ABSTRACT

WHEELER, JOSHUA JAMES. Characteristics and Kinetics of a Red-to-Green Photochemical Upconversion System utilizing a Perylene-3,4-dicarboximide Acceptor (Under the direction of Felix N. Castellano).

Red-to-Green photon upconversion was realized using platinum(II) meso-tetraphenyltetrabenzoporphyrin (PtTPBP) as a sensitizer and N-(2,5-di-tert-butylphenyl)-perylene-3,4-dicarboximide (PMI) as the acceptor. The ground state absorption extinction coefficients were measured for PMI and PtTPBP in toluene. Additionally, the quantum yield for PMI was determined relative to rhodamine 101. The Stern-Volmer constant, bimolecular quenching rate constant, and triplet-energy-transfer quantum yield were calculated from PtTPBP’s lifetime data. An excitation scan of a solution of PtTPBP and PMI was taken to determine the origin of the delayed fluorescence from PMI. Transient absorption spectra for PtTPBP and PMI were taken. The emission intensity power dependence of PMI’s delayed fluorescence was studied. The kinetics of the PtTPBP/PMI sensitized triplet-triplet annihilation upconversion system were determined. Specifically, the first order/pseudo-first order rate constant, $k_T$, and the second order annihilation rate constant, $k_{TT}$, were calculated. PMI’s triplet extinction coefficient was determined. The triplet-triplet annihilation quantum yield, total upconverted emission quantum yield, maximum conversion efficiency, and initial time-zero quantum yield were also calculated.
Characteristics and Kinetics of a Red-to-Green Photochemical Upconversion System utilizing a Perylene-3,4-dicarboximide Acceptor

by
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A thesis submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Master of Science

Chemistry

Raleigh, North Carolina

2015

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Joshua Wheeler was born in Syracuse, NY. He moved to Charlotte, NC just before his 6th birthday. He has always had an interest in science: first in birds, then in genetics/biochemistry, and finally chemistry. He obtained his undergraduate degree in Biochemistry from North Carolina State University. He then stayed at North Carolina State University to complete his masters degree in chemistry.
ACKNOWLEDGMENTS

I would like to thank my Mom and Dad for all of your support!

I would also like to thank my friends: Wil, Christian, Faye, AJ, Mary Catherine, Angela, and Katrina. You all are great, thanks for keeping me sane during the last few years.

I would also like to thank Dr. Castellano for his support during my time as a graduate student. I would also like to thank the members of the Castellano Group who helped me out during my tenure as a group member.
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CHAPTER 1

INTRODUCTION

Sensitized triplet-triplet annihilation based photochemical upconversion (TTA-UC), also known as anti-Stokes delayed fluorescence, is the process of converting low two low energy photons into one photon of higher energy via the energy stored in molecule’s excited triplet states\(^1\). Sensitized TTA-UC is appealing because it is able to use non-coherent light sources, such as the sun and was initially seen as a way to overcome the Shockley-Queisser\(^3\) limit of solar cells. Additionally sensitized TTA-UC has been proposed as a method to develop more efficient light sources\(^2\) along with a wide variety of applications: solar energy harvesting applications\(^4\)\(^{-10}\) into \textit{in vivo} imaging\(^11\)\(^{-14}\), incorporated into polymeric displays\(^15\), used to sensitize photoelectrochemistry\(^16\),\(^17\) and integrated into nanostructures\(^18\)\(^{-31}\). To facilitate the development of these applications, sensitized TTA-UC has also been studied in a large variety of polymer hosts\(^32\)\(^{-56}\).

Parker and Hatchard\(^57\) first described delayed fluorescence from anthracene in mixture of phenanthrene and anthracene\(^58\). Afterwards, Parker and Hatchard intentionally induced photon upconversion in naphthalene by exciting phenanthrene\(^58\). Additionally, Parker and Hatchard also detected anthracene fluorescence from selective excitation of proflavin hydrochloride. Parker and Hatchard described this phenomenon as “anti-Stokes delayed fluorescence” due to observed emission being blue shifted (an anti-Stokes shift) relative to the exciting wavelength. Normally, excitation of a molecule results in the emission of photons red shifted relative to the excitation wavelength. This red shift is called a Stokes shift\(^59\).
Sensitized photon upconversion using metal-based chromophores was first demonstrated in 2004. A metal-organic ruthenium compound was used to sensitize delayed fluorescence from anthracene\textsuperscript{60,62}. Using green light to excite the MLCT band of the ruthenium chromophore in solution with anthracene resulted in the detection of fluorescence from anthracene without the characteristic emission from the ruthenium sensitizer’s \textsuperscript{3}MLCT state. This first proof of concept with anthracene was expanded to include the anthracene derivative, 9,10-diphenylanthracene\textsuperscript{61}. Once it was established metal-organic compounds are able to sensitize anti-Stokes delayed fluorescence, the library of sensitizer molecules grew quickly; either through the use of established triplet emitters or through the development of novel triplet emitters. Sensitizer Development has focused on increasing the visible light absorption of platinum\textsuperscript{63-72}, iridium\textsuperscript{73-80}, ruthenium\textsuperscript{81-86}, and rhenium\textsuperscript{87,88} metal-organic compounds. Most recently, sensitizers utilizing the first row element copper have been designed\textsuperscript{89,90}. Porphyrins and phthalocyanins\textsuperscript{91-105} are also popular sensitizers, due to the large extinction coefficient of the Q-band structure allowing them to strongly absorb red and near-infrared light. Sensitized TTA-UC systems utilizing organic compounds as sensitizers have also been designed\textsuperscript{106-121}. Despite the large increase in possible sensitizers, the library of available acceptors remains small. Only recently has there been efforts to expand the library of possible acceptors\textsuperscript{122,123}. 
CHAPTER 2

2.1 MOLECULAR PROPERTIES

Sensitized TTA-UC relies on several intrinsic properties of the sensitizer and acceptor molecules. Firstly, the sensitizer must absorb strongly at the desired wavelength(s); this requirement corresponds to having a strong extinction coefficient, ε, at the desired wavelengths. Strong absorption generally corresponds to \( \varepsilon \geq 10^3 \text{ M}^{-1} \text{ cm}^{-1} \). In addition, the sensitizer should poorly absorb photons emitted by the acceptor. Poor absorption refers to having a low extinction coefficient, \( \varepsilon \leq 10^2 \text{ M}^{-1} \text{ cm}^{-1} \). Furthermore, it is desirable for the sensitizer should absorb strongly in regions where the solar spectrum is the strongest. Figure 2.1 shows the total solar irradiance spectrum for the sun\(^{130}\). As seen in figure 2.1, the largest total solar irradiance occurs just after 500 nm and continues through the red to infrared regions of the electromagnetic spectrum.

