ABSTRACT

EL ROZ, KARIM. Mechanistic Insights from Transient Spectroscopy leading to Hydrogen Evolving Photocatalysis and Photon Upconversion in Water. (Under the direction of Professor Felix N. Castellano).

Solar energy conversion represents a crucial component of the renewable energy resources that is aimed to reduce carbon-based emissions in the atmosphere. Utilizing sunlight to produce H₂ through reduction of water provides an environmentally sensible and naturally abundant fuel. The generation of hydrogen gas from water using solar photons remains a formidable challenge that requires multi-faceted approaches in order to develop new photocatalytic molecular compositions.

To address this issue, we have recently developed new homogenous molecular compositions capable of directly converting water, with the aid of solar photons, into hydrogen, a combustible fuel and precious high-energy chemical feedstock. For the water splitting reaction to proceed economically for large-scale applications, efficient light absorbing sensitizers and hydrogen evolution catalysts are required.

The formulations examined in this dissertation were water-soluble ruthenium(II) photosensitizers and cobalt(II) proton reduction catalysts in conjunction with ascorbic acid as an electron donor. Subsequent to light absorption, the detailed photoinduced electron transfer mechanisms leading to hydrogen production and all rate parameters were investigated by pump-probe nanosecond transient absorption spectroscopy. Charge separated cage-escape efficiencies were extracted from transient absorption, spectroelectrochemistry, and quenching rate constants between the donor and quencher in the photocatalytic cycle. The optimized compositions were also investigated using steady state and time-resolved spectroscopy as well as conventional analytical tools (HPLC, ESI-MS, etc).
In addition to the design and synthesis of various molecules that serve as either photosensitizers or catalysts in these solar energy conversion schemes, we have designed an apparatus for parallel high-throughput screening of these photocatalytic compositions. This combinatorial approach to solar fuel photocatalysis has already led to significant advances in the fundamental understanding of hydrogen gas generation from pure water.

The second project discussed in this dissertation demonstrated the direct observation of photochemical upconversion performed homogenously in pure water in the absence of hydrophobic or surfactant additives. Photon upconversion represents a phenomenon that yields high-energy emission from low-energy absorption through sensitized triplet-triplet annihilation (TTA).

The current investigation achieved this goal using combinations of water soluble Ru(II) metal-to-ligand charge transfer (MLCT) sensitizers \([\text{Ru(bpy)}_3]^{2+}\) (bpy = 2,2'-bipyridine) and \([\text{Ru(BPS)}_3]^{4+}\) (BPS = bathophenanthroline disulfonate), in concert with \(9\)-anthracenecarboxylate anion (\(\text{AnCO}_2^-\)) and \(1\)-pyrenecarboxylate anion (\(\text{PyCO}_2^-\)).

Triplet-triplet energy transfer was identified as the exclusive quenching pathway using transient absorption spectroscopy where the characteristic \(T_1 \rightarrow T_n\) absorption bands for \(3\text{AnCO}_2^-\) and \(3\text{PyCO}_2^-\) were unambiguously identified. Transient absorption spectroscopy was also used to determine the diffusion limited rate constants for TTA and demonstrated that 75% of the initially sensitized aromatic carboxylate triplets decay through bimolecular TTA.

As photochemical upconversion relies on sequential triplet energy transfer reactions, it comes as no surprise that nonpolar media has been exclusively used to host these processes to date. However, the work presented here illustrates that with the proper selection of donor
and acceptor molecules, photochemical upconversion can indeed be realized in pure water, potentially enabling chemistry from the resulting high-energy singlet excited state.
Mechanistic Insights from Transient Spectroscopy leading to Hydrogen Evolving Photocatalysis and Photon Upconversion in Water

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Chemistry

Raleigh, North Carolina
2017

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DEDICATION

To my father Adnan and my mother Iman

To my sister Ghida and my brother Jad

To all my family and loved ones

Thank you all for the love and support
BIOGRAPHY

Karim was born and raised in the beautiful capital city of Lebanon, Beirut. After finishing high school at Ahliah, he was accepted at one of the prestigious universities in the Middle East, the American University of Beirut (AUB). Following his father’s footsteps, he decided to pursue a degree in Chemistry. He received his Bachelor of Science Degree from AUB in 2012 and conducted undergraduate research under the supervision of Professor Bilal Kaafarani. Directly after graduating, Karim came to United States for graduate school to join the research group of Professor Felix N. Castellano. In 2013, he moved to Raleigh, North Carolina with the Castellano group to complete his PhD at North Carolina State University in 2017.
ACKNOWLEDGMENTS

The work presented in this dissertation would not have been possible without the continuous support and encouragement from the people in my professional and personal life.

First, I would like to express my gratitude to my advisor Professor Felix N. Castellano for the guidance and mentoring he provided me over the years as a graduate student in his group. I was privileged to be selected among the members that moved to Raleigh, NC with the Castellano group back in 2013. Thank you for all the opportunities and for the open-mindedness of ideas to inspire new approaches in photochemistry.

Second, I would like to thank my committee members and collaborators for their assistance and helpful discussions. I would also thank Professor J. Long and Professor C. Chang at University of California, Berkley for providing us with a series of pentadentate and tetradentate cobalt (II) water reduction catalysts to investigate their photocatalytic mechanisms and fidelity under long-term photocatalytic conditions. Many thanks to Professor W. Weare and his former graduate student (Dr. A. Francis) from North Carolina State University for providing us with a series of cobaloxyime catalysts to study their photocatalytic performance. I am also grateful for the guidance and collaborative work performed with Professor R. Khnayzer (former Postdoc in the Castellano group) and for building the original high-throughput setup for rapid screening of photocatalytic compositions.

I would also like to thank my group members in the Castellano group for their collaboration and helpful discussions. Thank you Dr. Arnab Chakraborty, Dr. Barry Pemberton, Dr. Evgeny Danilov, Dr. Joseph Deaton, Dr. Kate MucCusker, Dr. Michelle
McGorty, Dr. Mykhaylo Myahkostupov, Mr. James Yarnell, and Mrs. Sofia Garakyaraghi for all of your assistance throughout my graduate school career at both Bowling Green State University and North Carolina State University.

Lastly, my sincere appreciation goes to my family for their constant support and encouragement, which has never stopped. I would also like to thank Carolina Londono and all my friends for their love and motivation throughout the years especially Wissam Farhat, Sharif Kolailet, Dr. Nader lamaa, and Dr. Giuseppe Giammanco.
# TABLE OF CONTENTS

LIST OF TABLES......................................................................................................................... x
LIST OF FIGURES ........................................................................................................................ xi

CHAPTER 1. INTRODUCTION ........................................................................................................ 1
  1.1 Global Energy Demand......................................................................................................... 1
  1.2 Solar Energy and Hydrogen Fuel.......................................................................................... 2
  1.3 Earth Abundant Transition Metal Complexes ..................................................................... 4
  1.4 The Photochemistry of [Ru(bpy)_3]^{2+}............................................................................... 6
  1.5 Homogenous Photocatalysis .................................................................................................. 10
    1.5.1 Reductive and Oxidative Quenching ............................................................................. 11
    1.5.2 Homolytic versus Heterolytic Pathways ...................................................................... 12
    1.5.3 Recent Examples of Cobalt (II) Complexes as Water Reduction Catalysts .......... 13
  1.6 Photochemical Upconversion in Water ............................................................................... 17
    1.6.1 Generalized Photon Upconversion phenomenon ...................................................... 17
    1.6.2 Förster and Dexter Energy Transfer ........................................................................... 19
    1.6.3 Quantitative Analyses of Photon Upconversion ......................................................... 21
    1.6.4 Spin Statistical factors and Triplet-Triplet Annihilations Yields ............................... 25
    1.6.5 Encapsulation and Triplet Energy Migration in Water .............................................. 26
  1.7 References .......................................................................................................................... 29

CHAPTER 2. HOMOGENOUS PHOTOCATALYSIS: SENSITIZER DESIGN AND
  MECHANISTIC INSIGHTS FROM TRANSIENT SPECTROSCOPY ........................................... 37
  2.1 Abstract ............................................................................................................................... 37
  2.2 Photocatalysis Using Co^{II}(bpyPY2Me) as Water Reduction Catalyst ............................ 39
  2.3 Outperforming The Photostability of [Ru(bpy)_3]^{2+}....................................................... 41
  2.4 Quantum Yield of Hydrogen Production ............................................................................ 44
CHAPTER 3. EFFECT OF SALT ON PHOTOCATALYSIS AND CATALYTIC CURRENT

3.1 Abstract ................................................................................. 71
3.2 Effect of Salt on Hydrogen Photocatalysis .............................. 72
3.3 Stern-Volmer Quenching ....................................................... 74
3.4 Rate of Electron Transfer from Ru (I) to Co (II) ....................... 77
3.5 Decomposition Rates of Molecular Compositions with Salt vs No-Salt ........................................................................... 78
3.6 The Involvement of an Anation-Based Pathway for Co (II) Catalyst ............................................................. 80
3.7 Unprecedented Hydrogen Production for [Ru(phen)_3]^{2+} Photosensitizer ................................................................. 83
3.8 Conclusion ............................................................................. 84
3.9 References ............................................................................ 86
3.10 Supporting Information ..................................................................... 88

CHAPTER 4. TRIPLET-TRIPLET ANNIHILATION IN WATER USING BENCHMARK RU (II) SENSITIZERS AND CARBOXYLATE ACCEPTORS ......................................................... 94
4.1 Abstract ................................................................................. 94
4.2 Photochemical Upconversion in Water .................................... 95
4.3 Transient Absorption ................................................................. 100
4.4 Power Dependence Experiment on Photon Upconversion .......... 101
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>Excimer Formation</td>
<td>102</td>
</tr>
<tr>
<td>4.6</td>
<td>Quantum Yield of Photon Upconversion</td>
<td>105</td>
</tr>
<tr>
<td>4.7</td>
<td>Kinetic Parameters of Triplet Absorption Decay Data</td>
<td>106</td>
</tr>
<tr>
<td>4.8</td>
<td>Conclusion</td>
<td>109</td>
</tr>
<tr>
<td>4.9</td>
<td>Future Direction</td>
<td>111</td>
</tr>
<tr>
<td>4.10</td>
<td>References</td>
<td>112</td>
</tr>
<tr>
<td>4.11</td>
<td>Supporting Information</td>
<td>115</td>
</tr>
<tr>
<td>5.1</td>
<td>Synthesis</td>
<td>126</td>
</tr>
<tr>
<td>5.2</td>
<td>Hydrogen Production</td>
<td>129</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Photocatalytic Experiment</td>
<td>129</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Quantum Yield of Hydrogen Production</td>
<td>131</td>
</tr>
<tr>
<td>5.2.3</td>
<td>Deuterated Experiment for Photocatalysis</td>
<td>132</td>
</tr>
<tr>
<td>5.2.4</td>
<td>Steady-State Measurements</td>
<td>132</td>
</tr>
<tr>
<td>5.2.5</td>
<td>Transient Absorption Measurements for Photocatalytic Compositions</td>
<td>133</td>
</tr>
<tr>
<td>5.2.6</td>
<td>Fraction Quenched</td>
<td>133</td>
</tr>
<tr>
<td>5.2.7</td>
<td>Cage-Escape Calculations</td>
<td>134</td>
</tr>
<tr>
<td>5.2.8</td>
<td>Electrochemistry</td>
<td>135</td>
</tr>
<tr>
<td>5.2.9</td>
<td>Spectroelectrochemistry</td>
<td>135</td>
</tr>
<tr>
<td>5.2.10</td>
<td>Real-Time Absorption Measurements for Decomposition Rates</td>
<td>136</td>
</tr>
<tr>
<td>5.2.11</td>
<td>HPLC Study</td>
<td>137</td>
</tr>
<tr>
<td>5.2.12</td>
<td>Dynamic Light Scattering (DLS)</td>
<td>137</td>
</tr>
<tr>
<td>5.3</td>
<td>Photon Upconversion in Water</td>
<td>138</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Transient Absorption Spectroscopy for Upconversion Compositions</td>
<td>138</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Stern-Volmer Kinetics</td>
<td>139</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Upconversion Power Dependence Experiment</td>
<td>139</td>
</tr>
<tr>
<td>5.3.4</td>
<td>Quantum Yield of Upconversion</td>
<td>141</td>
</tr>
<tr>
<td>5.3.5</td>
<td>Triplet Extinction Coefficient of AnCO$_2^-$ and PyCO$_2^-$ in Water</td>
<td>142</td>
</tr>
</tbody>
</table>

CHAPTER 5. EXPERIMENTAL SECTION: SYNTHESIS, INSTRUMENTATION, AND MOLECULAR CHARACTERIZATION

5.1 Synthesis | 126 |
5.2 Hydrogen Production | 129 |
   5.2.1 Photocatalytic Experiment | 129 |
   5.2.2 Quantum Yield of Hydrogen Production | 131 |
   5.2.3 Deuterated Experiment for Photocatalysis | 132 |
   5.2.4 Steady-State Measurements | 132 |
   5.2.5 Transient Absorption Measurements for Photocatalytic Compositions | 133 |
   5.2.6 Fraction Quenched | 133 |
   5.2.7 Cage-Escape Calculations | 134 |
   5.2.8 Electrochemistry | 135 |
   5.2.9 Spectroelectrochemistry | 135 |
   5.2.10 Real-Time Absorption Measurements for Decomposition Rates | 136 |
   5.2.11 HPLC Study | 137 |
   5.2.12 Dynamic Light Scattering (DLS) | 137 |
5.3 Photon Upconversion in Water | 138 |
   5.3.1 Transient Absorption Spectroscopy for Upconversion Compositions | 138 |
   5.3.2 Stern-Volmer Kinetics | 139 |
   5.3.3 Upconversion Power Dependence Experiment | 139 |
   5.3.4 Quantum Yield of Upconversion | 141 |
   5.3.5 Triplet Extinction Coefficient of AnCO$_2^-$ and PyCO$_2^-$ in Water | 142 |
LIST OF TABLES

