstrated the presence of three major impurities, the first of which is the remaining 9-bromo-10-phenylanthracene, the second of which is the remaining 1-ethynyltoluene, and the last of which is likely a transition-state species. A solution of 10:1 hexanes:ethyl acetate was used to separate the product from the contaminates by flash column chromatography (FCC). The final purified product is a bright yellow crystalline power with blue fluorescence under solvation.

3.3 Preparation of Upconversion Solutions

Upconverting solutions were prepared for fluorescence spectroscopy. In solution, the wt% of the chromophores was established at 1:30:1 sensitizer:annihilator:sink. After the components were added, additional chlorobenzene was added in order to have the final concentration reach 0.75 mg/mL of annihilator, and 0.025 mg/mL of sensitizer and singlet sink. A stir bar was added, the cuvette was sealed, and an oxygen purge was performed using argon for 15 minutes.

3.4 Preparation of Upconverting Films

Stock solutions of PdOEP and PTEA were utilized in order to ensure accurate measurement of the components. All stock solutions utilized chlorobenzene as the solvent. In order to prevent moisture from being present, all glassware and stir rods were dried in an oven overnight at 120°C before use. Approximately 30 mg of PMMA was taken and placed into a dried 5 mL glass vial with a pierceable cap and stir rod inside. The respective amount of PdOEP, DPA, and PTEA were then added based on the desired wt% ratio. All ratios were in relation to the mass of PMMA. These values ranged from 0.1-0.25% for PdOEP, 0-0.25% for PTEA, and 30-35% for DPA. In solutions containing additional chlorobenzene due to the use of PTEA stock solution, an additional 250 microliters of chlorobenzene were added, and in solutions without the additional chlorobenzene, 300 microliters of chlorobenzene were added. This was done in order to ensure the same volume between samples. Vials containing solution were well sealed, placed onto a hotplate, and left to stir for a minimum of 3 hours at 65° C.

Standard microscope glass slides with 1 mm thickness were cleaned with ethanol and dried. After 3 hours the solutions were removed from heat, allowed to cool to room temperature, and then drop cast onto the glass slides in the vacuum oven. After all solutions were drop cast, they were left on vacuum at 80°C overnight to ensure evaporation of chlorobenzene.

The following day, the dried solutions that were drop cast onto glass slides were removed from the vacuum oven, and an additional, clean slide was placed on top. The slides were allowed to cool, and then were placed between heat resistant polyimide Kapton sheets to aid in the conduction of heat. The films were then pressed between two steel plates and placed into a compression molder set to 243°C. The addition of the sample into the compression molder caused a decrease in temperature, so time in the melt press was not measured until the temperature returned to 243°C. Samples were left in the melt press for 5 minutes with no additional pressure. Alternatively, if press temperature reached 253°C, samples were immediately removed and cooled due to risk of decomposition. Information regarding decomposition temperature was determined through thermogravimetric analysis (TGA). Cooling was performed by placing onto an ice bed immediately followed by coating the steel plates in a layer of ice at least 2 inches thick. Samples were left in the ice bed for a minimum of 5 minutes. After cooling, samples were dried and then observed in the presence of a 543 nm laser in order to determine if upconversion was visible.

After the above procedure was able to reliably produce upconverting films, DPA was replaced with pyrenebutanol. Following this switch, the same procedure was followed with one primary exception. When operating the melt press, the temperature used was lowered from 243° C to 190° C in order to prevent degradation of the pyrenebutanol. Additionally, if the temperature reached 200° C, the samples were immediately removed for quenching.

3.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was used in order to determine the decomposition temperature of materials. TGA was performed on both pyrenebutanol and a completed film. When performing the TGA, temperature was increased from 23°C (room temperature) to 500° C at a rate of 10° C/min. This was done in order to find a reasonable temperature to operate the melt press without risk of degradation as well as confirm the lack of solvent present in completed films.

3.6 Fluorimetry

Fluorimetry was utilized for two primary purposes: to obtain emission spectra of individual components and verify that upconversion was occurring in the system. An Agilent 1200 series fluorescence detector was utilized to measure emission intensity, with a helium-neon bulb used for excitation. To begin the loading process, samples were placed into different holders based on whether they were a solid film or a liquid solution in a cuvette. Solid films placed at an angle of 45° in order to ensure light could reach the detector, while solutions were loaded at an angle of 90°. Slit widths for both the excitation beam and detector were set to 5 nm for solid samples and 2 nm for solution-based samples. Solutions containing only pyrenebutanol were excited at 315 nm and the emission range analyzed was 325-600 nm. An excitation wavelength of 543 nm was directed onto upconverting solutions. In these solution-based upconverting systems, a laser light filter was utilized to prevent light of undesired wavelength from reaching the system and interfering with results. The emission range was observed from 300-710 nm to obtain both upconversion and phosphorescence intensities. Upconversion from pyrenebutanol was analyzed from 390-525 nm, upconversion from PTEA was analyzed from 425-500 nm, and phosphorescence from PdOEP was analyzed from 650-725 nm.

When analyzing upconverting films, both a laser line filter and short pass filter were utilized. The laser line filter utilized in order to regulate the wavelength of light reaching the sample to 543 nm, and the short pass filter was used to block all light above 500 nm from reaching the detector. This was because of a climbing effect that was present in solid samples which would saturate the detector. A potential cause of this climbing effect will be discussed in the results section, but the use of a laser light filter and short pass filter prevented its occurrence. Because of this, solid-state samples could only be analyzed from 300-500 nm, but this range still allowed for analysis of upconversion intensity.

Obtaining emission spectra of individual components followed the same procedure, with the only difference being the material preparation. Components were added into chlorobenzene at concentrations of 0.75 mg/mL. Pyrenebutanol was excited at 315 nm based on an excitation wavelength found in Handbook of fluorescence spectra of Aromatic Molecules.[22]

CHAPTER IV: RESULTS

4.1 TGA Results

The first material analyzed through the use of TGA was pyrenebutanol. Pyrenebutanol was analyzed in order to determine an optimal temperature at which the melt press could be operated. The temperature needed to be below the degradation point of any of the components utilized in the upconverting films. Figure 4 below contains the results of this analysis.