![Figure 2.1 - Total solar irradiance spectrum for the ultraviolet, visible, and infrared regions of the solar spectrum](image)

The second intrinsic property sensitized TTA-UC relies on is the intersystem crossing (ISC) ability of the sensitizer. ISC refers to how well the sensitizer goes from its excited singlet state into its metastable excited triplet state. There are two mechanisms for a
sensitizer to access its excited triplet state: i) use of a heavy atom, usually a transition metal, with a large spin-orbit coupling constant ($\zeta_{SO}$) or ii) a large overlap between the wavefunction of an excited singlet state and an excited triplet state. Transition metal sensitized TTA-UC complexes take advantage of the large spin-orbit coupling constant ($\zeta_{SO}$) provided by the metal atom (Table 2.1). Purely organic compounds used as sensitizers utilize the large overlap of the excited singlet state and excited triplet state wavefunctions\textsuperscript{124-126}. The most efficient sensitizers utilize either the large $\zeta_{SO}$ (transition-metal sensitizers) or the strong wavefunction overlap (organic sensitizers) to achieve ISC yields, $\Phi_{ISC}$, approaching unity.

<table>
<thead>
<tr>
<th>Atomic Number</th>
<th>Element</th>
<th>Mass (amu)$^a$</th>
<th>$\zeta_{SO}$ (cm)$^{127}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>Copper (Cu)</td>
<td>63.546</td>
<td>857</td>
</tr>
<tr>
<td>44</td>
<td>Ruthenium (Ru)</td>
<td>101.07</td>
<td>1042</td>
</tr>
<tr>
<td>46</td>
<td>Palladium (Pd)</td>
<td>106.42</td>
<td>1504</td>
</tr>
<tr>
<td>75</td>
<td>Rhenium (Re)</td>
<td>186.21</td>
<td>2903</td>
</tr>
<tr>
<td>77</td>
<td>Iridium (Ir)</td>
<td>192.22</td>
<td>3909</td>
</tr>
<tr>
<td>78</td>
<td>Platinum (Pt)</td>
<td>195.08</td>
<td>4481</td>
</tr>
</tbody>
</table>

The next property of a TTA-UC system is how well the triplet energy is transferred from the sensitizer to the acceptor. This energy transfer process is referred to as Triplet-Energy Transfer (TET). The mechanism of TET for TTA-UC is Dexter type energy transfer\textsuperscript{132}. In Dexter-type energy transfer, an excited molecule collides with a second ground state molecule, resulting in energy transfer to the second molecule. Figure 2.2 illustrates Dexter-type energy transfer. In Figure 2.2, a donor molecule in its excited state, $^3D^*$, collides with a ground state acceptor molecule, $^1A$. The collision causes the donor molecule to return to the ground state, $^1D$, and forcing the acceptor to take on an excited triplet state, $^3A^*$. Since the total spin of the system is preserved, this process is labeled as spin-allowed. Monguzzi
and coworkers confirmed Dexter-type energy transfer as the mechanism of triplet energy transfer in sensitized TTA-UC\textsuperscript{133,134} in 2008.

Sensitized TTA-UC is also dependent on the energy of the excited triplet state of the acceptor molecule. The triplet state energy of the acceptor molecule must lie below the triplet state energy of the sensitizer, thus ensuring triplet energy transfer from the sensitizer to the acceptor is exothermic\textsuperscript{128-130}. If the energy level of the acceptor’s excited triplet state is higher than the sensitizer’s excited triplet state, the energy transfer is endothermic and triplet energy transfer cannot occur. Additionally, the energy of the triplet state must also satisfy the requirement $2E_T \geq E_s$\textsuperscript{122,123}; where $E_T$ is the triplet level energy and $E_s$ is the excited singlet energy level. This inequality ensures there is enough excess energy in the annihilating triplet pair to access the acceptor’s excited singlet states. Finally, efficient acceptors have fluorescence quantum yields approaching unity and/or have a short (nanosecond) singlet lifetimes\textsuperscript{127} ensuring fluorescence as the dominant decay pathway.
One of the aims of this research is to address the deficiency in the acceptor library by studying N-(2,5-di-tert-butylphenyl)perylene-3,4-dicarboximide (PMI) as a new acceptor. The Castellano group has previously described a sensitized TTA-UC system using platinum(II) meso-tetraphenyltetrabenzoporphyrin (PtTPBP) as the sensitizer and perylene as the acceptor. Since perylene-3,4-dicarboximides are a derivative of perylene, PMI should function as a suitable acceptor for PtTPBP. Figure 2.3 shows the structures of PtTPBP and PMI.
Platinum(II) *meso*-tetraphenyldiophenyltetrabenzoporphyrin (PtTPBP) was originally synthesized for use as a triplet emitter for NIR OLEDs. The condensed phase photophysics of PtTPBP were determined in 2-methyl-THF (2MTHF). The extinction coefficients of PtTPBP in toluene were calculated for three different excitations wavelengths: 614 nm, 630 nm, and 635 nm. The concentrations of PtTPBP in the experiments performed were calculated from these extinction coefficients. The extinction coefficients were calculated using Beer’s Law (Equation 2.1) and are seen in Figure 2.4. In 2MTHF, the peak of PtTPBP’s Q-band is at 611 nm. In toluene, PtTPBP’s Q-band peak is red shifted slightly to 614 nm. The extinction coefficients for the two peaks agree well with each other—1.35 x 10^5 M\(^{-1}\)cm\(^{-1}\) in 2MTHF versus 1.42 x 10^5 M\(^{-1}\)cm\(^{-1}\) in toluene. The lifetime of PtTPBP in toluene was determined to be 41 μs in toluene. The intersystem crossing rate yield of PtTPBP determined by Borek et. al. is Φ\(_{\text{ISC}}\) = 0.7.
Figure 2.5 - Solar irradiance spectrum for the ultraviolet and visible portion (300 nm – 750 nm) of the 1.5 AM solar spectrum compared to the PtTPBP's absorbance spectrum.

Figure 1.4 shows the total solar irradiance spectrum\textsuperscript{130} of the sun compared to PtTPBP’s absorption spectrum. An effective sensitizer molecule will have strong absorption where the solar irradiance is the strongest. As seen in Figure 2.5, the Q-band of PtTPBP strongly absorbs between 575 nm and 650 nm a region of strong solar irradiance on a mW\textsuperscript{-1}cm\textsuperscript{-2} basis. PtTPBP’s ability to strongly absorb sunlight, combined with its long microsecond lifetime and high intersystem crossing yield make PtTPBP an ideal candidate as a TTA-UC sensitizer.

Perylene monoimide compounds were first synthesized in 1995\textsuperscript{137} and are typically used to study electron\textsuperscript{138-140} and energy transfer\textsuperscript{141-157} mechanisms and as dyes in dye-sensitized solar cells\textsuperscript{158-166}. Additionally, PMI’s are useful for studying photophysical processes\textsuperscript{167-178} due to their large extinction coefficients for the HOMO-LUMO transitions. Along with their large extinction coefficients, perylene monoimide complexes possess large fluorescence quantum yields (Φ\textsubscript{F}) where Φ\textsubscript{F} ≥ 0.90\textsuperscript{141,146,147,151,152,156,157,163,167,168,172,176}. 
Figure 2.6 - A) Absorption spectra with increasing [PMI] used for calculating extinction coefficients for PMI. B) Concentrations versus A\textsubscript{478} used to calculate \( \varepsilon_{478} \) for PMI. C) Concentration versus A\textsubscript{506} used to calculate \( \varepsilon_{506} \) for PMI.