Table 2.1 Comparison of Photophysical Properties of Ru (II) sensitizers and Performance Metrics for Hydrogen Production........................................................................................................ 52
Table 4.1 Performance Metrics of the Photochemical Upconversion Compositions .......... 99
Table 4.2 Parameters Obtained from the Fits of the Transient Absorption Decay Data ...... 107
LIST OF FIGURES

Chapter 1

1.1 Renewable sources of energy as a share of total primary energy consumption .......... 2
1.2 Redox reaction for water splitting............................................................................ 3
1.3 Generalized plot showing the abundance of different transition metals on earth........ 5
1.4 Jablonski diagram showing the energetic states and photophysical processes occurring in the excited state......................................................................................... 6
1.5 A general representation of a molecular orbital diagram for an octahedral geometry metal complexes such as [Ru(bpy)₃]²⁺ .................................................................................................. 8
1.6 Overall reactions between the excited state sensitizer (S) and ascorbic acid (H₂A) .... 10
1.7 Reductive and Oxidative quenching pathways ............................................................. 11
1.8 Homolytic and heterolytic pathways for hydrogen production through cobalt-based catalyst. ........................................................................................................................................ 13
1.9 Cobalt (II) water reduction catalysts with tetra-dentate polypyridine ligands used for homogenous photocatalysis .................................................................................................. 15
1.10 Bar graph showing the final amount of H₂ produced with six different Co (II) water reduction catalysts .................................................................................................................................. 16
1.11 Generalized Jablonski diagram illustrating the process of sensitized photochemical upconversion .................................................................................................................. 18
1.12 Representation of Förster and Dexter type of energy transfer................................. 20
1.13 Representation of the weak and strong annihilation limits as a function of laser power density ........................................................................................................................................ 23

Chapter 2

2.1 Chemical structures of the Ru (II) photosensitizers studied for photocatalysis........... 38
2.2 Structure of the water reduction cobalt (II) catalyst used in the photocatalytic experiments .................................................................................................................................. 39
2.3 Photocatalytic hydrogen production of four different Ru (II) sensitizers (O.D₄₅₂nm = 1) with 2 x 10⁻⁵ M Co₁(Ⅲ)bpyPY2Me in 0.3 M ascorbic acid (H₂A/HA) at pH 4 ........................................ 40
2.4 Regeneration experiment of hydrogen production following the addition of fresh aliquot of sensitizer ......................................................................................... 42
2.5 Absorbance spectra as a function of irradiation time under 442 nm laser excitation (He/Cd laser) at 68 mW incident power for a) [Ru(bpy)$_3$]$^{2+}$ and b) [Ru(BPS)$_3$]$^{4+}$ .................. 43

2.6 Transient absorption spectra of a degassed solution containing [Ru(bpy)$_3$]$^{2+}$ (O.D. 452 nm = 0.32) and 0.3 M of ascorbic acid at pH 4 excited at 452 nm (~ 4 mJ) at different delay times .......................................................... 48

2.7 Spectroelectrochemistry (SEC) data of a sample containing 2.4 x 10$^{-5}$ M [Ru(bpy)$_3$]$^{2+}$ in acetonitrile using a Pt honeycomb electrode operated in the glovebox .......................... 49

2.8 Kinetic transient absorption decay monitored at 505 nm as a function of catalyst Co$^{II}$(bpyPY2Me) concentration for a sample containing 2.5 x 10$^{-5}$ M [Ru(bpy)$_3$]$^{2+}$ (O.D. 452 nm = 0.36) and 0.3 M ascorbic acid at pH 4 in degassed water ...................................... 51

2.9 Mass spectrum of the headspace sample containing heavy water (D$_2$O). Conditions: 6.7 x 10$^{-5}$ M [Ru(bpy)$_3$]$^{2+}$, 2 x 10$^{-5}$ M Co(bpyPY2Me), 0.1 M H$_2$A/HA at pH=pD=4 under 452 nm excitation ........................................................................................................ 53

2.10 Hydrogen production experiment performed at different temperatures (7$^0$C – 20$^0$C – 30$^0$ C). Conditions: 1.0 x 10$^{-3}$ M [Ru(bpy)$_3$]$^{2+}$, 2 x 10$^{-5}$ M Co(bpyPY2Me), and 0.3 M H$_2$A/HA at pH 4 irradiated using blue LEDs at 452 nm ........................................... 54

2.S1 High-throughput screening for rapid optimization of hydrogen production for the compositions present in solution at pH 4 under blue LED excitation at 452 ± 10 nm. Conditions: a) [Ru(dpdpbyS)$_3$]$^{4+}$ sensitizer, 2 x 10$^{-5}$ M Co$^{II}$(bpyPY2Me), and 0.3 M H$_2$A/HA. b) [H$_2$A/HA] electron donor, 1 x 10$^{-4}$ M [Ru(dpdpbyS)$_3$]$^{4+}$, and 2 x 10$^{-5}$ M Co$^{II}$(bpyPY2Me). c) [Co$^{II}$(bpyPY2Me)], 1 x 10$^{-4}$ M [Ru(dpdpbyS)$_3$]$^{4+}$, and 0.3 M H$_2$A/HA ........................................................................................................ 61

2.S2 Regeneration experiment following the addition of fresh aliquot of Co(bpyPY2Me) under the following conditions: 0.5 M H$_2$A/HA at pH 4, 6.7 x 10$^{-5}$ M Ru II) sensitizer, and 2 x 10$^{-5}$ M Co(bpyPY2Me). Arrows indicate the time at which the sensitizer was introduced in an amount equivalent to the initial condition ........................................ 62

2.S3 UV-vis absorption spectra before and after photocatalysis for the optically matched Ru (II) sensitizers for a) [Ru(bpy)$_3$]$^{2+}$ b) [Ru(phen)$_3$]$^{2+}$ c) [Ru(dpdpbyS)$_3$]$^{4+}$ d) [Ru(BPS)$_3$]$^{4+}$. Conditions: 2x 10$^{-5}$ M Co(bpyPY2Me), 7.0 x 10$^{-5}$ M Ru(II), and 1 M H$_2$A/HA at pH 4 under 452 ± 10 nm blue LED excitation .......................................................... 63

2.S4 Transient absorption spectra of actinometer [Ru(bpy)$_3$]$^{2+}$ in degassed water (O.D. 452 nm = 0.32) excited at 452 nm (~ 4 mJ) at different delay times .................................................. 64

2.S5 Transient absorption spectra of [Ru(BPS)$_3$]$^{4+}$ in degassed water (O.D. 452 nm = 0.32) excited at 452 nm (~ 4 mJ) at different delay times .................................................. 64

2.S6 Transient absorption spectra of a degassed solution containing [Ru(BPS)$_3$]$^{4+}$ (O.D. 452 nm = 0.32) and 0.3 M of ascorbic acid at pH 4 excited at 452 nm (~ 4 mJ) at different delay times .......................................................................................... 65
2.8 Spectroelectrochemistry (SEC) data of a sample containing 2 x 10⁻⁵ M [Ru(BPS)₃]⁴⁻ in acetonitrile using a Pt honeycomb electrode operated in the glovebox.  

Chapter 3  

3.1 Hydrogen production as a function of different salts added with a) Ru(bpy)₃²⁺ and b) Ru(BPS)₃⁴⁺ sensitizer upon photoexcitation at 452 ± 10 nm.  

3.2 Dynamic photoluminescence quenching of the excited state a) [Ru(bpy)₃]²⁺ and b) [Ru(phen)₃]²⁺ with quencher ascorbic acid/ascorbate (H₂A/HA) at pH 4 in degassed water with 0.3 M of NaOtf (red) vs no salt (black).  

3.3 Dynamic photoluminescence quenching of the excited state a) [Ru(dpdpbyS)₃]⁺ and b) [Ru(BPS)₃]⁺ with quencher ascorbic acid/ascorbate (H₂A/HA) at pH 4 in degassed water with 0.3 M of NaOtf (red) vs no salt (black).  

3.4 Kinetic transient absorption decay monitored at 505 nm as a function of catalyst CoII(bpyPY2Me) concentration for a sample containing 0.3 M of NaOtf, 2.5 x 10⁻⁵ M [Ru(bpy)₃]²⁺ (O.D.₄5₂ nm = 0.36) and 0.3 M ascorbic acid at pH 4 in degassed water.
3.5 Absorption spectra showing the stability of the sensitizer as a function of irradiation time under 443 nm laser (He/Cd) at 68 mW incident power ........................................ 79

3.6 Electrochemical measurement for Co\textsuperscript{II}(bpyPY2Me) catalyst as a function of salt concentration of NaOtf. ................................................................. 82

3.7 Hydrogen production plot. Conditions: 6.7 x 10\textsuperscript{-5} M Ru(phen)\textsubscript{3}\textsuperscript{2+} sensitizer, 2 x 10\textsuperscript{-5} M Co(bpyPY2Me), and 0.3 M H\textsubscript{2}A/HA\textsuperscript{-} (ascorbic acid) at pH 4 with 0.3 M NaOtf ............. 84

3.8 Hydrogen production was not generated when 0.3 M of KNO\textsubscript{3} salt was added to the reaction mixture ...................................................... 88

3.9 H\textsubscript{2} production as a function of Co\textsuperscript{II}(bpyPY2Me) catalyst concentration .................. 89

3.10 H\textsubscript{2} production as a function of Co\textsuperscript{II}(bpyPY2Me) catalyst concentration with 0.3 M of NaOtf ................................................................. 90

3.11 Dynamic photoluminescence quenching of the excited state Ru(bpy)\textsubscript{3}\textsuperscript{2+} and quencher ascorbate in degased water with salt vs no salt. Excited state lifetime decay a) No salt added. b) with 0.3 M NaOtf ........................................ 91

3.12 HPLC study experiment demonstrating the stability of the Ru (II) sensitizer and Co (II) catalyst during photocatalysis ......................................................... 92

3.13 Cyclic voltammetry and differential pulse voltammetry of the Co\textsuperscript{II}(bpyPY2Me) catalyst with NaOtf (red line) and without salt (black line) ............................................ 93

Chapter 4

4.1 Sensitizers and acceptors/annihilators used in this study ........................................ 96

4.2 Absorption (solid lines) and normalized photoluminescence (dashed lines) spectra for sensitizers and acceptors/annihilators studied ................................................................. 97

4.3 Upconverted emission spectra sensitized by [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} (A\textsubscript{488 nm} \approx 0.2) in degassed water for a) 3.2 mM of AnCO\textsubscript{2}\textsuperscript{-} (blue line) and b) 3.6 mM PyCO\textsubscript{2}\textsuperscript{-} (green line). ............ 98

4.4 Transient absorption data of [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} with AnCO\textsubscript{2}\textsuperscript{-} and PyCO\textsubscript{2}\textsuperscript{-} respectively in H\textsubscript{2}O solvent ........................................................................................................... 100

4.5 Photoluminescence upconverted emission spectra of a) 3 mM of AnCO\textsubscript{2}\textsuperscript{-} and b) 3.2 mM of PyCO\textsubscript{2}\textsuperscript{-} respectively sensitized by [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} (A\textsubscript{488 nm} \approx 1) in degassed H\textsubscript{2}O using an Ar/Kr laser at 488 nm excitation at different power intensities .................................. 101

4.6 A qualitative Jablonski diagram illustrating the overall process of photochemical upconversion with two absorbed photons to generate one upconverted emission. ........ 103

4.7 Stability of the upconverted emission of AnCO\textsubscript{2}\textsuperscript{-} sensitized by [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} in degassed H\textsubscript{2}O under continuous-laser beam excitation at 488 nm for 3.5 hour. ........ 104
4.8 Transient absorption decay at 420 nm of $3.4 \times 10^{-5}$ M $[\text{Ru(bpy)}_3]^{2+}$ and 3.78 mM $\text{AnCO}_2^-$ in degassed water measured as a function of pulsed energy .................................. 108

4.1 S1 Upconverted emission spectra of 3.1 mM of $\text{AnCO}_2^-$ sensitized by $[\text{Ru(BPS)}_3]^{4+}$ ($\lambda_{514} \approx 0.2$) in degassed D$_2$O (blue line) as a function of 514 nm excitation .................................. 115

4.1 S2 Upconverted emission spectra of 2.8 mM of $\text{AnCO}_2^-$ sensitized by $[\text{Ru(bpy)}_3]^{2+}$ ($\lambda_{514} \approx 0.1$) in degassed D$_2$O (black line) and H$_2$O (blue line) at 514 nm excitation wavelength ................................................................. 115

4.1 S3 Dynamic photoluminescence quenching of Ru(II) photosensitizers by $\text{AnCO}_2^-$ and $\text{PyCO}_2^-$ respectively monitored at 625 nm in degassed D$_2$O ............................................. 116

4.1 S4 Dynamic photoluminescence quenching of Ru(II) photosensitizers by $\text{AnCO}_2^-$ and $\text{PyCO}_2^-$ respectively monitored at 625 nm in degassed H$_2$O ............................................. 117

4.1 S5 Stern-Vomer plots of samples prepared in degassed H$_2$O solvent. a) $[\text{Ru(bpy)}_3]^{2+}$ quenched by $\text{AnCO}_2^-$ (black square) and $\text{PyCO}_2^-$ (red circles). b) $[\text{Ru(BPS)}_3]^{4+}$ quenched by $\text{AnCO}_2^-$ (black square) and $\text{PyCO}_2^-$ (red circles) ............................................. 118