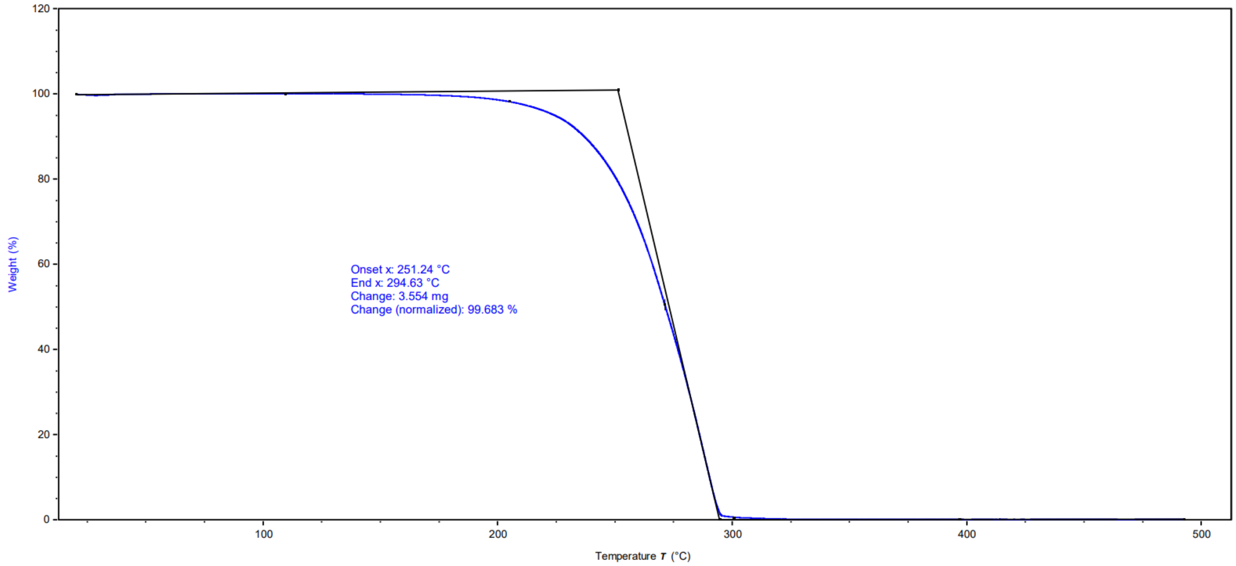


Figure 3. TGA of pyrenebutanol

Results from the pyrenebutanol TGA suggested degradation began between 170°C-200° C, with onset of major degradation beginning at 251° C. In order to determine an optimal temperature to operate the melt press, the melting points of all components must be considered. PTEA singlet sink does not melt until around 190° C.

Because of this, it was determined to run the melt press at 190° C, as it overshoots the target temperature by approximately 5° C. Following this, TGA was ran on a completed film with the results below.

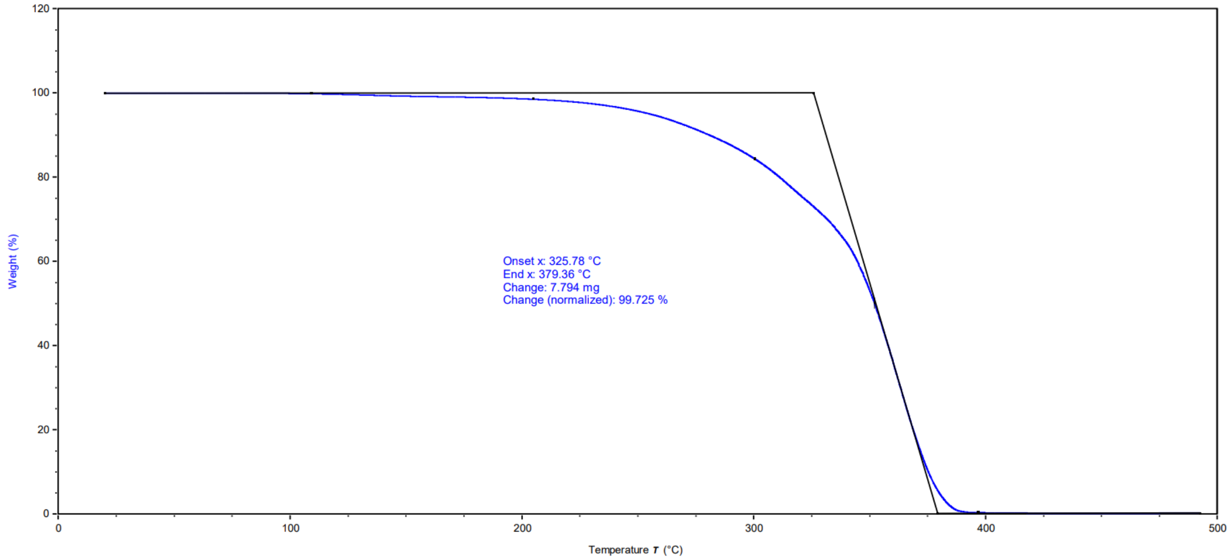


Figure 4. TGA of upconverting film at wt% ratio of 0.1:30:0.1

Degradation occurs in two primary segments: from 200-310 °C and 310-380 °C. The first section of degradation is likely reflective of the pyrenebutanol content in the film, as it makes up approximately 20% of the total weight of a film. The later section is consistent with the PMMA content of the film, comprising approximately 80% of the total weight and degrading in the expected range of PMMA based on previous literature.[23] Overall, results from TGA determined the optimal melt-pressing temperature was approximately 190 °C.

4.2 Fluorimetry Results

The first material analyzed through fluorimetry was pyrenebutanol. Its emission spectra were obtained through an excitation wavelength of 315 nm.