Like other perylene monoimide complexes, PMI possess a large extinction coefficient for the HOMO-LUMO transition that occurs at 506 nm (2.45 eV), \( \varepsilon_{506} = 37,265 \text{ M}^{-1} \text{ cm}^{-1} \), Figure 2.6B. In addition, a second HOMO-LUMO transition occurs at 478 nm (2.59 eV) also has a large extinction coefficient, \( \varepsilon_{478} = 37,079 \text{ M}^{-1} \text{ cm}^{-1} \), Figure 2.6C.

\[
A = \varepsilon \ast l \ast c \quad (2.1)
\]

\[
\Phi_{PMI} = \phi_S \frac{I_U}{I_S} \frac{A_S}{A_U} \frac{\eta_U^2}{\eta_S^2} 
\quad (2.2)
\]

The quantum yield for PMI was determined relative to Rhodamine 101 (\( \Phi_F = 1.0 \) in 200 proof ethanol) using Equation 2.2. In Equation 2.2, \( A_U \) is the absorbance of PMI and \( A_S \) is the absorbance of rhodamine 101 at the excitation wavelength, \( \lambda_{ex} = 478 \text{ nm} \); \( I_U \) is the integrated emission of PMI, \( I_S \) is the integrated emission of rhodamine 101; and \( \eta_U \) is the
refractive index of toluene ($\eta = 1.496$), and $\eta_S$ is the refractive index of ethanol ($\eta = 1.360$). Using equation 1.2, the quantum yield for PMI is $\Phi_T = 0.93$. Additionally the singlet lifetime of PMI was determined to be 5 ns. PMI is a suitable candidate for use as an acceptor in sensitized TTA-UC based on its high quantum yield and short singlet lifetime.

![Combined Absorption and Emission Spectrum for PtTPBP and PMI](image)

**Figure 2.7**-Combined absorption and emission spectrum for PtTPBP and PMI.

Figure 2.7 is the total absorption and emission spectrum for PtTPBP and PMI. The absorption spectra characteristics for PtTPBP and PMI were discussed previously. For sensitized TTA-UC applications, PMI’s absorption spectrum is important for determining the origin and energy of the delayed singlet fluorescence from triplet-triplet annihilation. For PMI this origin is at 2.45 eV (506 nm). The emission spectrum of the acceptor, PMI in this system, is important in determining how efficacy of the TTA-UC system. Higher overlap between the acceptor emission and sensitizer absorption reduces the TTA-UC efficacy due to the sensitizer reabsorbing the emitted photons before they can do work. PMI is a suitable acceptor for PtTPBP because it has low overlap with the Q-band of PtTPBP, resulting in little photon reabsorption.
The total energy difference of the anti-Stokes shift can be determined based on the chosen excitation wavelength and the origin of PMI’s fluorescence. The desired excitation for PtTPBP/PMI sensitized TTA-UC was 635 nm (1.95 eV). Based on this, the anti-Stokes energy shift for PtTPBP/PMI sensitized TTA-UC is 0.50 eV.

Figure 2.8 - A Jablonski diagram for the PtTPBP/PMI TTA-UC system. $1S^*$ is the singlet excited state of PtTPBP, $3S^*$ is the triplet excited state of PtTPBP, $3A^*$ is the triplet state of PMI, $1A^{**}$ is a higher lying singlet excited state of PMI, and $1A^*$ is the lowest singlet excited state of PMI. GS is an arbitrary ground state for the entire system. Solid lines are absorption or emission processes, wavy lines signify non-radiative processes; dashed lines indicate energy transfer steps. ISC is intersystem crossing, TET is triplet energy transfer and TTA is triplet-triplet annihilation.

The photophysical in sensitized TTA-UC are seen in the Jablonski diagram in Figure 2.8. The first TTA-UC process is the absorption of light by the sensitizer. When studying the total photophysics of the PtTPBP/PMI TTA-UC system, light absorption occurs at 1.95 eV (635 nm). Once PtTPBP absorbs light, it intersystem crosses into its excited triplet state. In the absence of PMI, $^3PtTPBP^*$ will undergo phosphorescence centered at 1.62 eV (765 nm). In the presence of sufficient PMI, $^3PtTPBP^*$ will transfer its excited triplet state energy to PMI, resulting in triply excited PMI, $^3PMI^*$. Once a large enough population $^3PMI^*$
molecules is achieved, two $^3\text{PMI}^*$ molecules will undergo triplet-triplet annihilation (TTA). Due to the excess of energy stored in the two $^3\text{PMI}^*$, the resulting singly-excited PMI molecule is in a higher lying excited singlet state, $^1\text{PMI}^*$. $^1\text{PMI}^*$ will then internally convert to its lowest excited singlet state, $^1\text{PMI}$*. Finally, $^1\text{PMI}$* fluoresces back to the ground state releasing the upconverted photon.

![Figure 2.9](image)

**Figure 2.9** - A) Stern-Volmer plot for PtTPBP/PMI. B) TET Quantum Yield plot for PtTPBP to PMI triplet energy transfer. C) Kinetic traces of PtTPBP taken at 765 nm used to calculate $K_{SV}$ in (A) and $\Phi_{TET}$ in (B).

To determine how well PMI quenches the triplet state of PtTPBP, the Stern-Volmer quenching constant, $K_{SV}$, was calculated (Equation 2.3). For the PtTPBP/PMI sensitized TTA-UC system $K_{SV} = 134,830 \text{ M}^{-1}$. Additionally, the bimolecular quenching rate constant, $k_q$, was calculated from $K_{SV}$ using Equation 2.4. For PtTPBP/PMI, $k_q = 3.26 \times 10^{9} \text{ M}^{-1} \text{ cm}^{-1}$. This value for $k_q$ is less than the diffusion limit in toluene, $1.2 \times 10^{10} \text{ M}^{-1} \text{ cm}^{-1}$, indicating that triplet energy transfer from PtTPBP to PMI is diffusion limited.
The lifetime data in Figure 2.9C used to calculate $K_{SV}$ can also be used to calculate the triplet energy transfer efficiency, $\Phi_{TET}$, using Equation 2.5\textsuperscript{179}. Using Equation 2.5 and the data in Figure 2.9C, $\Phi_{TET} = 0.94$ for the PtTPBP/PMI sensitized TTA-UC system.

\[
\frac{\tau_0}{\tau} - 1 = K_{SV}[Q] \quad (2.3)
\]

\[
K_{SV} = k_q \tau_0 \quad (2.4)
\]

\[
\Phi_{TET} = 1 - \frac{\tau}{\tau_0} \quad (2.5)
\]

Figure 2.10 - Normalized Absorption Spectrum for PtTPBP and normalized excitation spectra for a solution of PTTPB/PMI with the following concentrations: 10.1 μM PtTPBP, 22.4 μM PMI.