4.1 S6 Stern-Vomer plots of samples prepared in degassed D$_2$O solvent. a) $[\text{Ru(bpy)}_3]^{2+}$ quenched by $\text{AnCO}_2^-$ (black square) and $\text{PyCO}_2^-$ (red circles). b) $[\text{Ru(BPS)}_3]^{4+}$ quenched by $\text{AnCO}_2^-$ (black square) and $\text{PyCO}_2^-$ (red circles) ............................................. 118

4.1 S7 Nanosecond transient absorption spectroscopy of $[\text{Ru(bpy)}_3]^{2+}$ ($\lambda_{452} \approx 0.35$) excited at 452 nm ($\sim 3$ mJ/pulse) in D$_2$O vs H$_2$O solvent ............................................. 119

4.1 S8 Transient absorption data of $[\text{Ru(bpy)}_3]^{2+}$ with $\text{AnCO}_2^-$ and $\text{PyCO}_2^-$ respectively in D$_2$O solvent ................................................................. 120

4.1 S9 Nanosecond transient absorption spectroscopy of $[\text{Ru(BPS)}_3]^{4+}$ ($\lambda_{452} \approx 0.35$) excited at 452 nm ($\sim 3$ mJ/pulse) in D$_2$O vs H$_2$O solvent ............................................. 121

4.1 S10 Transient absorption data of $[\text{Ru(BPS)}_3]^{4+}$ with $\text{AnCO}_2^-$ and $\text{PyCO}_2^-$ respectively in H$_2$O solvent ................................................................. 122

4.1 S11 Transient absorption data of $[\text{Ru(BPS)}_3]^{4+}$ with $\text{AnCO}_2^-$ and $\text{PyCO}_2^-$ respectively in D$_2$O solvent ................................................................. 123

4.1 S12 Stability of the upconverted emission of 3 mM of $\text{PyCO}_2^-$ sensitized by 0.3 mM of $[\text{Ru(bpy)}_3]^{2+}$ in degassed H$_2$O upon 488 nm excitation for 1.5 hour ............................................. 124

4.1 S13 The triplet extinction coefficient of $\text{AnCO}_2^-$ ($\lambda^3 \epsilon = 39,000$ M$^{-1}$cm$^{-1}$) and $\text{PyCO}_2^-$ ($\lambda^3 \epsilon = 21,200$ M$^{-1}$cm$^{-1}$) were averaged as a function of pulsed energy ............................................. 125

Chapter 5

5.1 High-throughput screening apparatus for rapid optimization of hydrogen production compositions ................................................................. 125
5.2 A representation of the home-built real-time absorption experiment to monitor the absorption spectra for the photocatalytic solution under He/Cd laser (452 nm; 68 mW) irradiation .......................................................................................................................... 132

5.3 Illustration of the laser beam irradiated along the edge-geometry square cuvette to correct for the inner filter effect and avoid the reabsorption of the upconverted emission 136

APPENDIX

A.1 $^1$H NMR of Na$_4$[Ru(dp bpyS)$_3$] in MeOD solvent performed on 400 MHz.............. 145
A.2 MALDI of Na$_4$[Ru(dp bpyS)$_3$] .................................................................................. 146
A.3 $^1$HNMR of Na[AnCO$_2$] in D$_2$O solvent performed on 400 MHz ............................... 147
A.4 IR spectra of 9-Antracenecarboxylic acid and Sodium 9-Antracenecarboxylate .... 148
CHAPTER 1. INTRODUCTION

1.1 Global Energy Demand

The search for alternative sources of energy has captured the attention of many researchers over the years and has propelled scientists to seek better means in diversifying our planet’s energy supply. With the aid of medical developments, the population of earth continues to grow everyday. The United Nations predicts more than 11 billion people will inhabit earth in 2100. Consequently, this larger future population will encounter an increasing global energy demand.

Recent studies project an increase in energy consumption from the current rate of about 13 TW per year to 50 TW per year by the end of the century. Assuming that most individuals use fossil fuels and natural resources as a source of energy, the remaining by-product wastes would be unnecessary carbon-based emissions and exhausts that will put our global atmosphere at risk.

From Figure 1.1, the majority of the population’s energy supply comes from oil, natural gases, and coal. One disadvantage of using these natural resources is their expiration date. Hence, if we continue to extract oil, coal, petroleum, natural gases, and other natural resources, the earth’s reserve energy supplies will eventually be depleted. The other drawbacks are the aftermath and the remainder repercussions caused by the leftover by-products and their effects on living beings and global warming.

Based on these facts, it is essential to find alternative sources of energy that will energize our technological machines without deteriorating our global atmosphere. To date,
renewable energy represents less than 10 % of the total global energy consumption, due to the high cost of infrastructure (balance of systems) with respect to established carbonaceous technologies.\(^3\)

**Figure 1.1** Renewable sources of energy as a share of total primary energy consumption. Data was reproduced from reference (5).

### 1.2 Solar Energy and Hydrogen Fuel

Finding inexpensive, clean, and sustainable energy sources represents a promising solution to step away from the carbon-based emissions. Solar energy is one of several options that is considered a potential solution for this particular energy case.\(^1\) The sun delivers about $$1.2 \times 10^{34} \text{ J}$$ of energy per hour to earth. However, efficiently harvesting this energy remains a challenge.\(^6\)

Photochemical reactions may provide an avenue to mimic the solar energy conversion processes of photosynthesis.\(^7,8\) Many studies have taken inspiration from this process towards
the development of artificial photosynthetic schemes to convert solar energy into electric energy (photovoltaics) or potential energy in chemical bonds.\textsuperscript{9–11} Solar energy is a promising and appealing alternative to fossil fuels and other natural resources. First, it is viable and its driving force comes from photons originated from the sun. Second, it is a clean and an environmentally friendly source. Utilizing solar energy in the production of hydrogen gas via water splitting represents a promising route towards the large scale formation of solar fuels.\textsuperscript{11}

Hydrogen, a fuel with remarkable properties including high energy density and non-carbon based combustible by-products, is usually generated through steam reforming of natural gas or from coal in the refining industries.\textsuperscript{12} However, such procedures produce carbon monoxide and carbon dioxide as by-products and the respective cost of the obtained energy on an industrial scale is considered excessive.\textsuperscript{13}

Alternatively, molecular systems can be engineered to produce hydrogen gas from pure water through photocatalysis.\textsuperscript{14} Such approaches would result in a clean and applicable source of energy that has the potential to meet the growing global energy demand. Over the years, scientists have shown that molecular compositions can be understood in mechanistic

\[
\begin{align*}
4 \text{H}^+ + 4\text{e}^- & \rightarrow 2 \text{H}_2 & E_\text{Anode}^0 &= + 1.23 \text{ V} \\
\text{O}_2 + 4 \text{H}^+ + 4\text{e}^- & \rightarrow 2 \text{H}_2\text{O} & E_\text{Cathode}^0 &= 0 \text{ V} \\
2 \text{H}_2\text{O} & \rightarrow 2 \text{H}_2 + \text{O}_2 & E_\text{Cell}^0 &= [E_\text{Cathode}^0 - E_\text{Anode}^0] = - 1.23 \text{ V}
\end{align*}
\]

Figure 1.2 Redox reaction for water splitting
detail and therefore can be improved.\textsuperscript{15} Hydrogen gas can be generated from proton reduction in water using visible light, and this catalysis drives the thermodynamically uphill process to split water into $\text{H}_2$ and $\text{O}_2$. The same energy required to free the H-H from its stable carrier water can be used in the reverse reaction, Figure 1.2.\textsuperscript{7–12,14,15}

The combustion product of $\text{H}_2$ is water and heat energy. The heat energy can be collected and transformed into electrical power. The reverse of water splitting illustrates the closed-cycle, chemical-conversion sequence that is both green and sustainable. This process can provide insight and lay important foundations for further developments in the field of solar energy.\textsuperscript{15–17}

### 1.3 Earth Abundant Transition Metal Complexes

In order for water splitting to work efficiently, molecular compositions consisting of photosensitizer, electron donor, and water reduction catalyst need to be present in water to produce hydrogen gas. The photosensitizer absorbs a photon to generate an excited state sensitizer. First row transition metal-based photosensitizers that absorb photons in the visible spectrum such as copper, cobalt, iron, zinc, and nickel are earth abundant, Figure 1.3. However, they are not photo-stable and they tend to decompose or undergo geometrical distortions in their excited states.\textsuperscript{18–20}

The benchmark ruthenium(II) metal-to-ligand charge transfer (MLCT) complexes have been studied for decades as photosensitizers for hydrogen production in water because of their attractive electrochemical and photophysical properties.\textsuperscript{21–23} Although ruthenium is not among the most abundant elements on earth, the benchmark [$\text{Ru}(\text{bpy})_3]^{2+}$ MLCT
chromophore has been shown to possess appropriate energetics for both water oxidation and water reduction.\textsuperscript{24,25} As such, these complexes lay important groundwork for further development in designing more photo-stable and energetically favorable photosensitizers.\textsuperscript{26–30}

On the other hand, complexes of iridium, rhenium, and osmium, which are less earth abundant, have shown improved performance metrics as photosensitizers compared to [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} in select hydrogen production systems, mostly in organic solvent/water mixtures.\textsuperscript{31–34} However, despite their superiority in photocatalysis, many of these molecules have very low molar absorptivity in the visible region.\textsuperscript{34,35} In addition, platinum(II) and select organic chromophores have been shown to be promising candidates as photosensitizers for solar hydrogen production, but they tend to photo-bleach rapidly during photocatalysis.\textsuperscript{36–38}
1.4 The Photochemistry of [Ru(bpy)₃]²⁺

Upon photoexcitation, the molecule or chromophore gets excited from the ground state to the excited state. The most common representation of electronic states is demonstrated through a Jablonski diagram, showing the energetic states and the photophysical processes that can occur in the excited state, as seen in Figure 1.4. S₀ and S₁ are the singlet ground-state and the singlet excited-state respectively. T₁ corresponds to the first triplet-excited state. The triplet-excited state is lower in energy than the singlet-excited state.

The population of S₁, the singlet excited-state, occurs when one electron with an opposite spin gets excited to a higher energy level, whereas the triplet excited-state is produced when one electron with the same spin character is generated to the higher energy

Figure 1.4 Jablonski diagram showing the energetic states and photophysical processes occurring in the excited state.
level. Using the spin multiplicity 2s+1, if the spin quantum number (s) is 0, this generates a singlet state. If (s) is equal to 1, then the spin multiplicity becomes 3, signifying a triplet excited state formation.

Subsequent to light absorption, an electron gets excited from the ground state to the excited state through a Franck-Condon allowed transition occurring at a femtosecond time scale. These vertical transitions taking place have the same electronic spins, suggesting that the allowed transition is to a singlet-excited state. According to Kasha’s rule, the rate of internal conversion is much faster than the rate of radiative decay. Fluorescence is achieved when the radiative decay occurs from the lowest energy singlet excited state to the ground state.\(^{40}\)

The transition from the singlet excited state to the triplet excited state is spin-forbidden. But with the heavy atom effect, the spin-orbit coupling is enhanced because the rate of intersystem crossing becomes a feasible course. The presence of heavy atom increases the probability of the spin-forbidden transition from the singlet-excited state to the triplet-excited state, leading to electrons with identical spins (unpaired electrons). Next, the electrons can non-radiatively decay back to the ground state or radiatively decay as phosphorescence.\(^{41,42}\)

An interesting representation of such phenomenon can be observed with ruthenium(II) complexes.\(^{43}\) The photochemistry of Ru(II) complexes have attractive electrochemical and photophysical properties.\(^{21,44-50}\) These complexes have a (d\(^6\)) valence electronic configuration and tend to form octahedral geometry complexes with polypyridine ligands. The binding site is between the metal center ruthenium and the nitrogen on the
ligand. Upon ligand coordination, the octahedral geometry field splits the five degenerate (d) orbitals into two sets: three nonbonding ($t_{2g}$) in the lower energy and two antibonding (eg) in the higher energy levels. The nonbonding ($t_{2g}$) symmetry are formed from the orientations of $d_{xy}$, $d_{xz}$, and $d_{yz}$, whereas the latter antibonding ($e_g$) symmetry are represented by $d_{x^2-y^2}$ and $d_z^2$. The difference in energy between the nonbonding ($t_{2g}$) and the antibonding ($e_g^*$) is called the ligand field stabilization energy (LFSE).\textsuperscript{51,52}

The polypyridine ligands have $\sigma$ donor orbitals that are localized on the nitrogen atoms as well as $\pi$ bonding and $\pi^*$ antibonding orbitals that are usually delocalized on the

![Molecular Orbital Diagram](image)

**Figure 1.5** A general representation of a molecular orbital diagram for an octahedral geometry metal complexes such as [Ru(bpy)$_3$]$^{2+}$.
aromatic hydrocarbon ring. The six (d^6) electrons on the Ru(II) metal are favorably filled in the three lower energy levels (t_{2g}). Upon light absorption, an electron can get excited from the (d) orbitals on the metal to the π* orbital on the ligand demonstrating the metal to ligand charge transfer (MLCT) excited state, represented in Figure 1.5 as the lowest energy transition (3). The MLCT excited state in [Ru(bpy)_3]^{2+} is observed between 400-500 nm on the absorption spectra. The spin allowed π to π* transition designated as Ligand-Centered (LC) has a signature absorption feature between 250-300 nm. Other transition can be obtained by promoting an electron either as Metal-Centered (MC) or ligand to metal charge transfer (LMCT). All these excited states have mixed singlet and triplet excited states due to spin-orbit coupling.\(^{53-58}\)

Population of the antibonding (eg*) orbitals in the excited state suggests that the lowest energy transition is MC. As such, when placed at room temperature, the excited state lifetime becomes short-lived and no luminescence emission is observed. This clearly demonstrates that when electrons are promoted to the antibonding orbitals, fast radiationless decays are more likely to occur as well as ligand dissociation reactions. On the other hand, when the lowest energy transition is MLCT or LC, most of the electronic relaxations occur radiatively.