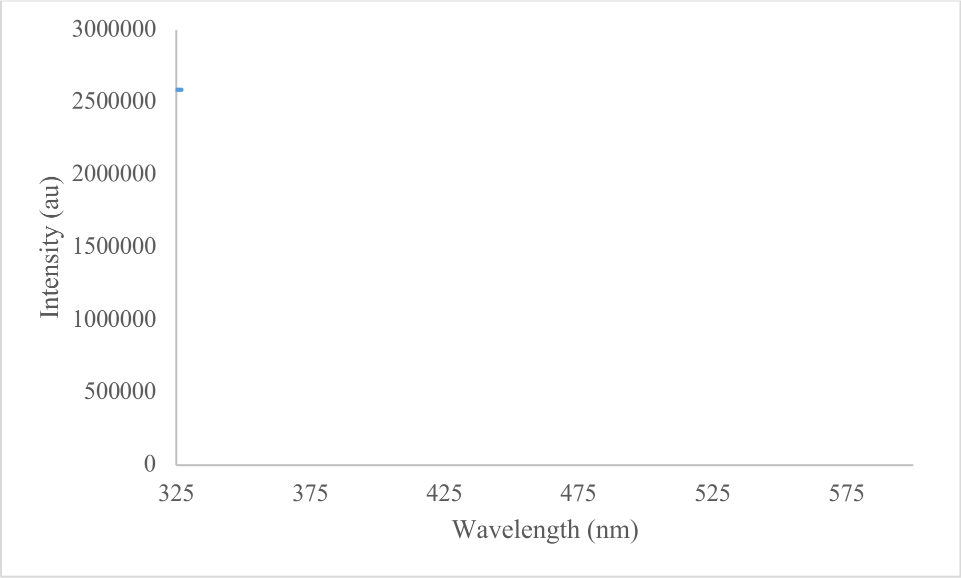


Figure 5. Emission spectra of pyrenebutanol

As seen in the above chart, pyrenebutanol emits most strongly at approximately 390 nm, but has a broad band of emission ranging from 375 nm to over 575 nm. This range of emissions includes the region in which the previously mentioned climbing effect occurred, from 480 nm through 510 nm. Because of this, it is hypothesized that emission from pyrenebutanol played a role in the presence of the climbing effect in solid samples.

Illustration 1. Image of upconverting solution containing PdOEP, Pyrenebutanol, and PTEA at a wt% ratio of 1:30:1 PdOEP:Pyrenebutanol:PTEA

Before films were analyzed, an upconverting system of only pyrenebutanol and PdOEP in solution was analyzed in order to prove the viability of pyrene functioning as an annihilator for PdOEP. The ratio of PdOEP to pyrenebutanol in this system was 1:30.

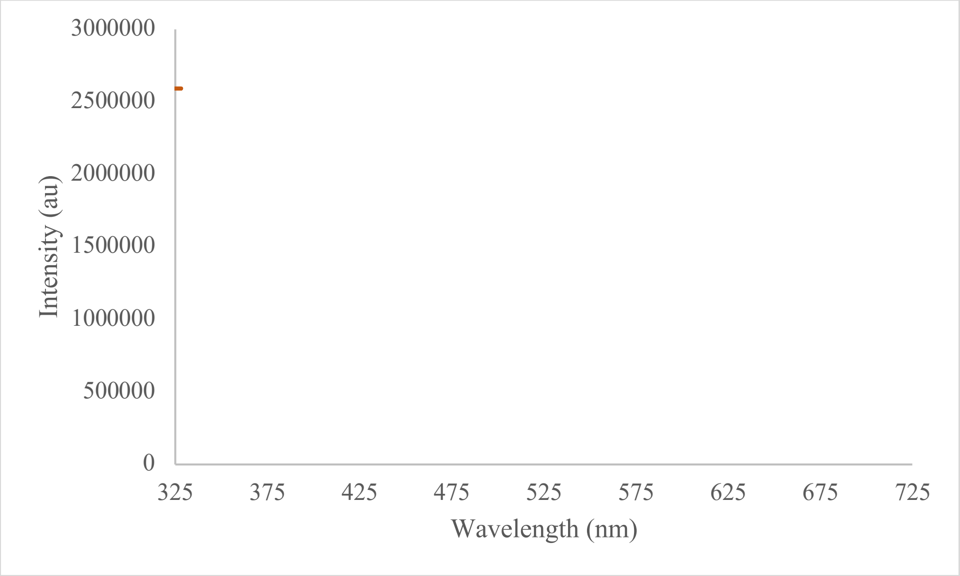


Figure 6. Emission spectra of an upconverting solution containing 1:30 PdOEP:Pyrenebutanol

Since excitation occurred at 543 nm, the peak present in that region is due to the excitation beam. The large peak centered at 660 nm is the phosphorescence of the sensitizer, PdOEP. While difficult to see due to its far smaller size, upconversion was detected in the expected emission range of pyrenebutanol (Figure 7).

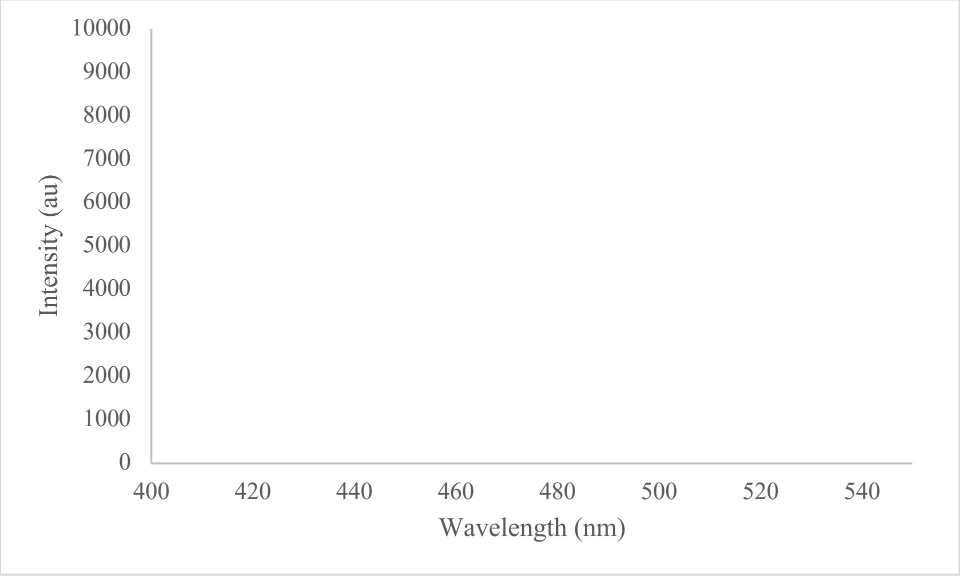


Figure 7. Enhanced spectra of two-component solution

The enhanced spectra align very closely with the emission band of pyrenebutanol obtained in Figure 5, so it was concluded that a small amount of upconversion was occurring in this system. With this in mind, an upconverting solution containing singlet sink was also examined. The ratio of components matched that of the PdOEP-pyrenebutanol system, being 0.1:3:0.1 sensitizer:annihilator:singlet sink. The emission spectrum of this system is as follows:

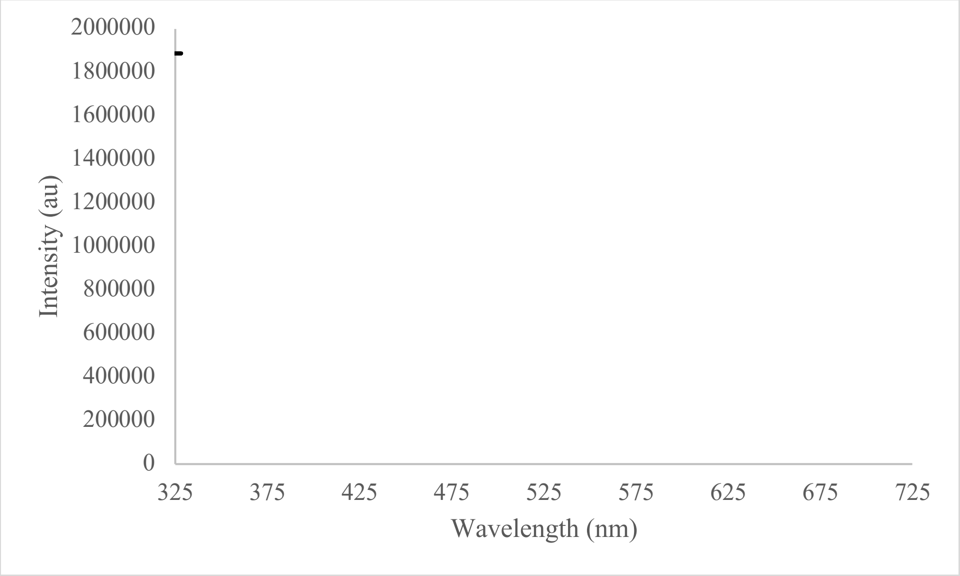


Figure 8. Emission spectra of three-component upconverting solution

As shown in Figure 8, the emission of PTEA is seen as a double peak located at 450 and 475 nm. This region unfortunately shares overlap with the emission of pyrenebutanol, so the exact amount of light in this region emitted by PTEA cannot be determined. Despite this, the differences in emission maxima between pyrenebutanol and PTEA systems can be used in order to determine if emission is occurring from the singlet sink. Results showed that emissions from systems containing singlet sink were higher than the systems without singlet sink.

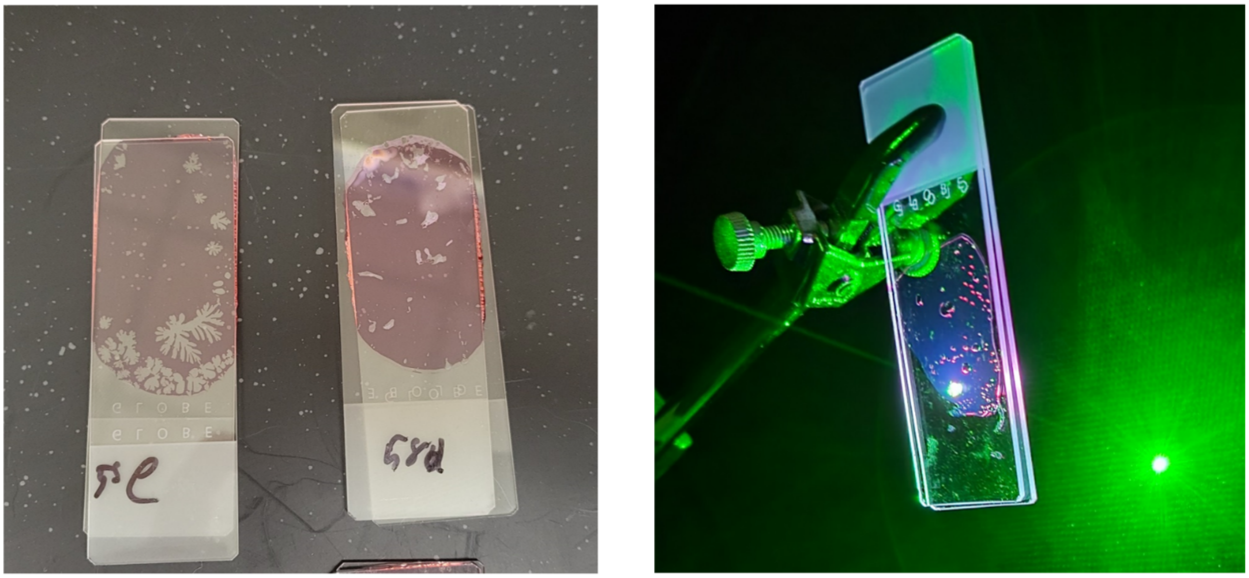


Illustration 2. Upconverting films c consisting of PdOEP, DPA, and PTEA in a PMMA matrix under ambient light (left) and excitation at 543nm (right).

With this information in mind, the emission spectra of 20 different films were obtained in total. They were separated into 4 graphs based on the concentration of pyrenebutanol and the presence of singlet sink. The results were separated this way in order to more easily examine the effects of altering sensitizer and singlet sink concentrations. These spectra are displayed in the following figures.