To determine the origin of PMI fluorescence in a deoxygenated solution of PtTPBP and PMI, and excitation scan was taken. In an excitation scan the intensity of one an emission wavelength is constantly monitored while the excitation wavelength is varied. An increase in emission intensity correlates to more molecules being excited by that wavelength which correlates with a stronger extinction coefficient at that wavelength. For a solution containing a single molecule the excitation scan should correlate with absorbance spectrum.
In sensitized TTA-UC, monitoring the delayed fluorescence of the acceptor molecule should generate an excitation spectrum matching the absorbance spectrum of the sensitizer molecule. An excitation scan of PtTPBP/PMI sensitized TTA-UC system is seen in Figure 2.10. The excitation scan of a solution containing PtTPBP and PMI generates an excitation spectrum that matches the Q-band of PtTPBP when the emission of PMI is monitored at 532 nm. The excitation scan shows that delayed fluorescence from PMI in a solution of PtTPBP and PMI is due to excitation of PtTPBP, providing evidence for energy transfer between PtTPBP and PMI.

![Normalized Emission Intensity vs Wavelength (nm)](image)

**Figure 2.11** - Prompt and Delayed fluorescence of PMI. Prompt PMI in the prompt fluorescence was excited at $\lambda = 478$ nm. Delayed fluorescence was sensitized via excitation of PtTPBP at $\lambda = 614$ nm.

Additional evidence for TTA-UC comes from comparing the delayed fluorescence spectrum with the prompt fluorescence spectrum, Figure 2.11. As seen in Figure 2.11, the delayed fluorescence spectrum contains the same $S_1 \rightarrow S_0$ features as the prompt fluorescence spectrum. The loss of the shoulder centered at 640 nm in the delayed fluorescence spectrum is due to PtTPBP reabsorbing the photons emitted by PMI. Additionally, the decrease in emission intensity of the second peak is due to the minor Q-band of PtTPBP absorbing the photons emitted by PMI.
The data in Figures 2.10 and 2.11 demonstrate that sensitized TTA-UC delayed fluorescence occurs due to energy transfer from PtTPBP to PMI. In de-oxygenated solutions, excited state PtTPBP exists as $^3$PtTPBP. Because energy transfer between two molecules requires the total spin of the system to be conserved, energy transferred from PtTPBP to PMI must involve the excited triplet state. Thus the interaction of PtTPBP and PMI results in $^3$PMI. In order to see any delayed fluorescence from PMI, two triplet molecules must interact to form $^1$PMI, thus proving that sensitized TTA-UC is occurring.

Figure 2.12 shows the nanosecond transient absorption (nsTA) spectrum for PtTPBP in toluene at varying time delays. The nsTA spectrum of PtTPBP contains characteristic ground state bleach between 400 nm to 450 nm and between 590 nm and 630 nm. The ground state bleach located between 400 nm and 450 nm corresponds to PtTPBP’s Soret band and the ground state bleach located between 590 nm and 630 nm corresponds to PtTPBP’s Q-band. The nsTA spectrum of PtTPBP has strong triplet-triplet absorption in between the Soret and Q band ground state bleaches. The nsTA spectrum of PtTPBP also has
triplet-triplet absorption features beyond the Q-band ground state bleach. These nsTA features follow the rules for porphyrin transient absorption spectra$^{180}$. In addition, the nsTA spectrum in Figure 2.12 matches the nsTA spectrum of PtTPBP taken in DMF$^{91}$.

Figure 2.13- Sensitized PMI triplet-triplet absorption spectrum sensitized with PtTPBP. Pulse energy was 2.4 mJ/pulse, 17.4 μM PMI, 2.9 μM PtTPBP, λex = 614 nm.

Figure 2.13 is the nsTA spectrum for PMI that has been sensitized by PtTPBP. The long delay times used ensure a large population of excited triplet state PMI has built up. In addition, the long time delay ensures that any residual $^3$PtTPBP* species have decayed to the ground state. The nsTA spectrum of PMI has two ground state bleaches located at 478 nm and at 506 nm corresponding to PMI’s ground state absorptions. The most notable feature of PMI’s nsTA spectrum is the strong triplet-triplet absorption that occurs right at 532 nm, almost immediately after the lowest energy ground state bleach. These nsTA features are similar to a nsTA spectrum published by the Wasielewski group$^{182}$. Additionally, the nsTA spectrum demonstrates that energy transfer does occur between PtTPBP and PMI due to the absence of PtTPBP transient absorption features in Figure 2.13.
CHAPTER 3

3.1 TRIPLET-TRIPLET ANNIHILATION SPIN STATISTICS

Delayed fluorescence from TTA-UC is ultimately dependent on the interaction of two acceptors in their excited triplet state. Figure 3.1 shows a general reaction scheme for the interaction of two molecules, A and B, with multiplicities of \( m \) and \( n \) interacting to form a product, \( P \). When A and B encounter each other in solution, the total number of spin states possible is the product of \( m \) and \( n \). For sensitized TTA-UC, \( m = n = 3 \) making \( mn = 9 \); meaning there are 9 possible spin combinations that arise from the interaction of two triplets.

\[
mA + nB \leftrightarrow mn(AB) \rightarrow P
\]

Equation 3.1 defines the spin multiplicity of a molecule, where \( M \) is multiplicity and \( S \) is the sum of the electron spin states. The sum of electron spin states accounts for up spin, \( \alpha \), equaling \(+\frac{1}{2}\) and the down spin, \( \beta = -\frac{1}{2} \), such that \( S = 0 \) for an \( \alpha \beta \) electron pair. Since electrons in triplet states are formally unpaired, \( \alpha \alpha \) or \( \beta \beta \), \( S = 1 \) making \( M = 3 \).

\[
M = 2S + 1 \tag{3.1}
\]

\[
SSF = \frac{M}{mn} \tag{3.2}
\]

Equation 3.1 can also be applied to determine the multiplicity of interacting molecules. Two excited state molecules interacting is referred to as an excimer. Figure 3.2
outlines the interaction of two excited state triplet molecules. Two interacting triplet states results in one of three outcomes: i) a quintet where the electrons are all up (αααα) or down (ββββ) spins which leads to $S = 2$ and $M = 5$, ii) a triplet state that has three up spins or three down spins and one opposing spin (ααβ or ββα) leading to $S = 1$ and $M = 3$, or iii) a singlet state that has two up spins interacting with two down spins, ααββ, leading to $S = 0$ and $M = 1$.