In this dissertation, the photosensitizers studied are ruthenium(II)-based complexes, and the water-reduction catalysts are cobalt(II)-based complexes. Cobalt is a first row transition element with high abundance. Inspired by the benchmark [Co(bpy)_3]^{2+}, the water-reduction catalysts have demonstrated strong redox activity appropriate for photocatalysis.
[Co(bpy)$_3$]$^{2+}$ has been studied for more than 30 years for catalysis, as it reacts with protons to produce hydrogen gas.$^{59-63}$

1.5 Homogenous Photocatalysis

Water-reduction reactions require a photosensitizer (S), a sacrificial electron donor (D), and a water-reduction catalyst (WRC) to produce hydrogen gas under visible light irradiation. The sacrificial electron donors are used to quench the excited state of the photosensitizer by donating an electron. Examples of sacrificial electron donors are amine derivatives such as tertiary amines, alcohols such as methanol and ethanol, or even ascorbic acid derivatives.$^{64,65}$

Previously, ascorbic acid (H$_2$A) has been shown to act as a mild reducing agent due to its reversible oxidation process to form dehydroascorbate (HA$^-$) and ascorbate radical (A$^-$).$^{66}$ Dehydroascorbate is usually hydrated and is converted irreversibly to other species. In this dissertation, ascorbic acid buffer (H$_2$A/HA$^-$) serves as a sacrificial electron donor that possesses antioxidant-redox properties with favorable energetics in acidic media to transfer an electron to the metal-centered hole generated in the excited state photosensitizer.$^{65}$

\[ H_2A \rightarrow HA^- + H^+ \]
\[ 2S^* + 2 HA^- \rightarrow 2 S^- + 2 HA^- \]
\[ 2 HA^- \rightarrow H^+ + HA^- + A \]
\[ 4 S^* + H_2A \rightarrow 2 S^- \]

**Figure 1.6** Overall reactions between the excited state sensitizer (S) and ascorbic acid (H$_2$A). Dehydroascorbate is (HA$^-$) and ascorbate radical is (A$^-$).
1.6 represents the quenching process of ascorbic acid and the Ru(II) photosensitizers.

1.5.1 Reductive and Oxidative Quenching

The general mechanism for producing hydrogen gas via photocatalysis can proceed through two different pathways: the reductive-quenching and the oxidative-quenching pathways as shown in Figure 1.7. The first initiated step for both pathways is the absorption of light by the photosensitizer to generate singlet excited states followed by intersystem crossing to form triplet excited states. The triplet excited state photosensitizer is lower in energy than the singlet excited state photosensitizer.

In the reductive-quenching pathway, the sacrificial electron donor (D) quenches the excited state of the photosensitizer (S) by filling the hole through a down hill reductive electron transfer, yielding the reduced ground state photosensitizer (S\( ^- \)) and the oxidized donor (D\( ^+ \)).\(^{62}\) From this higher energy reduced state photosensitizer, the electron in the

![Figure 1.7 Reductive and Oxidative quenching pathways. The terms are defined as sensitizer (S), sacrificial electron donor (D), and water reduction catalyst (WRC).](image-url)
HOMO level can be transferred to the catalyst (WRC) through a second down hill electron transfer step to form reduced catalyst and regenerate the ground state sensitizer (S), allowing the cycle to continue.

In the oxidative-quenching pathway, the excited-state photosensitizer donates an electron to the catalyst first, forming the reduced water-reduction catalyst and the oxidized photosensitizer \((S^+)\).\textsuperscript{32} Then, the sacrificial electron donor (D) donates an electron to the oxidized photosensitizer \((S^+)\) in the dark to regenerate the ground state photosensitizer.

To determine which quenching type is more dominant, analyses of kinetic rates of electron transfer are studied. The initial step in both quenching types requires the absorption of photon to generate the excited state photosensitizer. If the rate of electron-transfer from the sacrificial electron donor to the excited-state photosensitizer is faster than the quenching by the WRC, then this is most likely the reductive-quenching pathway. The inverse is true in the oxidative-quenching pathway. Kinetic rates are usually studied through Stern-Volmer analysis, as will be illustrated in this document. In addition, both pathways can be competitive when different factors and parameters such as concentration, temperature, and pH dependence are driving specific electron transfers to be faster than others\textsuperscript{16,24}

1.5.2 Homolytic versus Heterolytic Pathways

In conclusion to the reductive or oxidative quenching routes, an electron is finally delivered to the water-reduction catalyst, leading to the evolution of hydrogen gas. Cobalt-based catalysts were inspired by the early findings from \([\text{Co(bpy)}_3]^{2+}\) which displayed strong redox activity in homogenous catalysis and were studied for several years for their
impressive structural and electrochemical properties.\textsuperscript{62} There are two proposed approaches that the molecular catalyst can undergo to produce hydrogen: homolytic or heterolytic, Figure 1.8.\textsuperscript{67,68} Each approach requires two electrons and two protons to complete the catalytic cycle, and the sequential order is strongly dependent on the catalyst itself and the conditions at which the experiment is operating.\textsuperscript{16,69,70}

In the homolytic pathway, two metal hydride complexes come together in a bimolecular interaction and undergo a reductive elimination process for the di-hydride species to bond and evolve hydrogen gas. In essence, Co(II) is reduced to Co(I) followed by proton coordination at the less-hindered open coordination site of the metal center to form the Co(III) hydride intermediate, [Co(III)-H]. Then two [Co(III)-H] species approach at close proximity, breaking the metal-hydride bonds, forming hydrogen gas, and regenerating the

![Diagram of homolytic and heterolytic pathways for hydrogen production through cobalt-based catalyst.](image)

**Figure 1.8** Homolytic and heterolytic pathways for hydrogen production through cobalt-based catalyst.
initial Co(II) species.

Alternatively, in the heterolytic pathway, a dihydrogen-cobalt \( \sigma \) complex is formed as an intermediate after two electrons and two protons are delivered to the same metal center either consecutively or concertedly. The reduction of Co(II) to Co(I) and the formation of the [Co(III)-H] intermediate are the same as in the homolytic approach. However, from the [Co(III)-H] intermediate step, another proton is attracted to the metal center to form the proposed \( \sigma \)-H\(_2\) intermediate. Then, a metal-dihydrogen cleavage occurs to give hydrogen gas and the initial Co(II) species.

Reducing Co(II) to Co(I) initiates both pathways. The homolytic and heterolytic mechanisms are only suggested mechanisms for the photocatalytic systems. And since both pathways operate simultaneously with relative weights depending on the conditions of the reaction, it is hard to predict which one is dominant. A proposed tactic to study which pathway is more likely to occur is to identify and isolate the metal hydride intermediates that proceed with the hydrogen evolution cycle, but, as discussed earlier, this is only possible in few cases.\(^{71}\) Chao and Espenson have studied this several years ago and concluded that the bimolecular homolytic mechanism is several fold more likely to occur than the heterolytic mechanism, and that the latter is only competitive at very low concentrations of catalyst or high acid concentrations.\(^{72-75}\)

1.5.3 Recent Examples of Cobalt (II) Complexes as Water Reduction Catalysts

The Long, Chang, and Castellano groups have reported a library of Co(II) water reduction catalysts with tetra-dentate and penta-dentate ligands with improved
electrochemical and photochemical properties for hydrogen production. Results were described in our recent publication (*Energy Environ. Sci.*, 2014, 7, 1477-1488).

In Figure 1.9, the tetra-dentate Co(II) catalysts (1,2,3,4) share an open *cis* coordination site, whereas Co(II) catalysts (5,6) have an open *trans* coordination site to abstract protons from water and yield hydrogen gas. Under identical conditions and irradiation flux, these six different catalysts were compared photocatalytically. To date, catalyst 1 remains the champion tetra-dentate Co(II) water-reduction catalyst in homogenous hydrogen production.

![Figure 1.9](image)

**Figure 1.9** Cobalt (II) water reduction catalysts with tetra-dentate polypyridine ligands used for homogenous photocatalysis.
The H$_2$ bar graph shown in Figure 1.10 demonstrates the photoactivity of the six Co(II) catalysts present in solution with [Ru(bpy)$_3$]$^{2+}$ (sensitizer) and ascorbic acid buffer in water under blue LED excitation. The presence of a methyl (CH$_3$) group on the ligand backbone of the champion catalyst 1 instead of methoxy (OMe) in 3 or hydroxy (OH) in 4 has lead to the enhancement of hydrogen production. Due to the sterically hindered trans coordination site in catalysts 5 and 6, the final amount of H$_2$ accumulated was less. Incorporating electron-withdrawing groups (CF$_3$) to catalyst 2 has weakened the pyridine-Cobalt bond interactions, resulting in decreased hydrogen production performance. As such, this remarkable sensitivity of catalytic performance allows further investigations of ligand modification to improve hydrogen generation.

**Figure 1.10** Bar graph showing the final amount of H$_2$ produced with six different Co(II) water reduction catalysts. The conditions are 2 x $10^{-5}$ M of [Co(II)], 3.3 x $10^{-4}$ M [Ru(bpy)$_3$]$^{2+}$, 0.3 M ascorbic acid at pH 4 after 14 hours of irradiation under blue LEDs excitation at 452 nm. Data was reproduced from reference (45).
1.6 Photochemical Upconversion in Water

1.6.1 Generalized Photon Upconversion phenomenon

Photon upconversion represents a phenomenon that yields high-energy emission from low-energy absorption through a combination of donor and acceptor molecular pairs extending from excited state chemistry, intersystem crossing (ISC), triplet-triplet energy transfer (TTET), and triplet-triplet annihilation (TTA) processes. This wavelength-shifting technology truly glances into the future of utilizing low energy photons into higher energy light that has applications in solar energy conversion, biomedical imaging, and photovoltaics.\(^76\)–\(^78\) This technology is predicted to increase the efficiency of energy conversion in photovoltaics exceeding the Shockley-Queisser limit.\(^79\)

Parker and Hatch were the first to introduce photochemical upconversion back in the 1960s. The sensitizer and acceptor pair used were organic-based compounds with low intersystem crossing that yielded inefficient photon upconversion.\(^80\)–\(^83\) More recent investigations into this phenomenon have taken advantage of the fast intersystem crossing rates inherent to transition metal photosensitizers such as Ru(II) and Ir(III) sensitizers as well as metallloporphyrins.\(^84\)–\(^89\) And using advanced excitation and detection sources of today’s technologies,\(^90\) photochemical upconversion is now realized as a research of applicable science to detect higher energy light that is visualized by the naked eye.
In this dissertation, Ruthenium(II) photosensitizers were selected for the broad MLCT band absorption that extends to the green visible spectrum. Subsequent to light absorption, the photosensitizer gets excited to the singlet excited state followed by fast intersystem-crossing (ISC), close to near unity, to generate triplet excited states. The organic acceptors were chosen so that their triplet energy is lower than that of the sensitizer to allow for energy transfer from the latter. Thus, when the difference in energy between the triplet sensitizer and the triplet acceptor is large enough, the higher the driving force to yield triplet excited state acceptors through energy transfer process. Furthermore, as long as the energy of two combined triplet acceptors is equal to or higher in energy than the singlet fluorescence state acceptor, triplet-triplet annihilation (TTA) becomes a favorable course to yield photon upconverted emission. As such, the singlet of the acceptor is purposely nested higher in

![Figure 1.11 Generalized Jablonski diagram illustrating the process of sensitized photochemical upconversion (S = sensitizer, A = acceptor, ISC = intersystem crossing, TTET = triplet-triplet energy transfer, TTA = triplet-triplet annihilation). Note: 2 absorbed photons are required to yield 1 upconverted-emitted photon.](image)
energy than the singlet of the photosensitizer to obtain a higher energy emission from a lower energy absorption. The observation of fluorescence photon upconversion is achievable for any donor and acceptor pair as long as these energetic criteria are met, Figure 1.11.

1.6.2 Förster and Dexter Energy Transfer

In photon upconversion systems, energy transfer is the first interaction between the donor and acceptor pair, which occurs subsequent to light absorption. First, the donor (D) forms the triplet excited state (D*) and transfers energy to the acceptor (A) to form triplet-excited state acceptors (A*). The kinetic rates of energy transfer are calculated using Stern-Volmer analyses to determine the quenching rate constant (k_{sv}) and the bimolecular quenching rate (k_{q}) resulting between the donor and acceptor pair. A dynamic quenching process is defined as one that interferes with the spontaneous emission decay of the donor, thus lowering the lifetime of photoluminescence of the sensitizer. Quenching can be observed by monitoring the time resolved emission intensity or photoluminescence of the donor.

Energy transfer mechanisms can be described as dipole induced (Förster type) or exchange-induced (Dexter type) interactions\textsuperscript{91,92} Förster type is responsible for the long-range resonance interaction whereas the latter is responsible for the short-range exchange interaction. In both types, a radiationless transfer of energy occurs between the donor and acceptor.