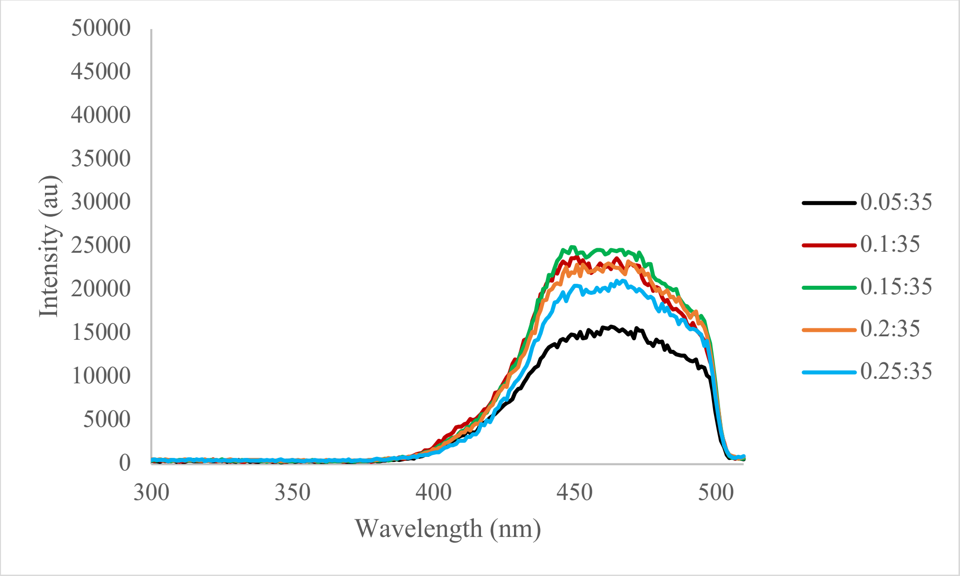


Figure 9.a. Emission of films without singlet sink at 35 wt% pyrenebutanol

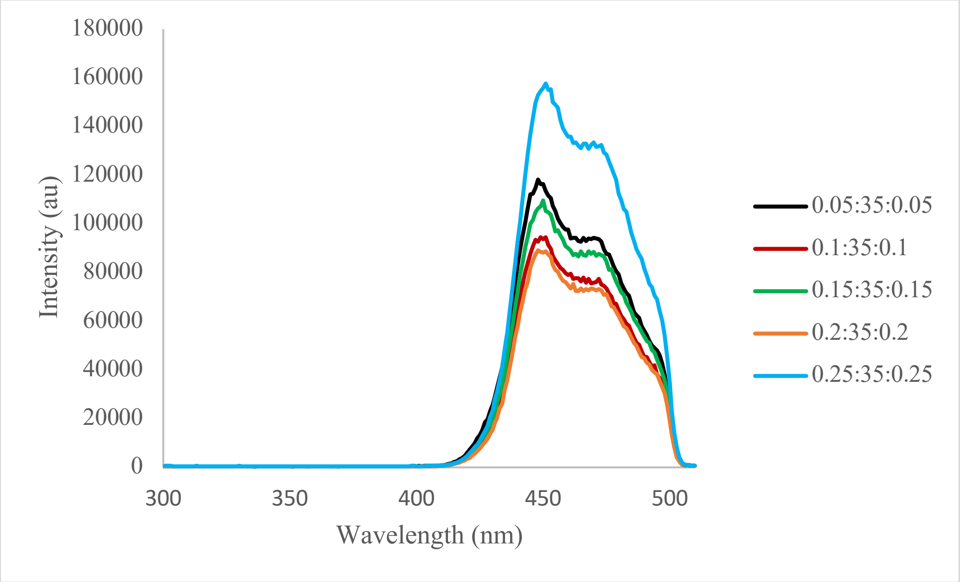


Figure 9.b. Emission of films with singlet sink at 35 wt% pyrenebutanol

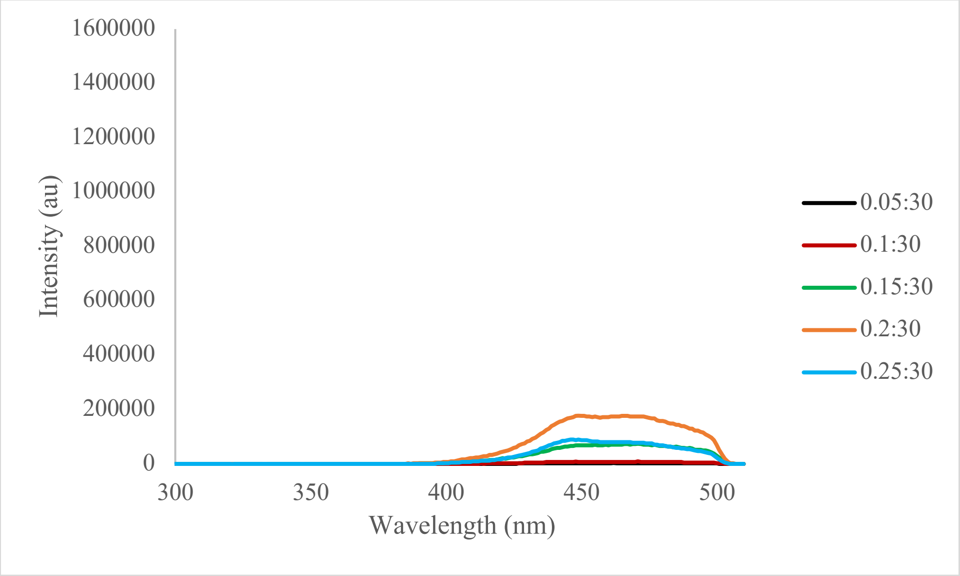


Figure 10.a. Emission of films without singlet sink at 30 wt% pyrenebutanol

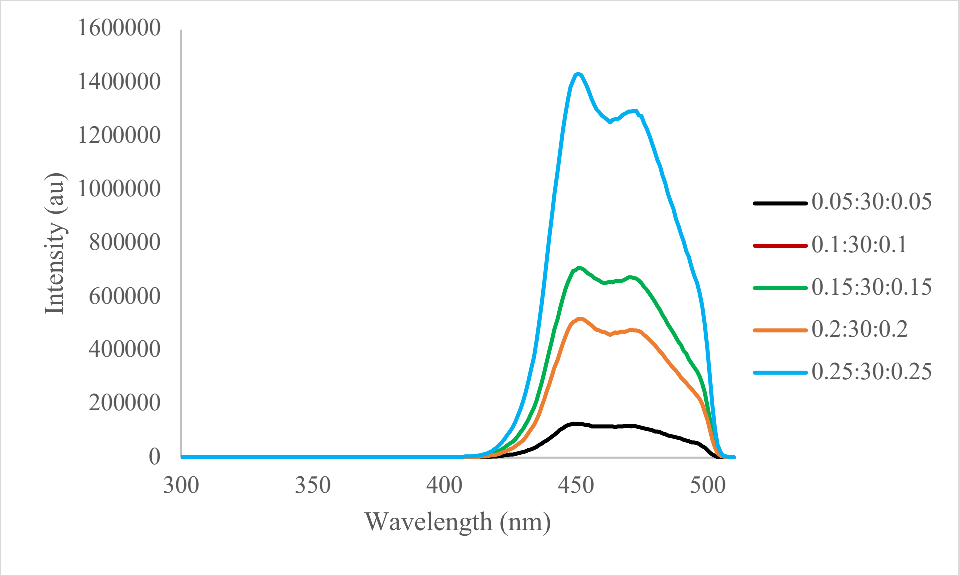


Figure 10.b. Emission of films with singlet sink at 30 wt% pyrenebutanol

The above spectra all have emission in the expected range of 400-500 nm, the expected emission range of both pyrenebutanol and PTEA. When examining the above data, both systems containing singlet sink exhibited far greater upconversion than their equivalents without singlet sink. The increase in upconversion intensity suggests that the singlet sink is functional and effective in the upconverting systems. Systems containing 0.2-0.25 wt%

sensitizer and singlet sink demonstrated the greatest upconversion in the above figures. Typically, as sensitizer concentration increases, aggregation induced quenching can occur and greatly impact upconversion efficiency. Because 0.25 wt% exhibited the greatest intensity of upconverted light, it can be determined that the critical point of sensitizer loading for this system is past 0.25 wt%. Finally, the emission spectra of 30 wt% systems displayed far greater emission intensity than 35 wt% systems. This suggests that increasing pyrenebutanol concentration beyond 30 wt% has a negative effect on the upconversion intensity of the system. The most likely reason for this is due to aggregation of pyrenebutanol and increase in self-quenching.