![Diagram of possible outcomes of the interaction of two triplet states]

**Figure 3.2**- Schematic of the possible outcomes of the interaction of two triplet states

The probability of forming a quintet, triplet, or singlet state is determined by the spin statistical factor, SSF, Equation 3.2. In Equation 3.2, $M$ is the multiplicity determined by Equation 2.1 and $mn$ is the total number of states calculated as seen in Figure 3.1. Using equation 3.2 with $m = n = 3$ demonstrates two interacting triplet states form a quintet state 5/9 of the total encounters, a triplet state 3/9 of the total encounters and a singlet state 1/9 of the total encounters. Based on this SSF analysis, the desired singlet excited state occurs once in every nine encounters casing the maximum theoretical quantum yield obtainable is $\Phi_{UC} = 0.11$.

A more recent kinetic analysis of sensitized TTA-UC has determined that the upper limit of $\Phi_{UC}$ is $\Phi_{UC} = 0.40$ corresponding to a maximum conversion efficiency, $\eta_c = 0.40$. In
solution, the excimeric quintet state immediately dissociates back into the two constituent triplet states. This leaves the interaction of triplet excimers or singlet excimers as potential second order deactivation pathways for the triplets involved in sensitized TTA-UC. The efficiency of the second order decays processes is defined as $\eta_c$, Equation 3.3. In Equation 3.3, $k_{TTA-S}$ is the triplet-triplet annihilation pathways resulting in the singlet state and $k_{TTA-T}$ is the triplet-triplet annihilation pathway resulting in one singlet and one triplet state. Spin statistics suggest $k_{TTA-T} = 3k_{TTA-S}$. The prefactor of three is due to two different triplet deactivation pathways: i) standard triplet-triplet annihilation pathway, which removes two triplet states from solution and ii) the formation of a doubly excited triplet state and a ground state, which removes only one triplet state from solution. Plugging in $k_{TTA-T} = 3k_{TTA-S}$ into Equation 3.3 results in Equation 3.4, which simplifies down to $\eta_c = 0.4$.

$$
\eta_c = \frac{2k_{TTA-S}}{2k_{TTA-S} + k_{TTA-T}}
$$

$$
\eta_c = \frac{2k_{TTA-S}}{2k_{TTA-S} + 3k_{TTA-S}} = \frac{2k_{TTA-S}}{5k_{TTA-S}} = \frac{2}{5} = 0.40
$$
3.2 TRIPLET-TRIPLET ANNIHILATION KINETICS

Triplet-triplet annihilation kinetics was first studied using the delayed fluorescence emission from pyrene excimers. A thorough investigation of triplet-triplet annihilation occurring in other molecules was carried out in the early 1970’s. It was later proven that triplet-triplet annihilation is both concentration dependent and diffusion limited. In the first instance of sensitizing a molecule to obtain the triplet-triplet annihilation rate constant, Yekta and Turro used camphorquinone to produce triplet 1,2-benzanthracene to calculate the triplet-triplet annihilation rate constant for 1,2-benzanthracene. The first kinetic study of a sensitized TTA-UC system was carried out in 2009. Studying the kinetics of sensitized TTA-UC systems is necessary to determine the highest possibly efficiencies.

The rate equation for triplet-triplet annihilation has contributions from first order and pseudo-first order triplet decay pathways, \( k_T \), and the second-order triplet-triplet annihilation decay pathway, \( k_{TT} \), Equation 3.5. In Eq. 3.5, \( [^3M^*] \) is the concentration of excited-triplet state acceptor.

\[
\frac{d[^3M^*]}{dt} = -k_T[^3M^*] - k_{TT}[^3M^*]^2 \tag{3.5}
\]

Since triplet-triplet annihilation consists of two competing pathways, the observed kinetics becomes dependent on which rate constant, \( k_T \) or \( k_{TT} \), is dominant resulting in two different kinetic regimes. The first regime is a quadratic regime where \( k_T \) is dominant and the emission intensity is dependent on the square of the incident light. The second regime is a
linear regime where \( k_{TT} \) is dominant and the emission intensity scales linearly with the intensity of the incident light.

In the first kinetic regime when \( k_T \) is dominant (\( k_T \gg k_{TT} \)), Equation 3.5 becomes a standard first order rate equation, Equation 3.6. The analytical solution to Equation 3.6 is Equation 3.7, where \([^3M^*]_0\) is the initial concentration of excited-triplet state molecules and \(k_T\) is the first order rate constant. The second kinetic regime, where \( k_{TT} \gg k_T \), Equation 3.5 becomes a standard second order rate equation, Equation 3.8. Integration of Equation 3.8 results in Equation 3.9, where \([^3M^*]_0\) is the same as before and \(k_{TT}\) is the triplet-triplet annihilation rate constant.

\[
\frac{d[^3M^*]}{dt} = -k_T[^3M^*] \tag{3.6}
\]

\[
[^3M^*]_t = [^3M^*]_0 e^{-k_T t} \tag{3.7}
\]

\[
\frac{d[^3M^*]}{dt} = -k_{TT}[^3M^*]^2 \tag{3.8}
\]

\[
[^3M^*]_t = \frac{[^3M^*]_0}{1 + k_{TT}[^3M^*]_t} \tag{3.9}
\]

Using the kinetic equations calculated above, the characteristics of sensitized TTA-UC delayed fluorescence can be determined. Equation 3.10 is the equation used to calculate the intensity of delayed fluorescence, \( N_F \). In Equation 3.10, \( \Phi_F \) is the fluorescence quantum yield of the sensitized TTA-UC acceptor, \( k_{TT} \) is the triplet-triplet annihilation rate constant of the acceptor, and \([^3M^*]_t\) is the kinetic rate equation. Since sensitized TTA-UC has two kinetic regimes, the observed sensitized TTA-UC delayed fluorescence will also have two emission regimes. The two regimes for sensitized TTA-UC are a quadratic regime, where the delayed fluorescence is dependent of the square of \([^3M^*]\) and a linear regime where the delayed
fluorescence linearly scales with the concentration of $[^3M^*]$. The first emission regime occurs when $k_T$ is the dominant kinetic decay pathway. The kinetic rate equation when $k_T$ is dominant is Equation 3.7. Inserting Equation 3.7 into Equation 3.10 and integrating results in Equation 3.11. In Equation 3.11, $N_F$ is dependent on the square of $[^3M^*]_0$ — the initial triplet concentration at time zero. The second sensitized TTA-UC regime occurs when $k_{TT}$ is the dominant triplet decay pathway. The equation for $[^3M^*]_t$, Equation 3.9, is inserted into Equation 3.10 resulting in Equation 3.12. In Equation 3.12, $N_F$ scales linearly with $[^3M^*]_0$.

$$N_F = \int_0^\infty I_F(t) \, dt = \int_0^\infty \Phi_F k_{TT}[^3M^*]^2_t \, dt$$  \hspace{1cm} (3.10)

$$N_F = \frac{\Phi_F k_{TT}[^3M^*]^2_0}{2k_T}$$  \hspace{1cm} (3.11)

$$N_F = \Phi_F[^3M^*]_0$$  \hspace{1cm} (3.12)
3.3 TRIPLET-TRIPLET ANNIHILATION

RESULTS AND DISCUSSION

Figure 3.3 - A) Double logarithmic plot of PtTPBP/PMI. PtTPBP was excited at 635 nm and delayed fluorescence from PMI was detected between 450-650 nm.