Förster energy transfer, also referred to as Fluorescence Resonance Energy Transfer (FRET), is based on dipole-dipole coupling between the donor and acceptor pair. Over the
course of 50 years, FRET has been used more and more frequently in the biomedical research and drug discovery field, as it relies on the distance between the donor and acceptor pair to transfer energy.\textsuperscript{93} Therefore, the emission of the donor should overlap with the absorption of the acceptor to efficiently shuttle energy via a FRET mechanism. Several factors affect FRET, including the oscillator strength of the D* to D transition and the A to A* transition. Förster demonstrated that the efficiency of energy transfer is inversely proportional to the sixth-order of magnitude of the distance between the donor and acceptor, making FRET sensitive to the slightest changes in distance.

Dexter-type transfer, also referred to as Dexter electron exchange or Dexter energy transfer, occurs when an exited electron is simultaneously transferred from the donor to the acceptor while a ground state electron is transferred to the donor through an exchange transition. The overall spin state in Dexter interactions does not change. As a result the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1}
\caption{Representation of Förster and Dexter type of energy transfer.}
\end{figure}
energy transfer from singlet-to-singlet or triplet-to-triplet states becomes highly efficient and spin-allowed. Similar to Förster, it also occurs when the distance between the donor and acceptor is small (orbital overlap occurs) and mostly happens at diffusion-controlled rates. However, the Dexter mechanism is largely independent on the oscillator strength of the transition from (A) to (A*). Representation scheme of Förster and Dexter types are presented in Figure 1.12.

In photon upconversion systems, the Dexter type mechanism is responsible for the energy transfer between the donor and acceptor/annihilator pair. Since the Dexter type mechanism preserves the overall spin state of the system, triplet-triplet energy transfer (TTET) from the donor to the acceptor becomes possible. Many organic chromophores cannot access triplet states and take advantage of the long-lived triplets because of the low intersystem crossing (ISC). But utilizing the spin-allowed energy transfer from a higher energy donor in Dexter type would allow the population of that triplet excited state acceptor, inspiring further research in excited state chemistry.

1.6.3 Quantitative Analyses of Photon Upconversion

As illustrated in the photon upconversion scheme above in Figure 1.9, simultaneous two-photon excitations are required to emit one upconverted photon. Hence, the maximum efficiency of upconversion that can be achieved is 50 %. Subsequent to populating the triplet-excited state acceptors, two competing kinetic decays occur in parallel. There is the first-order decay that represents the triplet decay rate constant (kT), and the second-order decay
that corresponds to the triplet-triplet annihilation rate constant \(k_{TTA}\) as seen in Eq 1.1. \([^3M^*]\) is the concentration of the triplet excited state acceptor.

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

Eq 1.1

The integration of Eq 1.1 suggests that the kinetic rates are dependent on laser power intensity. At low power densities, the triplet decay rate \(k_T\) is much larger than \(k_{TTA}[^3M]^2\), resulting in weak triplet-triplet annihilation. Hence, the dissociation of that triplet excited state acceptor is mostly dominated by the relaxation of that excited triplet back to the ground state. It was also expressed in Eq 1.2 as \(N_f\) is the upconverted emission, and \(\Phi_f\) is the fluorescence quantum yield of the acceptor.

\[
N_f = \frac{\phi_f k_{TTA}[^3M^*]^2}{2k_T}
\]

Eq 1.2

At high power densities, triplet-triplet annihilation is strong. Instead of relaxing back to ground state, the excited state triplet acceptor finds another excited triplet to annihilate. Hence, the second-order \(k_{TTA}\) rate constant becomes larger than the triplet kinetic rate \(k_T[^3M^*]\) resulting in photochemical upconversion. It is also expressed in Eq 1.3, the integration of Eq 1.1, as the upconverted fluorescence is directly proportional to the excited state acceptors \([^3M^*]\).

\[
N_f = \phi_f[^3M^*]
\]

Eq 1.3
A representation of the upconverted emission intensity as a function of power density is shown in Figure 1.13. This graph is plotted as a double logarithmic plot to illustrate the weak annihilation limits at low laser power and the strong triplet-triplet annihilation at high power. At low power densities, the slope of 2 is an indication of a quadratic kinetic dependence as a function of laser intensity, extrapolated from Eq 1.2, where the upconverted emission \( N_f \) is directly proportional to \( [^3\text{M}^*]^2 \). As the laser the power increases, the slope deviates until it reaches a slope of 1 at high power, an indication of a linear kinetic dependence as extrapolated from Eq 1.3, \( N_f \) is directly proportional to \( [^3\text{M}^*] \). At that linear region, the quantum yield of TTA is maximized and limited by the concentration of triplet excited state acceptors/annihilators. 76

Figure 1.13 Representation of the weak and strong annihilation limits as a function of laser power density. The graph is plotted as a double logarithmic plot of upconverted emission vs power density.
Ideally, to maximize the overall quantum yield of upconversion ($\Phi_{UC}$), it is necessary to improve the efficiency of each step: intersystem-crossing ($\Phi_{ISC}$), triplet-triplet energy transfer ($\Phi_{TTET}$), triplet-triplet annihilation ($\Phi_{TTA}$), and fluorescence quantum yield of acceptor ($\Phi_f$) as seen in Eq 1.4.\textsuperscript{97,98} In most cases, the donor is selected with an intersystem-crossing ($\Phi_{ISC}$) efficiency close to near unity, and the concentration of acceptor is chosen to quench (TTET) at least 90% of the donor’s excited state, yielding ($\Phi_{TTET}$) close to unity.

$$
\Phi_{UC} = \Phi_{ISC} \times \Phi_{TTET} \times \Phi_{TTA} \times \Phi_f
$$

Eq 1.4

Quantum yield of upconversion ($\Phi_{UC}$) can be measured as a product of all the quantum yield efficiencies. Experimentally, ($\Phi_{UC}$) can be deduced relative to a known emissive standard ($\Phi_{std}$) as shown in Eq 1.5. Because the maximum upconversion yield is 50% as explained above, the expression in Eq 1.5 was multiplied by a factor of 2 to obtain a maximum conversion of 100% efficiency.

$$
\phi_{UC} = 2\phi_{std} \left( \frac{A_{std}}{A_{UC}} \right) \left( \frac{I_{UC}}{I_{std}} \right) \left( \frac{\eta_{UC}}{\eta_{std}} \right)^2
$$

Eq 1.5

Here, $A_{std}$ and $A_{UC}$ are the absorbance of the standard sample and the upconverted sample respectively. $I_{UC}$ and $I_{std}$ are the emission intensities of the upconverted sample and the standard sample respectively. And, $\eta_{uc}$ and $\eta_{std}$ are the refractive index of the upconverted sample and standard sample respectively.
1.6.4 Spin Statistical factors and Triplet-Triplet Annihilations Yields

When two triplet excited state acceptors/annihilators collide, several products can emerge as a result of that triplet fusion.\(^9\) Salteil and Atwark reported a spin-statistical analysis that gives 9 possible spin probabilities such as singlet excited state (\(^1\text{A}^*\)), triplet excited state (\(^3\text{A}^*\)), and quintet excited state (\(^5\text{A}^*\)) (Eq 1.6-1.8).\(^{100,101}\) The total nine possible spin-state outcomes were weighed according to their multiplicity product that is a total of \(1+3+5 = 9\).

In upconversion systems, the spin-statistical factors predict a maximum yield of quantum upconversion of 11.1\% (1/9) generated from the initial dissociation of the singlet excited state. However, since the quintet state is much higher in energy than the triplet state, most of those quintets will relax back to the pool of triplet excited state acceptors/annihilators.\(^9\) And by considering all these factors and taking them into account all the recycled excited triplets; the photon upconversion efficiency reaches a maximum limit of 50 \%, based on two absorbed photons.

Several research groups such as Schmidt and Castellano, have presented quantum yields of TTA above the predicted limit of spin-statistical factors by experimentally comparing the delayed (upconverted) fluorescence to the prompt fluorescence within the same solution.\(^{76,89,95,102–104}\)
To obtain precise yields for TTA, the conditions of the upconverted solution would be saturated with high concentrations of donor (O.D ≥ 2) to absorb up to 100% of the incident light and generate generous amount of excited states. The concentration of acceptor should also be high enough to quench at least 90% of sensitizer’s triplet excited state. Either quantum yield of TTA or upconversion is dependent on laser power intensity. Hence, using a pulsed laser at different power intensities allows the calculation of quantum yield of TTA according to Eq 1.9.

\[ \phi_{TTA} = \frac{2F_d E_p \lambda_d}{F_p E_d \lambda_p} \]  

Eq 1.9

Here, the upconverted sample is excited at two different excitation wavelengths separately; one excites the donor to give the delayed fluorescence (F\(_d\)), and the other directly excites the acceptor/annihilator to yield the prompt fluorescence (F\(_p\)). (E\(_p\)) and (E\(_d\)) are the corresponding laser pulse energies; (\(\lambda_p\)) and (\(\lambda_d\)) are the excitation wavelengths of the prompt and delayed experiments, respectively. By comparing the integrated emission profile of the delayed fluorescence to the prompt fluorescence at different laser pulsed energies, the quantum yield of TTA can be calculated. In general, at high-pulsed power, the TTA approaches maximum yields, rendering the strong annihilation.

1.6.5 Encapsulation and Triplet Energy Migration in Water

Most studies that investigate photochemical upconversion involve organic solvent mediums. In the past, our group has demonstrated a significant improvement
of triplet-triplet annihilation (TTA) upconversion in deareated organic non-polar solvents to facilitate the energy transfer between the donor and acceptor pair. In such non-aqueous solvents, it is possible to annihilate and populate singlet states of acceptors due to the effect of solvent and dipole interactions.

Photochemical upconversion was a challenge to achieve in water solvent alone, preventing further utilization of higher energy upconversion in the related aqueous fields. However, recent studies have demonstrated photon upconversion by having surfactant hosts or polymer-based matrices in water to permit TTA and generate singlet fluorescence. Kim and co-workers have reported photochemical upconversion in nanocapsulated materials in water that was later used towards photocatalysis. These encapsulated materials contain a solution of sensitizer and acceptor pair in an organic solvent that would retain the favorable photophysics but does not interact with the outside environment. Limited diffusion or even absolute zero diffusion occurred between the inner sphere and the outer sphere of the capsule, utilizing the advantageous kinetic properties of the donor and acceptor/annihilator in the organic non-polar solvent. These encapsulations also have low permeability of oxygen that prevents triplet excited state quenching and thus further annihilation and upconversion.

The Kim group has studied Pd(II) porphyrins as sensitizers along with perylene acceptors and other precursors in polymerized polystyrene shells. Although the capsules were surrounded by aqueous suspension, triplet-triplet energy transfer
(TTET) and triplet-triplet annihilation (TTA) were still of high efficiency because the energy transfer and triplet fusion were occurring inside the sphere of the shell.

Alternative to encapsulation of sensitizer and acceptor pair solutions in polymerized shells, Kimizuka and collaborators have demonstrated upconversion in molecular self-assembled matrices. Utilizing the concept of photon upconversion and the concept of molecular aggregations, they were able to emit higher energy photons from lower energy absorption in aqueous mediums. They have demonstrated upconverted emission in aerated water by exploring triplet energy migration in an amphiphilic molecular self-assembled environment that allowed the sensitization of acceptors and made TTA possible.\textsuperscript{105,111–114}

These nanocapsulations or aggregate environments were used to shuttle energy from the water-soluble chromophores to sensitize acceptors inside the assemblies. Although upconverted emission in these mediums is of high efficiency, it is still limited by diffusion or migration of energy, precluding further advances in solar energy conversion. To date, our group has successfully employed direct sensitization and TTA in degassed water in the absence of any micelle patterns or polymer surfactant hosts to generate blue upconverted light, inspiring new approaches in the aqueous solar research.
1.7 References


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CHAPTER 2. HOMOGENOUS PHOTOCATALYSIS: SENSITIZER DESIGN AND MECHANISTIC INSIGHTS FROM TRANSIENT SPECTROSCOPY

2.1 Abstract

Ruthenium(II) photosensitizers were studied for photocatalytic performance in conjunction with a cobalt(II) catalyst Co\textsuperscript{II}(bpyPY2Me) and ascorbic acid/ascorbate (H\textsubscript{2}A/HA) acting as electron donor. Under blue light irradiation, the benchmark [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} was demonstrated to be labile during photocatalysis and decomposed during the course of the experiment. Here, we describe Ru(II) molecular sensitizers, [Ru(BPS)\textsubscript{3}]\textsuperscript{4-} and [Ru(dpbpys)\textsubscript{3}]\textsuperscript{4-}, with an overall negative charge that revealed enhanced hydrogen production and better photostability.

The quantum yield of hydrogen production under blue LED excitation at 452 nm was 7.5 ± 0.8 % for [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} based on two absorbed photons. Using Stern-Volmer analyses, a fast electron transfer rate was observed between the Ru(II) sensitizers and the ascorbic acid/ascorbate quencher (k\textsubscript{q} \approx 10\textsuperscript{7}-10\textsuperscript{8} M\textsuperscript{-1} s\textsuperscript{-1}), values below the diffusion limit. The quantum yield was limited by the combination of the cage-escape yield of each electron transfer step as well as by the outer-sphere charge recombination.

The mechanism of hydrogen production was further investigated using pump-probe transient absorption (TA) spectroscopy. Using TA, cage-escape yields were calculated for each electron transfer step. The cage-escape yield (Φ\textsubscript{CE}) for the initial reductive quenching pair [Ru(bpy)\textsubscript{3}\textsuperscript{+}/HA] was found to be 55 % and for the second electron transfer product pair [Ru(bpy)\textsubscript{3}\textsuperscript{2+}, Co(I)], the cage-escape yield was above 85 %. [Ru(phen)\textsubscript{3}]\textsuperscript{2+} sensitizer has
resulted in no hydrogen production due to the low cage-escape efficiency of the initial electron transfer pair \([\text{Ru(phen)}_3^+/\text{HA}^-]\), which was as low as 2%. Figure 2.1 shows the structures of the Ru(II) photosensitizers investigated for hydrogen production.