The greatest source of error in film creation was the presence of voids in completed films. The rapid quenching technique utilized could introduce small amounts of water into films, which promoted voids after evaporation. These voids were not capable of upconversion and resulted in non-homogenous films. Solutions to this issue are proposed in the future work section, but time constraints prevented a solution from being implemented in this process.

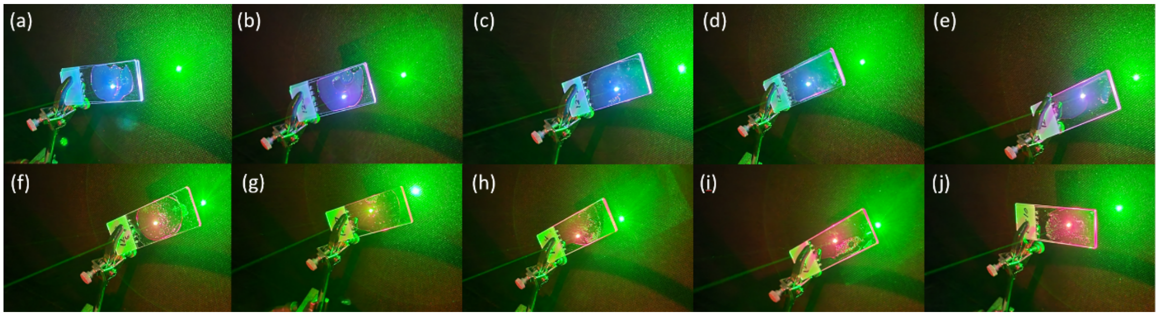


Illustration 3. Upconverting films containing excited by a 543nm laser. Composition in Figure 11.

Sample	PdOEP (Wt%)	Pyrenebutanol (Wt%)	PTEA (Wt%)
a	0.05	30.0	0.05
b	0.10	30.0	0.10
c	0.15	30.0	0.15
d	0.20	30.0	0.20
e	0.25	30.0	0.25
f	0.05	30.0	0.00
g	0.10	30.0	0.00
h	0.15	30.0	0.00
i	0.20	30.0	0.00
j	0.25	30.0	0.00

Figure 11. Composition of films in Illustration 3.

Sample Ratio	Maximum Intensity (au)	Sample Ratio	Maximum Intensity (au)
0.5:35:0.5	118171	0.05:30:0.05	127119.7
0.1:35:0.1	94479.6	0.1:30:0.1	197294.9
0.15:35:0.15	109580	0.15:30:0.15	708496.9
0.2:35:0.2	89141.7	0.2:30:0.2	518380
0.25:35:0.25	157604	0.25:30:0.25	1433852
0.05:35	15803.7	0.05:30	4747.424
0.1:35	23862.1	0.1:30	9682.104
0.15:35	24933.9	0.15:30	75081.99
0.2:35	23295	0.2:30	178223.1
0.25:35	21071.3	0.25:30	90543.07

Figure 12. Maximum intensities of each sample.