To effectively visualize the two sensitized TTA-UC delayed fluorescence regimes, a double logarithmic plot of pulse energy versus the emission intensity, Figure 3.3, was created. At low laser energies, only a fraction of $^3$PtTPBP$^*$ molecules are generated, consequently only a small population of $^3$PMI$^*$ is formed. With a small $[^3$PMI$^*]$, $k_T$ is the dominant decay pathway and the sensitized TTA-UC delayed fluorescence is dependent on the square of $^3$PMI$^*$ concentration. In a double logarithmic plot, quadratic dependence appears as a line with a slope of 2. At low laser powers in Figure 3.3, the fit of the experimental data is equal to 1.9, indicating a quadratic dependence of the delayed fluorescence. As the laser power is increased, the steady state threshold $^{102}$ (where $k_T = k_{TT}$) is reached at approximately 8 mJ/pulse. After this threshold, $k_{TT}$ is the dominant decay pathway.
and delayed fluorescence from sensitized TTA-UC scales linearly with increasing $[^3\text{PMI}^*]$. In a double logarithmic plot linear dependence appears as a line with a slope of 1. The fit of the data after the steady state threshold in Figure 2.1 has a slope of 1.0, indicating linear scaling of sensitized TTA-UC delayed fluorescence from PMI.

To demonstrate the quadratic and linear nature of the two sensitized TTA-UC delayed fluorescence regimes, the data for the low laser powers and high laser powers were normalized to the highest value of each regime, Figure 3.4. In both panels in Figure 3.4, the red line corresponds to the quadratic equation $y = x^2$ and the blue line corresponds to the linear equation $y = x$. If the sensitized TTA-UC delayed fluorescence of PMI follows first order kinetics at low pulse energies, the normalized data should fall along the $y = x^2$. In panel A of Figure 3.4, the data from the second order kinetic regime has been normalized to the largest value along the $m = 1.9$ line. The resulting data does indeed fall along the $y = x^2$ line, indicating that delayed fluorescence from PMI does follow first order sensitized TTA-UC kinetics at low laser energies. Additionally, at higher pulse energies the normalized data for the second order sensitized TTA-UC kinetic regime should fall along the line $y = x$. In panel

![Figure 3.4](image-url)
B of Figure 3.4, the normalized values for delayed fluorescence emission does fall along the \( y = x \) line, indicating that the sensitized TTA-UC delayed fluorescence of PMI does follow second order kinetics at higher pulse energies.

![Figure 3.5](image)

**Figure 3.5** - A) Triplet-Triplet Annihilation Quantum yield based on pulse energy. B) Spectra used to calculate the TTA Quantum Yield. Prompt emission was excited at \( \lambda_p = 478 \text{ nm} \). The sensitized delayed fluorescence was excited at \( \lambda_d = 614 \text{ nm} \). OD at both wavelengths was OD \( \approx 2.0 \).

\[
\Phi_{TTA} = \frac{2 F_d E_p \lambda_d}{F_p E_d \lambda_p} / \Phi_{TET} \tag{3.13}
\]

To measure the efficiency of the TTA process, it is necessary to calculate the quantum yield for triplet-triplet annihilation, \( \Phi_{TTA} \), Equation 3.13. In Equation 3.13, \( F_d \) and \( F_p \) are the integrated emission intensities for the delayed and prompt fluorescence.
respectively; $E_p$ and $E_d$ are the pulse energies of the prompt (p) and delayed (d) excitation; $\lambda_d$ is the delayed pulse wavelength; $\lambda_p$ is the prompt pulse energy; and $\Phi_{TET}$ is the quantum yield of the triplet energy transfer step. Since two excited state molecules are required for TTA, the maximum value of $\Phi_{TTA}$ is 0.5. The factor of two in Equation 3.13 normalizes $\Phi_{TTA}$ so that $\Phi_{TTA} = 1.0$. In order to get an accurate assessment of $\Phi_{TTA}$, virtually every photon emitted by the laser source must be absorbed by the sample, as a result the OD of the PtTPBP/PMI sample at the prompt ($\lambda_p = 478$ nm) and delayed ($\lambda_d = 614$ nm) excitation wavelengths was $\sim 2.0$. Figure 3.5A shows $\Phi_{TTA}$ versus increasing energy density of $\lambda_d$. For the PtTPBP/PMI TTA-UC system, $\Phi_{TTA}$ increases with increasing energy density until a plateau is reached at near 3 mW cm$^{-2}$, after which $\Phi_{TTA}$ decreases with increasing pulse energy. At the plateau, $\Phi_{TTA} = 0.62$ for PtTPBP/PMI.

Kinetically speaking, the increase in $\Phi_{TTA}$ is due to the increase in $^3$PMI$^*$ concentration. As the pulse energy increased, the more $^3$PtTPBP$^*$ molecules are generated. Because $\Phi_{TET}$ for PtTPBP/PMI is efficient, an increasing $^3$PtTPBP$^*$ concentration increases the concentration of $^3$PMI$^*$. A higher population of $^3$PMI$^*$ makes it more likely for the desired triplet-triplet annihilation product, $^1$PMI$^*$, to be formed.

<table>
<thead>
<tr>
<th>$\Phi_{ISC}$</th>
<th>$\Phi_{TET}$</th>
<th>$\Phi_{TTA}$</th>
<th>$\Phi_F$</th>
<th>$\Phi_{UC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.70</td>
<td>0.94</td>
<td>0.62</td>
<td>0.93</td>
<td>0.37</td>
</tr>
</tbody>
</table>

$\Phi_{UC} = \Phi_{ISC}\Phi_{TET}\Phi_{TTA}\Phi_F$  \hspace{1cm} (3.14)

Knowing $\Phi_{TTA}$, $\Phi_F$, $\Phi_{ISC}$, and $\Phi_{TET}$ makes it possible to calculate the upper limit for $\Phi_{UC}$ using Equation 3.14$^{180}$. Table 3.1 contains the values for $\Phi_{TTA}$, $\Phi_F$, and $\Phi_{TET}$ obtained in
this work along with $\Phi_{ISC}$ for PtTPTP obtained by Borek et. al\textsuperscript{136}. Using the values from Table 3.1 and Equation 3.14, $\Phi_{UC} = 0.37$, which agrees with the theoretical maximum.

![Figure 3.6](image_url)

**Figure 3.6** - Kinetic trace for 2-Acetonaphthone taken at 430 nm and the kinetic trace for a solution of 2-Acetonaphthone and PMI taken at 532 nm used to calculate $\varepsilon_T$ for PMI.