![Chemical structures of the Ru(II) photosensitizers studied for photocatalysis.](image)

**Figure 2.1** Chemical structures of the Ru(II) photosensitizers studied for photocatalysis.
2.2 Photocatalysis Using $\text{Co}^{II}(\text{bpyPY2Me})$ as Water Reduction Catalyst

Using a combinatorial high-throughput setup,\textsuperscript{1} homogenous mixtures consisting of ascorbic acid buffer (sacrificial electron donor), ruthenium(II)-based photosensitizer, and cobalt(II)-based water reduction catalyst were investigated in photocatalytic reactions in the presence of pure water under visible light. The introduction of high-throughput screening of photocatalytic systems was inspired by the Bernhard group, who paved the way for extensive comparison and combinatorial evaluation of molecular compositions designed for hydrogen generation.\textsuperscript{2–4} Many researchers have adopted this combinatorial approach because it has rapidly lead to optimized conditions (concentration, pH, temperature, etc.) for both homogenous and heterogeneous systems.\textsuperscript{5,6}

In collaboration with the Long and Chang groups, a newly conceived series of Co(II) catalysts with penta-dentate and tetra-dentate ligands were studied for proton reduction.\textsuperscript{7–9} The best performing Co(II) catalyst was determined to be the $\text{Co}^{II}(\text{bpyPY2Me})$, bearing the

\[ \text{Co(bpyPY2Me)} \]

**Figure 2.2** Structure of the water reduction cobalt(II) catalyst used in the photocatalytic experiments.
tetra-dentate ligand 2-(bis(2-pyridyl)(methyl)methyl-6-pyridylpyridine, as seen in Figure 2.2. This champion water reduction catalyst has achieved turnover numbers (TON) up to 10,000 (H₂/Co) in a mixture containing [Ru(bpy)₃]²⁺ sensitizer and ascorbic acid solution under blue-light irradiation. In this chapter, Co²⁺(bpyPY2Me) was the water-reduction catalyst studied side-by-side with the Ru(II) photosensitizers and ascorbic acid.

A comparison of the final amount of hydrogen production accumulated in the headspace for the optically matched (O.D.₄₅₂ nm = 1) Ru(II) sensitizers were presented in Figure 2.3. The samples contained Ru(II) sensitizers, 2 x 10⁻⁵ M Co²⁺(bpyPY2Me), and 0.3 M H₂A/HA in 10 ml solution, and were irradiated with a 540 mW LED excitation at 452 ± 10 nm.

The results from the H₂ plot suggested that, at identical conditions, the best

![Graph a) Photocatalytic hydrogen production of four different Ru(II) sensitizers (O.D₄₅₂nm = 1) with 2 x 10⁻⁵ M Co²⁺(bpyPY2Me) in 0.3 M ascorbic acid (H₂A/HA) at pH 4. b) Mass spectrum of the analyzed headspace at the end of the experiment.](image-url)
photosensitizer performance was ranked accordingly \([\text{Ru(dp bpyS)}_3]^4+ > [\text{Ru(BPS)}_3]^4+ > [\text{Ru(bpy)}_3]^2+ > [\text{Ru(phen)}_3]^{2+}\). The first and second best, \([\text{Ru(dp bpyS)}_3]^4+\) and \([\text{Ru(BPS)}_3]^4+\), have achieved TON up to 650 \((\text{H}_2/\text{Ru})\), whereas \([\text{Ru(bpy)}_3]^2+\) reached a lower TON of 230.

Turnover numbers were strongly dependent on the concentrations utilized. Hence, under optimized conditions, the negatively charged photosensitizers achieved a TON up to 5000, Figure 2.S1. \(\text{Co}^{II}\)(bpyPY2Me) has achieved a TON of 10,000 \((\text{H}_2/\text{Co})\) at low concentrations.\(^7\)

**2.3 Outperforming The Photostability of [Ru(bpy)_3]^2+**

The benchmark \([\text{Ru(bpy)}_3]^2+\) photosensitizer has previously been shown to decompose upon light irradiation especially in the presence of other coordinating electron donors.\(^{10-13}\) In this study, \([\text{Ru(bpy)}_3]^2+\) was found to be unstable and short-lived during photocatalysis due to ligand loss and other degradation species. The photostability of the sensitizer was examined through a series of \(\text{H}_2\) regeneration experiments, UV-vis spectroscopy, and HPLC study (detailed discussion is in chapter 3).

The “plateau” region that was observed after few hours of irradiation in the \(\text{H}_2\) plot was a clear indication that the hydrogen production has stopped evolving due to the decomposition of one (or many) components during photocatalysis. The \(\text{H}_2\) regeneration plot in Figure 2.4 revealed that the limiting component in the photocatalytic mixture was the Ru (II) photosensitizer.

At eight hour-intervals after the experiment has “plateaued” and no more hydrogen production was detected, a fresh aliquot of Ru(II) sensitizer was added to the sample mixture. The hydrogen production cycle resumed its activity when identical amount of sensitizer was
These data revealed that the stability of [Ru(bpy)$_3$]$^{2+}$ was weaker than [Ru(BPS)$_3$]$^{4-}$ during the course of the experiment, as the latter demonstrated a continuous increase of hydrogen production before the addition of fresh sensitizer. Significantly, upon the addition of any other molecular component, the hydrogen production cycle failed to resume its activity, Figure 2.S2.

Figure 2.4 Regeneration experiment of hydrogen production following the addition of fresh aliquot of sensitizer under the following conditions: 0.5 M H$_2$A/HA at pH 4, 2 x 10$^{-5}$ M Co(bpyPY2Me), and Ru(II) sensitizer at 6.7 x 10$^{-5}$ M under 452 nm excitation. Arrows indicate the time at which the sensitizer was introduced in an amount equivalent to the initial condition.

When the photocatalytic samples were placed in the dark for days at room temperature and under inert atmosphere, the molecular compositions remained stable as no change was observed in the UV-vis spectrum. It was only during photoexcitation that the intrinsic instability of the sensitizer played a significant role in determining the limitations of the homogenous hydrogen production.
In our recent publication, the decomposition of $[\text{Ru(bpy)}_3]^{2+}$ to other by-products was investigated using ESI-MS. One of the bipyridine ligands on the Ru(II) complex was substituted with an ascorbte ion (from ascorbic acid dissociation), confirmed via 589 amu corresponding to $[\text{Ru(bpy)}_2\text{HA}]^+$. Another minor degradation product that was demonstrated to be inactive for photocatalysis was $[\text{Ru(bpy)}_2(\text{H}_2\text{O})_2]^{2+}$, also resulting from this ligand exchange.

**Figure 2.5** Absorbance spectra as a function of irradiation time under 442 nm laser excitation (He/Cd laser) at 68 mW incident power for a) $[\text{Ru(bpy)}_3]^{2+}$ and b) $[\text{Ru(BPS)}_3]^{4+}$. Conditions: Optically matched Ru(II) sensitizers at identical concentration of $\text{Co}^{II}\text(bpyPY2Me)} (4 \times 10^{-5}$ M) and $\text{H}_2\text{A/HA (0.5 M, pH 4)}$. Graph c) shows the decomposition rate taken at absorbance 442 nm as a function of irradiation time.
To glean insight into the relative rates of decomposition of the Ru(II) sensitizers, a real-time absorption experiment was performed as a function of a continuous-wave 442 nm laser excitation (He/Cd laser) at 68 mW incident power, Figure 2.5. [Ru(bpy)$_3$]$^{2+}$ decomposed much faster than [Ru(BPS)$_3$]$^{4-}$ in solution containing ascorbic acid/ascorbate and the Co(II) catalyst. The stability of the sensitizers was also assessed using UV-vis before and after catalysis when placed with 1 M ascorbic acid and 2 x 10$^{-5}$ M Co$^{II}$(bpyPY2Me) under blue LED excitation, Figure 2.53.

Essentially, our recent developments suggested that having a strong hydrophobic core (diphenyl phenanthroline) near the metal center would prevent this ligand substitution from occurring. In addition, the negative charge imparted on the complex from the sulfonated functional groups, for solubility purposes, have aided in shielding the complex from the ascorbate radical (HA$^-$), leading to a more photostable sensitizer.

### 2.4 Quantum Yield of Hydrogen Production

The quantum yields of photocatalysis were deduced from the initial rates of hydrogen production by taking into account the amount of hydrogen generated and the output power of the excitation source. During the first stages of photocatalysis, before the “plateau” region and the decomposition of the molecular components, the kinetic rates of hydrogen production were linear as a function of irradiation time. Hence, the quantum yield calculations were

\[
\Phi_{H_2} = \frac{2 \times n_{H_2}}{n_{\text{photons}}} \quad \text{Eq 2.1}
\]

\[
n_{\text{photons}} = \frac{P_{\text{abs}} \times t}{E_{\text{photons}} \times N_a} \quad \text{Eq 2.2}
\]
based on the amount of hydrogen production accumulated in the headspace at those initial rates with respect to the photons being absorbed according to Eq 2.1 and Eq 2.2.\textsuperscript{9,14,15}

Here, \((n_{H_2})\) is the number of moles of hydrogen gas accumulated in the headspace. \((n_{\text{Photons}})\) is the number of moles of photons absorbed. \((P_{\text{abs}})\) is the optical power (W) measured from the incident excitation source using a power meter. \((t)\) is the irradiation time in seconds (s). \((E_{\text{Photons}})\) is the energy of photons (J), and \((N_a)\) is the Avogadro’s number. Since two electrons were required to reduce the Co(II) catalyst and generate hydrogen gas, then two photons were needed to complete the cycle. Hence, the factor of 2 was included in the numerator of Eq 2.1.

Under optimized conditions, the quantum yield of hydrogen production was measured using 442 nm He/Cd laser and averaged at three different incident power densities (68 mW, 47 mW, and 25 mW). The irradiation time used to calculate the quantum yield was 30 minutes, where the hydrogen production rate was still linear. When using the same excitation source used for photocatalysis, blue LEDs at 452 ± 10 nm, identical results of quantum yields were found.

The quantum yield of hydrogen production for \([\text{Ru(phen)}_3]^{2+}\) was found to be less than 1 %, as no hydrogen production was accumulated in the headspace. For \([\text{Ru(dp bpyS)}_3]^{4+}\) and \([\text{Ru(BPS)}_3]^{4+}\) it was found to be almost identical, 6.0 ± 0.9 % and 5.9 ± 1 % respectively. The quantum yield of hydrogen production for the sample containing \([\text{Ru(bpy)}_3]^{2+}\) was about 7.5 ± 0.8 %. Due to the higher cage-escape efficiency calculated for \([\text{Ru(bpy)}_3]^{2+}\), the rate of hydrogen production was higher than the other sensitizers in the initial stages, hence the higher quantum yield of H\textsubscript{2}.
2.5 Cage-Escape Yields of The Ru(II) Sensitizer and Ascorbate Quencher

The mechanism of hydrogen production was investigated by nanosecond pump-probe transient absorption (TA) spectroscopy. Subsequent to light absorption, the Ru(II) sensitizer quantitatively yields long-lived triplet excited state sensitizers (μs), rendering them susceptible to electron transfer quenching. A series of static and dynamic spectroscopic measurements were performed to elucidate the electron transfer dynamics and evaluate the factors limiting the performance of the composition.

The excited state Ru(II) sensitizer was reductively quenched by ascorbate at pH 4 with a bimolecular rate constant of $k_q \approx 3.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, which was measured using dynamic Stern-Volmer quenching. To fully understand the rates and quantum yields of hydrogen production, cage-escape efficiencies between the donors and acceptors were obtained.

Under optimized conditions and in the absence of cobalt catalyst, the reduced sensitizer, $[\text{Ru(bpy)}_3]^+ (\varepsilon_{505\text{nm}} = 12,000 \text{ M}^{-1} \text{ cm}^{-1})$, quantitatively recombines with the oxidized ascorbate (HA$^-$) species. The cage-escape yield for the initial electron transfer product formation between $[\text{Ru(bpy)}_3]^{2+}$ and HA$^-$, termed as $[\text{Ru(bpy)}_3]^+, \text{HA}^-$, was found to be $55 \pm 5 \%$, ascertained from transient absorption and spectroelectrochemical data.

On the other hand, the cage-escape yield for the termed product $[\text{Ru(phen)}_3]^+, \text{HA}^-$ was calculated to be less than 2 %. After being quenched by (HA$^-$), the reduced radical sensitizer, $[\text{Ru(phen)}_3]^+$, did not separate from the charge transfer cage. No electrons were further transferred to reduce the Co(II) to Co(I) and complete the cycle, leading to the inactive performance of hydrogen production. A near-complete recombination of charges
was the result of back-electron transfer rate to the initial oxidized donor (HA\(^{+}\)), rates above the diffusion limit \((k_0 \approx 10^{10} - 10^{11} \text{ M}^{-1} \text{ s}^{-1})\). The cage-escape for the reduced negatively charged sensitizers, \([\text{Ru(dpbpyS)}_3]^{5-}\) and \([\text{Ru(BPS)}_3]^{5-}\), and the oxidized (HA\(^{+}\)) had similar yields of 23% and 21% respectively.