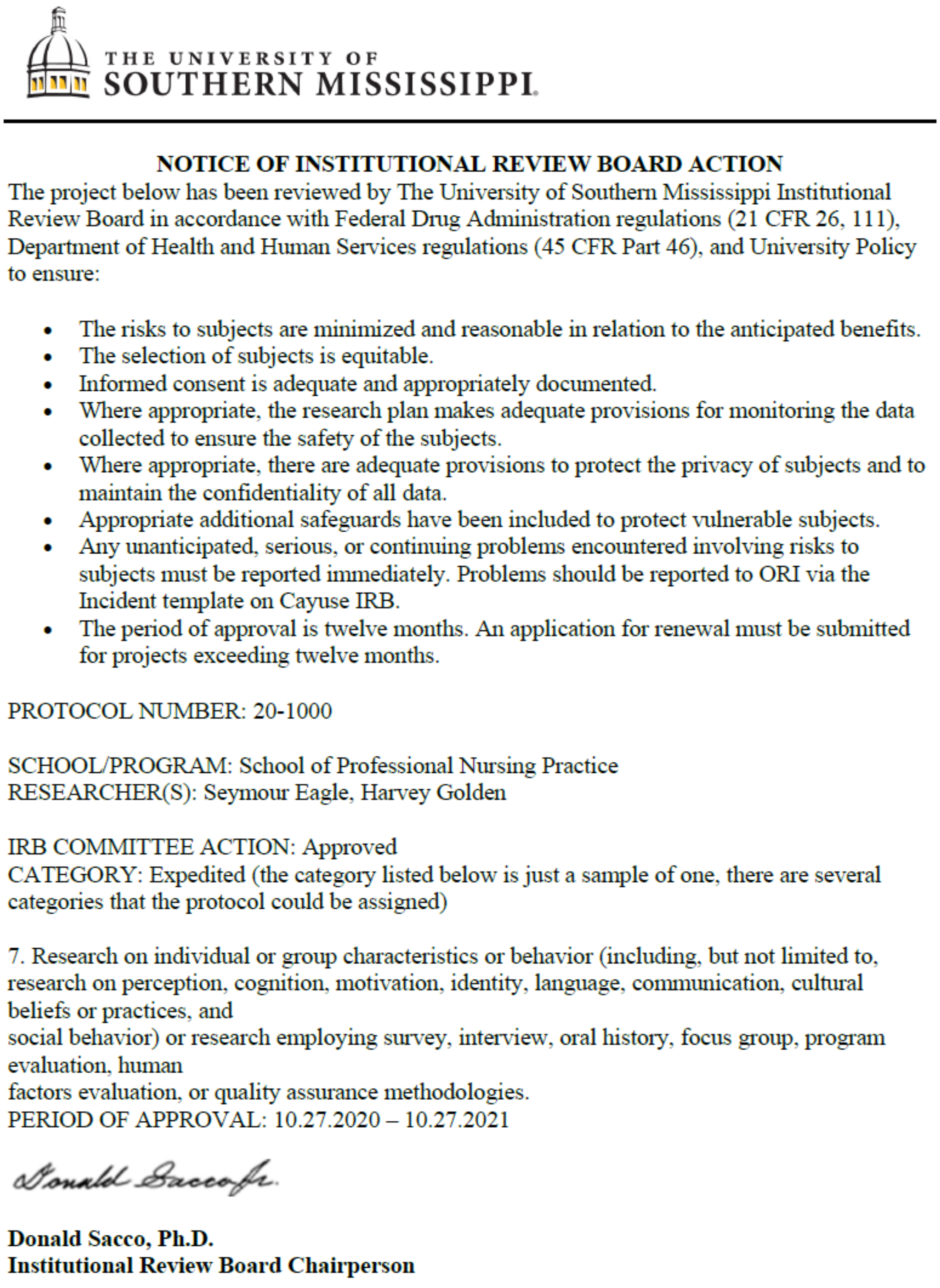
CHAPTER V: CONCLUSION/FUTURE WORK

This project demonstrated the viability of pyrenebutanol as an annihilator with the use of PdOEP as a sensitizer. In addition, the singlet sink PTEA was shown to increase the emission intensity of the upconverting system. When developing a processing procedure for this chromophore system dispersed in a PMMA matrix, several analytical techniques needed to be used. TGA was utilized in order to determine degradation temperatures of pyrenebutanol and an upconverting film in order to optimize the temperature in melt press processing. DSC was also performed on pyrenebutanol in order to determine a melting temperature. Characterization of the chromophore system in solution demonstrated that upconversion occurred in systems with and without singlet sink. For both solid and solution-based systems, upconversion was observed at greater intensities in systems containing singlet sink versus those without singlet sink. An optimal concentration of annihilator was determined to be 30 wt%. Utilizing 0.25 wt% of sensitizer and singlet sink at this concentration resulted in films emitting upconverted light with the highest intensity of all systems tested.

Due to time and instrumental constraints, alterations could not be made to this procedure in order to improve consistency of film creation. First and foremost, the prevention of water from reaching samples in the cooling process would reduce void formation in films. One proposed method of achieving this is through the use of a watertight, heat resistant Kapton bag. By placing samples in such a bag, water could be prevented from reaching the system without the loss of processing temperature. Adjustments to the time samples are being melt pressed may need to be made based on the heat conductivity of the bag, but this would improve film consistency.

There are several ways in which the results of this project could be utilized in future studies. The singlet sink and procedure utilized in this project have applications in other upconverting systems. The singlet sink must meet the criteria listed above in order to be utilized, but the procedure can be modified to be used in virtually any upconverting film containing a glassy polymer matrix. Solid-state upconverting materials containing a glassy polymer matrix show potential for a wide range of future applications.

APPENDIX A: IRB APPROVAL LETTER



THE UNIVERSITY OF
SOUTHERN MISSISSIPPI.

NOTICE OF INSTITUTIONAL REVIEW BOARD ACTION

The project below has been reviewed by The University of Southern Mississippi Institutional Review Board in accordance with Federal Drug Administration regulations (21 CFR 26, 111), Department of Health and Human Services regulations (45 CFR Part 46), and University Policy to ensure:

- The risks to subjects are minimized and reasonable in relation to the anticipated benefits.
- The selection of subjects is equitable.
- Informed consent is adequate and appropriately documented.
- Where appropriate, the research plan makes adequate provisions for monitoring the data collected to ensure the safety of the subjects.
- Where appropriate, there are adequate provisions to protect the privacy of subjects and to maintain the confidentiality of all data.
- Appropriate additional safeguards have been included to protect vulnerable subjects.
- Any unanticipated, serious, or continuing problems encountered involving risks to subjects must be reported immediately. Problems should be reported to ORI via the Incident template on Cayuse IRB.
- The period of approval is twelve months. An application for renewal must be submitted for projects exceeding twelve months.

PROTOCOL NUMBER: 20-1000

SCHOOL/PROGRAM: School of Professional Nursing Practice
RESEARCHER(S): Seymour Eagle, Harvey Golden

IRB COMMITTEE ACTION: Approved
CATEGORY: Expedited (the category listed below is just a sample of one, there are several categories that the protocol could be assigned)

7. Research on individual or group characteristics or behavior (including, but not limited to, research on perception, cognition, motivation, identity, language, communication, cultural beliefs or practices, and
social behavior) or research employing survey, interview, oral history, focus group, program evaluation, human
factors evaluation, or quality assurance methodologies.
PERIOD OF APPROVAL: 10.27.2020 – 10.27.2021

Donald Sacco Jr.