In order to calculate the remainder of the kinetic parameters for TTA-UC, the triplet extinction coefficient, $\varepsilon_T$, for PMI had to be determined. Using 2-Acetonaphthone (2-Acn) as a standard, $\varepsilon_T$ for PMI was calculated using equation 3.15\textsuperscript{91,196,197}. In equation 3.15, $\varepsilon_T$ is the triplet extinction coefficient, $\Delta A$ is the maximum change in optical density of the sample, (A) represents the acceptor (PMI), and (D) represents the donor (2-Acn). The established triplet extinction coefficient for 2-Acn is $\varepsilon_T = 10,500 \text{ M}^{-1} \text{ cm}^{-1}$ at 430 nm\textsuperscript{197}. Solving Equation 3.15 for $\varepsilon_T(A)$ results in a triplet extinction coefficient of $\varepsilon_T = 8354 \text{ M}^{-1} \text{ cm}^{-1}$ for PMI at 532 nm.
Figure 3.7 - Kinetic trace of PMI taken at 532 nm. Obtained by exciting PtTPBP at 614 nm (1.0 mJ/pulse) and then collecting transient absorption spectra of PMI starting 75 µs after the laser pulse and every 10 µs intervals extending out to 2000 µs after the laser pulse. The red line is the line of best fit using Equation 3.16.

\[ \Delta A_t = \frac{\Delta A_0 (1 - \beta)}{e^{k_T t} - \beta} \]  

(3.16)

\[ \beta = \frac{k_{TT}[^3M^*]_0}{k_T + k_{TT}[^3M^*]_0} \]  

(3.17)

The final piece of kinetic data necessary in understanding the TTA-UC process of PtTPBP/PMI is a kinetic trace of \(^3\)PMI\(^\ast\), Figure 3.7. In Figure 3.7 a kinetic trace of \(^3\)PMI\(^\ast\) sensitized by PtTPBP is seen. The kinetic trace for \(^3\)PMI\(^\ast\) was fit using Equation 3.16, which is the integrated solution of Equation 3.5 as described by Bachilo and Weismann\(^{198}\). Fitting the kinetic trace of \(^3\)PMI\(^\ast\) with Equation 3.16 determines the values of \(k_T\), the first order and pseudo-first order triplet decay pathways, and \(\beta\), the percentage of triplet molecules decaying through the triplet-triplet annihilation pathway (Equation 3.17\(^{190,195}\)). The pulse energy used
to obtain the values in Table 3.2 was 1.0 mJ/pulse was selected due to $\Phi_{\text{TTA}}$ being close to its maximum value at this pulse energy.

<table>
<thead>
<tr>
<th>Pulse Energy (mJ)</th>
<th>$\Delta A_0$</th>
<th>$[^3\text{M}^*]_0$ (M)</th>
<th>$k_T$ (s$^{-1}$)</th>
<th>$\beta$ (s$^{-1}$)</th>
<th>$\alpha$ (s$^{-1}$)</th>
<th>$k_{\text{TT}}$ (M$^{-1}$s$^{-1}$)</th>
<th>$f_T$</th>
<th>$f_{\text{TT}}$</th>
<th>$\eta_c$</th>
<th>$\Phi_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.0174</td>
<td>2.08 x 10$^{-6}$</td>
<td>180</td>
<td>6.20 x 10$^3$</td>
<td>2.97 x 10$^9$</td>
<td>0.10</td>
<td>0.90</td>
<td>0.69</td>
<td>0.67</td>
<td></td>
</tr>
</tbody>
</table>

Obtaining $k_T$ and $\beta$ allows for the calculation of $k_{\text{TT}}$, the triplet-triplet annihilation rate constant. In addition, $\alpha, f_T, f_{\text{TT}}, \eta_c$ and $\Phi_0$ can be calculated. The parameter $\alpha$ is the rate of molecules decaying via first order and pseudo-first order kinetics, $k_T$. The parameters $f_T$ and $f_{\text{TT}}$ represent the fraction of molecules decaying via first order pathways and the triplet-triplet annihilation pathways, respectively. The parameter $\eta_c$ is the efficiency of the triplet-triplet annihilation decay pathway. Finally, the $\Phi_0$ parameter is the initial efficiency of the triplet-triplet annihilation process; essentially representing $\eta_c$ at the highest concentration of $[^3\text{PMI}^*]$.

To calculate the sensitized TTA-UC parameters, the initial concentration of $[^3\text{PMI}^*]$ had to be calculated using the maximum $\Delta A$ value obtained from the kinetic trace in Figure 3.7 and the $\varepsilon_T$ calculated previously using Equation 3.18. Once the value of $\beta$ was determined, $f_{\text{TT}}$ can be calculated using Equation 3.19. Knowing $f_{\text{TT}}$ allows for the calculation of $f_T$ using Equation 3.20. The rate parameter $\alpha$ is calculated using $\beta$ and $k_T$ using Equation 3.21. The most important rate constant for sensitized TTA-UC, $k_{\text{TT}}$, is calculated based on $\alpha$ and $[^3\text{M}^*]$ using equation 3.22. For PMI, $k_{\text{TT}}$ is 2.97 x 10$^9$ M$^{-1}$ s$^{-1}$. This value of $k_{\text{TT}}$ is below the diffusion limit in toluene$^{127}$, 1.2 x 10$^{10}$ M$^{-1}$ s$^{-1}$, signifying that PMI triplet-triplet annihilation is diffusion limited. The triplet-triplet-annihilation efficiency parameter, $\eta_c$, can be calculated knowing $\Phi_{\text{TTA}}$ (Table 3.1) and the fraction of $[^3\text{PMI}^*]$ undergoing triplet-
triplet annihilation using Equation 3.23. The final parameter, $\Phi_0$, is dependent on the percentage of molecules undergoing triplet-triplet annihilation, $\beta$, and the triplet-triplet annihilation efficiency parameter, $\eta_c$, Equation 3.24.

\[
\begin{align*}
\left[^3M^\ast\right]_0 &= \frac{\Delta A_0}{\varepsilon_T} \\
 f_{TT} &= 1 - \frac{\beta - 1}{\beta} \ln(1 - \beta) \\
 f_T &= 1 - f_{TT} \\
 \alpha &= \frac{\beta k_T}{1 - \beta} \\
k_{TT} &= \frac{\alpha}{\left[^3M^\ast\right]_0} \\
 \eta_c &= \frac{\Phi_{TTA}}{f_{TT}} \\
 \Phi_0 &= \beta \eta_c
\end{align*}
\]

The results seen in Table 3.2 indicate sensitized TTA-UC using PtTPBP and PMI operates with high efficiency. Using $\beta$ and Equation 3.19, the percentage of molecules undergoing triplet-triplet annihilation is $f_{TT} = 0.9$, much higher than previously reported\(^{196}\). Additionally, the large $\beta$ value indicates that nearly all $^3$PMI decay through the triplet-triplet annihilation pathway as opposed to first order and pseudo-first order kinetic pathways. The large values of $f_{TT}$ and $\beta$ explain why $k_T$ appears to be much lower than the values reported previously for anthracene\(^{196}\), rubrene\(^{199}\), and a BODIPY dye\(^{94}\).