2.5.1 Representation of Cage-Escape Yield for \([\text{Ru(bpy)}_3]^{2+}\) and HA\(^{+}\)

The cage-escape yields \((\Phi_{CE})\) for the reduced Ru (II) sensitizers and the oxidized ascorbate (HA\(^{+}\)) were determined using a series of experiments of transient absorption spectroscopy, spectroelectrochemistry, and Stern-Volmer quenching. The yields were calculated relative to an actinometer, \([\text{Ru(bpy)}_3]^{2+}\) in water, according to Eq 2.3.\(^{16-19}\)

\[
\Phi_{CE} = \frac{\frac{\Delta A_{sample}}{\Delta A_{actinometer}}}{\frac{\Delta \epsilon_{sample}}{\Delta \epsilon_{actinometer}}} \times (1 - 10^{A_{actinometer}}) \times \frac{\Delta A_{actinometer}}{\Delta \epsilon_{actinometer}} \times (1 - 10^{A_{sample}}) \times \text{fraction quenched}
\]

Eq 2.3

Here, \(\Delta A_{sample}\) represents the maximum of the decay of the radical anion. \(\Delta \epsilon_{sample}\) corresponds to the maximum extinction coefficient of that radical anion at the same wavelength for \(\Delta A_{sample}\), data estimated from spectroelectrochemistry. \(\Delta A_{actinometer}\) is the maximum transient observed for the \([\text{Ru(bpy)}_3]^{2+}\) actinometer under identical excitation conditions. \(\Delta \epsilon_{actinometer}\) was previously reported as ~ 22,000 M\(^{-1}\)cm\(^{-1}\) at 370 nm.\(^{19,20}\) The fraction quenched was extrapolated from the Stern-Volmer relation.

Figure 2.6 presented the transient absorption spectra of a sample containing \([\text{Ru(bpy)}_3]^{2+}\) and 0.3 M of ascorbic acid at pH 4 at different delay times following the laser
pulse. *[Ru(bpy)_3]^{2+}\) was designated for the excited state absorption feature at 370 nm. The negative absorption feature in the TA spectrum (black line) centered at 450 nm was assigned for the ground-state bleach of the *[Ru(bpy)_3]^{2+}\) sensitizer. The formation of the reduced radical *[Ru(bpy)_3]^+\) sensitizer following the electron transfer from HA\(^-\) to *[Ru(bpy)_3]^{2+}\) had reached a maximum \(\Delta A\) at 505 nm.

The kinetic decay of the reduced radical *[Ru(bpy)_3]^+\) at 505 nm was presented in Figure 2.6. In the absence of cobalt catalyst, the reduced sensitizer recombines with the oxidized (HA\(^-\)) through a second-order kinetic decay. The back-electron transfer for *[Ru(bpy)_3]^+\) and HA\(^-\) achieved a rate constant of \(k_b \approx 10^9 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}\), indicating a diffusion-limited process.

![Figure 2.6](image)

**Figure 2.6** a) Transient absorption spectra of a degassed solution containing *[Ru(bpy)_3]^{2+}\) (O.D.\(_{452 \text{ nm}}\) = 0.32) and 0.3 M of ascorbic acid at pH 4 excited at 452 nm (~ 4 mJ) at different delay times. b) Kinetic decay of the radical anion *[Ru(bpy)_3]^+\) at 505 nm. The inset shows the second-order kinetic linear fit of the decay (red line).
Spectroelectrochemistry (SEC) data provided the spectral features of the reduced Ru(I) sensitizer that was equivalent to the signature bands seen on TA. Using electrochemistry and cyclic voltammetry, the first reduction potential that was localized on the (bpy) ligand occurred at -1.28 V (vs SCE).\textsuperscript{21,22} The same voltage was applied in the spectroelectrochemical experiment, where the absorbance of the reduced radical species was recorded as a function of electrolysis time, Figure 2.7. When all the ground-state sensitizer present in solution was reduced, the molar extinction coefficient ($\Delta\varepsilon$) of $[\text{Ru}(\text{bpy})_3]^+$ was back-calculated from the absorbance and the concentration of the reduced Ru(I). $\Delta\varepsilon$ of the reduced sample was further used in the cage-escape efficiency in Eq 2.3.

An example of the cage-escape yield being calculated for the initial electron transfer

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.7.png}
\caption{a) Spectroelectrochemistry (SEC) data of a sample containing $2.4 \times 10^{-5}$ M $[\text{Ru}(\text{bpy})_3]^{2+}$ in acetonitrile using a Pt honeycomb electrode operated in the glovebox. The reference used was Ag/AgNO$_3$ and the electrolyte was 0.1 M TBAPF$_6$. The potential applied to generate reduced radical $[\text{Ru}(\text{bpy})_3]^+$ was -1.75 V as a function of electrolysis time. b) Extinction coefficient ($\Delta\varepsilon$) of $[\text{Ru}(\text{bpy})_3]^+$ deduced at the end of the electrolysis experiment according to the Beer-Lambert law.}
\end{figure}
termed product, [Ru(bpy)$_3$]$^+$, HA], was found to be 55%. To summarize the factors present in Eq 2.3: $\Delta A_{\text{sample}}$ was 0.028 at maximum reduced sensitizer [Ru(bpy)$_3$]$^+$ at 505 nm. $\Delta \varepsilon_{\text{sample}}$ was extrapolated from spectroelectrochemical data as 12,000 M$^{-1}$ cm$^{-1}$ at 505 nm. From Stern-Volmer analyses, the fraction quenched was found to be 0.85 when 0.3 M of H$_2$A/HA (quencher) was used. The actinometer, [Ru(bpy)$_3$]$^{2+}$ in degassed water, at optically matched conditions had $\Delta A_{\text{actinometer}} = 0.112$ and $\Delta \varepsilon_{\text{actinometer}} = 22,000$ M$^{-1}$ cm$^{-1}$ at 370 nm. The TA and SEC data of the actinometer and the other Ru(II) sensitizers along with ascorbic acid were presented in the supporting information, Figures 2.S4 - 2.S11.$^{23,24}$

### 2.5.2. Cage-Escape Yield for [Ru(bpy)$_3$]$^{2+}$ and Co (I)

In the presence of Co(II) catalyst, the reduced sensitizer Ru(I) transferred an electron to produce Co(I) species. The transient absorption feature for the reduced Co(I) had a weak broadband absorbance over the entire visible spectrum. Spectroelectrochemical measurements also confirmed the signature features identical to the TA as was previously reported.$^7$ Due to this overlap absorbance of the formed Co(I), the decay of the reduced sensitizer became a function of two competing rates that allowed us to obtain the rate of electron transfer to the Co(II).

When Co$^{II}$(bpyPY2Me) was added to the sensitizer-ascorbic acid mixture, the kinetic decay of the reduced Ru(I) possessed a function of a bi-exponential decay fit under pseudo-first order conditions. The long-lived component was determined to be the Co(I) with a lifetime of 57 µs as was measured at 650 nm, where only the Co(I) catalyst absorbs exclusively as seen in Figure 2.S12.
Instead of \([\text{Ru(bpy)}_3]^+\) recombining with HA\(^-\), fitting the decay at 505 nm as a sum of two exponential functions yielded a rate constant of \(1.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}\) with increased concentration of Co\(^{II}\)(bpyPY2Me) as shown in Figure 2.8. The negatively charged reduced sensitizers, \([\text{Ru(dpbpyS)}_3]^5^-\) and \([\text{Ru(BPS)}_3]^5^-\), had a slightly higher electron rate transfer to the positively charged Co(II).

The cage-escape yield for the Ru(II) sensitizers with the Co(I) catalyst, [Ru(II), Co(I)], was found to be as high as 85 % for all combinations, indicating that the hydrogen production was not limited by the charge separation between the reduced sensitizer and the cobalt catalyst. Subsequent to Co(I) formation, the hydrogen production was the result of an extraction of a proton source from water through several essential steps that were mentioned in Chapter 1.\(^{25,26}\)
Table 2.1 summarizes the photophysical parameters and the rates of forward and back-electron transfers between the sensitizer and ascorbic/ascorbate. The cage-escape efficiencies were also presented to provide mechanistic understanding of the kinetics and quantum yields of hydrogen production.

Table 2.1 Comparison of Photophysical Properties of Ru(II) sensitizers and Performance Metrics for Hydrogen Production

<table>
<thead>
<tr>
<th>Complex</th>
<th>MLCT $\lambda_{max}$ (nm)</th>
<th>Emission $\lambda_{max}$ (nm)</th>
<th>$\tau$ (µs)</th>
<th>$k_q$ (x $10^7$ M$^{-1}$s$^{-1}$)</th>
<th>$k_b$ (x $10^9$ M$^{-1}$s$^{-1}$)</th>
<th>$\Phi_{CE}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)$<em>3$]$</em>{2^{+}}$</td>
<td>452</td>
<td>14,500</td>
<td>625</td>
<td>0.6</td>
<td>3.36</td>
<td>1.0</td>
</tr>
<tr>
<td>[Ru(phen)$<em>3$]$</em>{2^{+}}$</td>
<td>447</td>
<td>19,000$^{27}$</td>
<td>605</td>
<td>1.05</td>
<td>20.8</td>
<td>50</td>
</tr>
<tr>
<td>[Ru(BPS)$<em>3$]$</em>{4^{+}}$</td>
<td>462</td>
<td>27,000$^{24}$</td>
<td>630</td>
<td>3.69</td>
<td>8.19</td>
<td>5.0</td>
</tr>
<tr>
<td>[Ru(dp bpyS)$<em>3$]$</em>{4^{-}}$</td>
<td>477</td>
<td>25,000</td>
<td>645</td>
<td>0.77</td>
<td>6.77</td>
<td>6.0</td>
</tr>
</tbody>
</table>

$\varepsilon$ is the molar absorptivity at the higher absorbance wavelength

$k_q$ is the bimolecular quenching rate constant as extrapolated from Stern-Volmer (data enclosed in Chapter 3)

$k_b$ is the second-order rate constant of the back-electron transfer recombination (TA data)

2.6 Varying Experimental Conditions

To verify the homogenous nature of the photocatalytic system, mercury-poisoning experiments were executed. Considerable change in hydrogen production was observed for a sample containing 0.1 ml of mercury (Hg) in the photocatalytic mixture, Figure 2.S13. This result suggested that no particle formation was supporting the hydrogen production, validating the homogenous nature of the system.

Dynamic light scattering (DLS) was also conducted to prove that no nanoparticles were present in solution during photocatalysis. Samples before and after four hours of
irradiation were measured on the DLS, demonstrating that no change was observed and no light scattering was detected due to the absence of particles in solution, Figure 2.S14.

2.6.1 Replacing Water (H\textsubscript{2}O) with Heavy Water (D\textsubscript{2}O)

The source of protons for hydrogen production in the photocatalytic experiments was identified using Mass Spectrometry (MS) analysis. When H\textsubscript{2}O was replaced with heavy water (D\textsubscript{2}O), the majority of gas produced in the headspace was D\textsubscript{2} gas, signifying that the proton source was from water and not any other molecular composition.\textsuperscript{5,7}

Figure 2.9 represented the deuteration experiment that was performed for a sample containing [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} sensitizer, Co\textsuperscript{II}(bpyPY2Me) catalyst, and ascorbic acid/ascorbate electron donor in D\textsubscript{2}O solvent. The pH of the sample was adjusted to 4 using sodium deuteroxide base (NaOD) instead of sodium hydroxide (NaOH), as the optimized conditions

![Mass spectrum](image)

**Figure 2.9** Mass spectrum of the headspace sample containing heavy water (D\textsubscript{2}O). Conditions: 6.7 x 10\textsuperscript{-5} M [Ru(bpy)\textsubscript{3}]\textsuperscript{2+}, 2 x 10\textsuperscript{-5} M Co(bpyPY2Me), 0.1 M H\textsubscript{2}A/HA at pH=pD=4 under 452 nm excitation.
were analyzed for photocatalysis, Figure 2.S15. The sample was irradiated using blue LED at 452 ± 10 nm and the headspace was analyzed with a residual gas analyzer.

The amount of gaseous products generated revealed that the major gas produced was 85 % D₂. The other hydrogen-incorporated gases (14% HD, and 1% H₂) with a proton source were a result of proton-exchange between the ascorbic acid and D₂O solvent. The small amount of H₂ evolved was attributed to the minor traces of H₂O present in solution.

2.6.2 Temperature Dependence on Photocatalysis

The temperature change has significantly affected the photocatalytic sample on hydrogen production. From Figure 2.10, the final amount of hydrogen gas produced in the headspace decreased when the temperature of the sample increased. At high temperatures, the total hydrogen produced in the headspace was less than the sample at room temperature.

![Figure 2.10](image)

**Figure 2.10** Hydrogen production experiment performed at different temperatures (7°C – 20°C – 30°C). Conditions: 1.0 x 10⁻⁴ M [Ru(bpy)₃]²⁺, 2 x 10⁻⁵ M Co(bpyPY2Me), and 0.3 M H₂A/HA at pH 4 irradiated using blue LEDs at 452 nm.
(20 °C), which was attributed to the fast decomposition rate of the photosensitizer. As previously discussed in this chapter, the ligand exchange leading to the decomposition of the sensitizer could have been facilitated when the temperature increased.

At lower temperatures, the final amount of hydrogen gas was higher than that at room temperature. This suggests that the sensitizer was still active and did not decompose as quickly during the duration of the experiment. However, the initial kinetic rate of H₂ production was slower; this outcome was attributed to the slower rates of electron transfer steps and catalytic proton reduction steps when the temperature decreased.