Donald Sacco, Ph.D.
Institutional Review Board Chairperson

REFERENCES

1. Jiang, X.; Guo, X.; Peng, J.; Zhao, D.; Ma, Y. Triplet–Triplet Annihilation Photon Upconversion in Polymer Thin Film: Sensitizer Design. *ACS Applied Materials & Interfaces* **2016**, *8* (18), 11441–11449.
2. Raišys, S.; Kazlauskas, K.; Juršėnas, S.; Simon, Y. C. The Role of Triplet Exciton Diffusion in Light-Upconverting Polymer Glasses. *ACS Applied Materials & Interfaces* **2016**, *8* (24), 15732–15740.
3. Raišys, S.; Juršėnas, S.; Simon, Y. C.; Weder, C.; Kazlauskas, K. Enhancement of Triplet-Sensitized Upconversion in Rigid Polymers via Singlet Exciton Sink Approach. *Chemical Science* **2018**, *9* (33), 6796–6802.

4. Schmidt, T. W.; Castellano, F. N. Photochemical Upconversion: The Primacy of Kinetics. *The Journal of Physical Chemistry Letters* **2014**, *5* (22), 4062–4072.

5. Kafle, B. P. In *Chemical analysis and material characterization by Spectrophotometry*; Elsevier: Amsterdam, **2020**; pp 269–296.
6. Valeur, B.; Berberan-Santos, M. N. *Molecular fluorescence*; Wiley-VCH: Weinheim, Germany, **2013**.
7. Tan, S. G.; A., J. M. B. In *Introduction to the physics of nanoelectronics*; Woodhead Publishing: Oxford, **2016**; pp 23–77.
8. You, Z.-Q.; Hsu, C.-P.; Fleming, G. R. Triplet-Triplet Energy-Transfer Coupling: Theory and Calculation. *The Journal of Chemical Physics* **2006**, *124* (4), 044506.

9. Cravcenco, A.; Ye, C.; Gräfenstein, J.; Börjesson, K. Interplay between Förster and Dexter Energy Transfer Rates in Isomeric Donor–Bridge–Acceptor Systems. *The Journal of Physical Chemistry A* **2020**, *124* (36), 7219–7227.

10. Fan, C.; Wu, W.; Chruma, J. J.; Zhao, J.; Yang, C. Enhanced Triplet–Triplet Energy Transfer and Upconversion Fluorescence through Host–Guest Complexation. *Journal of the American Chemical Society* **2016**, *138* (47), 15405–15412.

11. Ahmad, W.; Wang, J.; Li, H.; Ouyang, Q.; Wu, W.; Chen, Q. Strategies for Combining Triplet–Triplet Annihilation Upconversion Sensitizers and Acceptors in a Host Matrix. *Coordination Chemistry Reviews* **2021**, *439*, 213944.

12. Edhborg, F.; Bildirir, H.; Bharmoria, P.; Moth-Poulsen, K.; Albinsson, B. Intramolecular Triplet–Triplet Annihilation Photon Upconversion in Diffusionally Restricted Anthracene Polymer. *The Journal of Physical Chemistry B* **2021**, *125* (23), 6255–6263.

13. Zhou, J.; Liu, Q.; Feng, W.; Sun, Y.; Li, F. Upconversion Luminescent Materials: Advances and Applications. *Chemical Reviews* **2014**, *115* (1), 395–465.

14. Hollauf, M.; Zach, P. W.; Borisov, S. M.; Müller, B. J.; Beichel, D.; Tscherner, M.; Köstler, S.; Hartmann, P.; Knall, A.-C.; Trimmel, G. Dye Functionalized-ROMP Based Terpolymers for the Use as a Light up-Converting Material via Triplet–Triplet Annihilation. *Journal of Materials Chemistry C* **2017**, *5* (30), 7535–7545.

15. Edhborg, F.; Bildirir, H.; Bharmoria, P.; Moth-Poulsen, K.; Albinsson, B. Intramolecular Triplet–Triplet Annihilation Photon Upconversion in Diffusionally Restricted Anthracene Polymer. *The Journal of Physical Chemistry B* **2021**, *125* (23), 6255–6263.

16. Tan, S. G.; A., J. M. B. In *Introduction to the physics of nanoelectronics*; Woodhead Publishing: Oxford, 2016; pp 23–77.

17. Simon, Y. C.; Weder, C. Low-Power Photon Upconversion through Triplet–Triplet Annihilation in Polymers. *Journal of Materials Chemistry* **2012**, *22* (39), 20817.

18. Meroni, D.; Monguzzi, A.; Meinardi, F. Photon Upconversion in Multicomponent Systems: Role of Back Energy Transfer. *The Journal of Chemical Physics* **2020**, *153* (11), 114302.

19. Singh-Rachford, T. N.; Castellano, F. N. Photon Upconversion Based on Sensitized Triplet–Triplet Annihilation. *Coordination Chemistry Reviews* **2010**, *254* (21-22), 2560–2573.

20. Zhao, J.; Ji, S.; Guo, H. Triplet–Triplet Annihilation Based Upconversion: From Triplet Sensitizers and Triplet Acceptors to Upconversion Quantum Yields. *RSC Advances* **2011**, *1* (6), 937.

21. Zhao, W.; Castellano, F. N. Upconverted Emission from Pyrene and Di-Tert-Butylpyrene Using Ir(PPY)3 as Triplet Sensitizer. *Journal of Physical Chemistry A* **2006**, *110*, 11440–11445.

22. Berlman, I. B. *Handbook of fluorescence spectra of Aromatic Molecules*; Academic Press, **1971**.

23. Nikolaidis, A.; Achilias, D. Thermal Degradation Kinetics and Viscoelastic Behavior of Poly(Methyl Methacrylate)/Organomodified Montmorillonite Nanocomposites Prepared via in Situ Bulk Radical Polymerization. *Polymers* **2018**, *10* (5), 491.