Another interesting set of data in Table 3.2 are the values of $\eta_c$ and $\Phi_0$. In theory, the maximum value for $\eta_c = 0.40$. With this theoretical maximum value for $\eta_c$ and a molecule for
which $\beta = 1.0$, the maximum achievable value of $\Phi_0$ is also 0.40. For PMI, $\eta_c = 0.69$ and $\Phi_0 = 0.67$, much higher than the theoretical maximum for these parameters. Exceeding the theoretical maximum values of $\eta_c$ and $\Phi_0$ has been seen in a sensitized TTA-UC system using rubrene as the annihilating species\textsuperscript{199}. For the rubrene system, it is hypothesized that the energetics of rubrene’s $T_2$ state affect $\eta_c$ and, by extension, $\Phi_0$.

In rubrene, two annihilating species in the lowest triplet excited state, $T_1$, can annihilate to form a rubrene in the second highest triplet excited state, $T_2$. The energy of rubrene’s $T_2$ triplet state lies above the energy of rubrene’s singlet excited state. Because rubrene’s $T_2$ state is both energetically accessible by triplet-triplet annihilation and higher in energy than the excited singlet state, it is hypothesized this second pathway also contributes to $\eta_c$, resulting in values larger than $\eta_c = 0.40$ when added to the traditional triplet-triplet annihilation pathway.

It is possible PMI’s $T_2$ triplet state is energetically accessible through triplet-triplet annihilation and for the $T_2$ state to be located energetically above PMI’s excited singlet state. If this is the case, then there are two possible pathways for PMI to generate delayed fluorescence via triplet-triplet annihilation, resulting in $\eta_c$ values above the theoretical $\eta_c = 0.40$ maximum. However, the triplet states of PMI remain unstudied, so it is not possible to determine if the large $\eta_c$ is due to additive effects from the $T_2 \rightarrow \text{1S}^*$ pathway.
CHAPTER 4

CONCLUSION

The photophysics of a new acceptor molecule, PMI, were studied. This new acceptor was used in a new sensitized TTA-UC system designed using PtTPBP and PMI. Energy transfer from PtTPBP to PMI was found to be efficient based on the Stern-Volmer constant and the triplet-energy-transfer quantum yield. The delayed fluorescence of PMI via sensitized TTA-UC was verified using an excitation scan of a solution of PtTPBP and PMI and then comparing it with PtTPBP’s absorption spectrum. Comparing the prompt PMI fluorescence with the delayed fluorescence of PMI also helps verify that sensitized TTA-UC is responsible for the production of delayed fluorescence. PMI fluorescence of de-oxygenated solutions of PtTPBP and PMI were found to follow the standard quadratic-to-linear response with increasing laser power. The triplet-triplet annihilation quantum yield of the PMI was determined. The overall quantum yield of delayed fluorescence from PMI was calculated using based on the quantum yields of the various steps and was found to agree with the theoretical maximum quantum yield. Analysis of triplet-triplet annihilation kinetics revealed that \(^3\text{PMI}\) appears to prefer to decay through triplet-triplet annihilation as opposed to decaying through first-order and pseudo-first-order kinetics. Based on the values obtained for \(\eta_c\) and \(\Phi_0\), PMI appears to support the assertion by Schmit and co-workers stating \(\eta_c\) approaching unity is possible.
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APPENDIX A: SUPPLIES AND EQUIPMENT

Chemicals. Platinum(II) meso-tetraphenyltetrabenzoalphyrin (PtTPBP) was purchased from Frontier Scientific. Spectroscopic grade Toluene was purchased from Alpha Aesar and used as is. Spectroscopic grade 200 proof ethanol and spectroscopic grade methanol was purchased from Sigma Aldrich and used as is. N-(2,5-di-tert-butylphenyl)perylene-3,4-dicarboximide (PMI) was synthesized by another graduate student in the Castellano group\textsuperscript{1-3}. Rhodamine 101, Rhodamine B, and 2-Acetonaphthone was purchased from Sigma Aldrich and used as is.

Absorption and Emission Spectra. Absorption spectra for PMI and PtTPBP were collected on an Agilent 8453 UV/Vis spectrophotometer. Absorption spectra used to calculate extinction coefficients were collected using a Cary-60 UV-Vis spectrophotometer. Emission spectra of PtTPBP and PMI were collected on a FS920 fluorimeter built by Edinburgh Instruments.

Lifetime Measurements. Stern-Volmer and Triplet Energy Transfer Quantum Yields were calculated using lifetime data. Lifetime measurement data was collected on a homebuilt nitrogen dye laser described previously\textsuperscript{4}. Rhodamine B ($\lambda_{em,max} = 622$ nm, 2.13 g/L concentration in spectroscopic grade methanol) or Rhodamine 101 ($\lambda_{em,max} = 649$ nm, 2.36 g/L concentration in spectroscopic grade methanol) was excited at 337 nm and the emission wavelengths were used to excite in PtTPBP’s Q-band. The PtTPBP emission lifetime was monitored at 765 nm. Lifetime measurements were fit to a single exponential function using IGOR 6.3.
Nanosecond Transient Absorption. Nanosecond transient absorption (nsTA) data was collected using a LP920 from Edinburgh Instruments. Kinetic traces were collected on a LP920-K PMT. Total spectra were collected using either an Andor iCCD camera or an Andor iStar iCCD camera. The pump excitation source was a Vibrant optical parametric oscillator (OPO) from OPOTek Inc. Pulse energies were measure using a Coherent PowerMax powermeter or a Nova II powermeter from OPHIR Photonics Group. When necessary, the pulse energy was varied using neutral density filters. Kinetic traces (Figure 2.5) were fit using Origin2015. This system was used to collect the transient absorption spectra for PtTPBP and PMI. Additionally, this set-up was used to calculate PMI’s triplet extinction coefficient.

Power Dependence. A solution of PtTPBP/PMI was excited at 635 ± 10 nm using a continuous-watt (CW) diode laser (LHR635-001EC) from Lasermate. The energy of the laser beam was varied using neutral density filters. The pulse energy was measured on a Nova II power meter from OPHIR Photonics Group. Emission spectra for the system were collected on the same FS920 mentioned previously. Integration of the spectra was done using IGOR 6.3. The laser peak was manually removed from the data by deleting the emission values for 625 nm to 645 nm from the emission spectrum.

Quantum Yields. Spectra for the fluorescence quantum yield of PMI and were collected on the FS920. PMI’s triplet-triplet annihilation quantum yield spectra were collected on the LP920 system.

All experiments were done in de-oxygenated solutions. Solutions used in Stern-Volmer analysis and used to calculate PMI’s triplet extinction coefficient were de-oxygenated by bubbling nitrogen gas through the cuvette for a minimum of 30 minutes. All
other solutions were de-oxygenated by subjecting them to a minimum of three freeze-pump-thaw cycles in a custom-made freeze-pump-thaw cuvette fitted with a side arm.

References