2.7 Conclusion

Using high-throughput screening, four representative Ru(II) photosensitizers were examined for photocatalytic activity in conjunction with the robust Co<sup>II</sup>(bpyPY2Me) catalyst and ascorbic acid electron donor under visible light irradiation. The best photosensitizer performance was ranked accordingly [Ru(dp bpyS)<sub>3</sub>]<sup>4+</sup> > [Ru(BPS)<sub>3</sub>]<sup>4+</sup> > [Ru(bpy)<sub>3</sub>]<sup>2+</sup> > [Ru(phen)<sub>3</sub>]<sup>2+</sup>.

The benchmark [Ru(bpy)<sub>3</sub>]<sup>2+</sup> was demonstrated to be unstable and labile during photocatalysis as it undergoes ligand substitution in the presence of coordinating donor ascorbate. Essentially, our recent developments suggested that having a strong core ligand design near the metal center with sulfonated groups, for solubility purposes, has lead to a more photostable photosensitizer that was less prone to ligand exchange.

Through designing more rigid ligand frameworks with fast forward electron transfer rates, [Ru(dp bpyS)<sub>3</sub>]<sup>4+</sup> and [Ru(BPS)<sub>3</sub>]<sup>4+</sup> were considerably promising candidates for
enhancing hydrogen production in conjunction with the Co$^{II}$ (bpyPY2Me) catalyst. Under visible light illumination, [Ru(dpbpyS)$_3$]$^{4+}$ and [Ru(BPS)$_3$]$^{4+}$ have achieved similar TON up to 5,000 (H$_2$/Ru) under optimized conditions, whereas [Ru(bpy)$_3$]$^{2+}$ reached significantly lower TON.

The quantum yield of H$_2$ was higher for [Ru(bpy)$_3$]$^{2+}$ ~ 7.5 \pm 0.8 \% vs ~ 5.9\% for [Ru(dpbpyS)$_3$]$^{4+}$ and [Ru(BPS)$_3$]$^{4+}$ when two photons were absorbed. The initial rates of hydrogen production were greatly manifested by the cage-escape efficiencies as the quantum yield of charge separated reduced [Ru(bpy)$_3$]$^+$ and oxidized ascorbate HA$^-$ was approximately 55 \%. These yields were deduced from pump-probe transient absorption spectroscopy and spectroelectrochemical measurements.

[Ru(phen)$_3$]$^{2+}$ sensitizer had a low cage-escape yield of 2\% for the initial electron transfer product, [Ru(phen)$^+$, HA$^-$], leading to no hydrogen being produced despite the favorable energetics. Its inability to separate its respective radical Ru(I) from the charge transfer cage, due to the fast back-electron recombination rate $k_b \sim 10^{10} – 10^{11}$ M$^{-1}$s$^{-1}$, has resulted in limited number of electrons being donated to the positively charged Co(II). Hence, Co(II) was not quantitatively reduced to Co(I) to produce H$_2$ and complete the catalytic cycle.

The negatively charged sensitizers [Ru(dpbpyS)$_3$]$^{4+}$ and [Ru(BPS)$_3$]$^{4+}$ had similar cage-escape yield with oxidized ascorbate HA$^-$ at about 23 \% and 21 \% respectively. The second electron transfer product between the reduced Ru(I) and Co(II) was as high as 85 \% for all sensitizers, suggesting that this electron transfer was not limiting the overall performance metrics of hydrogen production.
In conclusion, this combinatorial approach to solar fuel photocatalysis has lead to significant advances in the fundamental understanding of hydrogen gas generation from pure water. Using optimized conditions, the molecular components were mechanistically investigated using transient absorption spectroscopy to determine electron transfer rates and cage-escape yields, as well as analytical methods to study photostability.
2.8 References


4803–4810.


2.9 Supporting Information

**Figure 2.S1** High-throughput screening for rapid optimization of hydrogen production for the compositions present in solution at pH 4 under blue LED excitation at 452 ± 10 nm. Conditions: a) [Ru(dpbpyS)$_3$]$^{4+}$ sensitizer, 2 x 10$^{-5}$ M Co$^{II}$(bpyPY2Me), and 0.3 M H$_2$A/HA. b) [H$_2$A/HA] electron donor, 1 x 10$^{-4}$ M [Ru(dpbpyS)$_3$]$^{4+}$, and 2 x 10$^{-5}$ M Co$^{II}$(bpyPY2Me). c) [Co$^{II}$(bpyPY2Me)], 1 x 10$^{-4}$ M [Ru(dpbpyS)$_3$]$^{4+}$, and 0.3 M H$_2$A/HA.
Figure 2.S2 Regeneration experiment following the addition of fresh aliquot of Co$^{II}$(bpyPY2Me) under the following conditions: 0.5 M H$_2$A/HA at pH 4, 6.7 x 10$^{-5}$ M Ru(II) sensitizer, and 2 x 10$^{-5}$ M Co$^{II}$(bpyPY2Me). Arrows indicate the time at which the sensitizer was introduced in an amount equivalent to the initial condition.
Figure 2.53 UV-vis absorption spectra before and after photocatalysis for the optically matched Ru(II) sensitizers for a) \([\text{Ru(bpy)}_3]^{2+}\) b) \([\text{Ru(phen)}_3]^{2+}\) c) \([\text{Ru(dpypyS)}_3]^{4+}\) d) \([\text{Ru(BPS)}_3]^{4+}\). Conditions: 2x 10^{-5} M \text{Co}^{3+}(bpyPY2Me), 7.0 x 10^{-5} M \text{Ru(II)}, and 1 M \text{H}_2\text{A}/\text{HA} at pH 4 under 452 ± 10 nm blue LED excitation.
**Figure 2.S4** a) Transient absorption spectra of actinometer $[\text{Ru(bpy)}_3]^{2+}$ in degassed water (O.D. at 452 nm = 0.32) excited at 452 nm (~ 4 mJ) at different delay times. b) Kinetic decay excited state *$[\text{Ru(bpy)}_3]^{2+}$* at 370 nm. The red line corresponds to the single exponential decay fit and the green line is the residual of the fit.

**Figure 2.S5** a) Transient absorption spectra of $[\text{Ru(BPS)}_3]^+$ in degassed water (O.D. at 452 nm = 0.32) excited at 452 nm (~ 4 mJ) at different delay times. b) Ground-state bleach decay at 420 nm. The red line corresponds to the single exponential decay fit and the green line is the residual of the fit.
**Figure 2.86**  a) Transient absorption spectra of a degassed solution containing $[\text{Ru(BPS)}_3]^{4-}$ (O.D. at 452 nm = 0.32) and 0.3 M of ascorbic acid at pH 4 excited at 452 nm (~4 mJ) at different delay times. b) Kinetic decay of the radical anion $[\text{Ru(BPS)}_3]^{4+}$ at 520 nm. The inset shows the second-order kinetic linear fit of the decay (red line).

**Figure 2.87**  a) Spectroelectrochemistry (SEC) data of a sample containing $2 \times 10^{-5}$ M $[\text{Ru(BPS)}_3]^{4+}$ in acetonitrile using a Pt honeycomb electrode operated in the glovebox. The reference used was Ag/AgNO$_3$ and the electrolyte was 0.1 M TBAPF$_6$. The potential applied to generate reduced radical $[\text{Ru(BPS)}_3]^{5-}$ was -1.65 V as a function of electrolysis time. b) Extinction coefficient ($\Delta \varepsilon$) of $[\text{Ru(BPS)}_3]^{5-}$ deduced at the end of the electrolysis experiment according to the Beer-Lambert law.
Figure 2.S8 a) Transient absorption spectra of [Ru(phen)$_3$]$^{2+}$ in degassed water (O.D.$_{452\, \text{nm}}$ = 0.32) excited at 452 nm (~ 4 mJ) at different delay times. b) Ground-state bleach decay at 420 nm. The red line corresponds to the single exponential decay fit and the green line is the residual of the fit.

Figure 2.S9 a) Transient absorption spectra of a degassed solution containing [Ru(phen)$_3$]$^{2+}$ (O.D.$_{452\, \text{nm}}$ = 0.32) and 0.3 M of ascorbic acid at pH 4 excited at 452 nm (~ 4 mJ) at different delay times. b) Kinetic decay of the radical anion [Ru(phen)$_3$]$^+$ at 520 nm. The inset shows the second-order kinetic linear fit of the decay (red line).
**Figure 2.S10** a) Transient absorption spectra of $[\text{Ru(dpbyS)}_3]^+$ in degassed water (O.D. $452$ nm = 0.32) excited at 452 nm (~ 4 mJ) at different delay times. b) Kinetic decay of the excited state $*\left[\text{Ru(dpbyS)}_3\right]^+ 550$ nm. The red line corresponds to the single exponential decay fit and the green line is the residual of the fit.

**Figure 2.S11** a) Transient absorption spectra of a degassed solution containing $[\text{Ru(dpbyS)}_3]^+$ (O.D. $452$ nm = 0.32) and 0.3 M of ascorbic acid at pH 4 excited at 452 nm (~ 4 mJ) at different delay times. b) Kinetic decay of the radical anion $[\text{Ru(dpbyS)}_3]^+$ at 540 nm. The inset shows the second-order kinetic linear fit of the decay (red line).
Figure 2.S12 Kinetic decay at 650 nm where Co(I) absorbs exclusively. The lifetime was 57 µs as extrapolated from the single exponential fit of the decay (red line). Conditions: [Ru(bpy)_3]^{2+} (O.D. 452 nm = 0.36), 0.3 M ascorbic acid, and 6 x 10^{-5} of Co^{II}(bpyPY2Me) at pH 4 in degassed water under 452 nm laser pulse excitation.

Figure 2.S13 Homogenous hydrogen production confirmed using mercury (0.1 ml of pure Hg) poisoning experiment. Conditions: 6.7 x 10^{-5} M [Ru(bpy)_3]^{2+}, 2 x 10^{-5} M Co^{II}(bpyPY2Me), 0.3 M H_2A/HA at pH 4 under 452 ± 10 nm.
Figure 2.S14 Dynamic Light Scattering (DLS) before and after 4 hours of irradiation under 452 ± 10 nm (540 mW). Filtering each sample with 0.45 μm syringe filters was done before taking the measurement. Conditions: 3.3 x 10^{-4} M [Ru(bpy)_3]^{2+}, 2 x 10^{-5} M Co^{II}(bpyPY2Me), 0.3 M ascorbic acid at pH 4. 10^{-5} M of degussa p25 Titanium dioxide was used as the standard with its autocorrelation fit to detect the particles through light scattering. However, the absence of nanoparticles in the mixture above 0.5 nm in radius, before and after catalysis, resulted in no light scattering.

Figure 2.S15 H₂ production as a function of pH in a solution containing 0.78 M H₂A/HA, 1x 10^{-4} M [Ru(dpdpypS)]^{4+}, and 2 x 10^{-5} M Co^{II}(bpyPY2Me) under blue LED excitation at 452 ± 10 nm.
Figure 2.S16 a) Molar absorptivity of the photosensitizer [Ru(dpbpyS)$_3$]$^{4-}$ over the visible spectrum. b) Normalized intensity absorption and emission.
CHAPTER 3. EFFECT OF SALT ON PHOTOCATALYSIS AND CATALYTIC CURRENT

3.1 Abstract

Adding salt to the homogenous solution of Ru(II) sensitizer, Co(II) proton reduction catalyst, and ascorbic acid/ascorbate electron donor has affected the overall hydrogen production. The supplement of salt to the reaction mixture was “salt-specific”. Different salts have influenced the catalytic current of the Co(II) catalyst differently, results deduced from electrochemical data.

The current investigations examined in this chapter indicated that the addition of sodium trifluoromethanesulfonate (NaOTf) to the charged photocatalytic solution has enhanced the H₂ generation to almost double the amount, relative to that without salt. However, adding other salts such as Potassium Nitrate (KNO₃) in solution has failed to produce any gaseous products, illustrating the effect of certain solutes on catalysis.

Using pump-probe transient spectroscopy, the cage-escape yields for the termed product pairs, [Ru(I), HA⁻] and [Ru(II), Co(I)], were found to be almost identical, relative to the samples containing salt. The decomposition rate of either Ru(II) sensitizer or Co(II) catalyst in the presence of NaOTf was unaffected during the photocatalysis experiment. In addition, the rate of electron transfer from the reduced Ru(I) to the positively charged Co(II) catalyst remained untouched with NaOTf additives. Although a higher amount of hydrogen production was observed when NaOTf was added, this clearly showed that the cage-escape yields, decomposition rate constants, and electron transfer kinetics were not influenced by the
Using Electrochemistry, NaOTf demonstrated an increase in catalytic current of the cobalt(II) catalyst, enhancing its photocatalytic activity. These results provide a mechanistic understanding to the involvement of an anation-based pathway, as was previously illustrated by Chang and coworkers (*Chem. Sci.*, 2013, 4, 1578-1587), inspiring new approaches for hydrogen production.

As already discussed in this dissertation, \([\text{Ru(phen)}_3]^{2+}\) sensitizer failed to produce any hydrogen gas in conjunction with Co\(^{II}\)(bpyPY2Me) and ascorbic acid buffer solution. But when NaOTf was added to the mixture, hydrogen gas production was developed in the headspace vial in an unprecedented fashion. The cage-escape yield for the \([\text{Ru(phen)}^+, \text{HA}^-]\) remained as low as 2%, but the presence of NaOTf showed an improved catalytic activity of Co\(^{II}\)(bpyPY2Me) that led to higher amount of hydrogen production.

### 3.2 Effect of Salt on Hydrogen Photocatalysis

In an attempt to stabilize the charges in the photocatalytic solution, different salts were added to the mixture to investigate the effect of ionic strength on the yield of hydrogen evolution. Using a similar approach to Hoffman’s method,\(^2\)\(^3\) realizing an increase in efficiency of charged separated species, especially between the initial termed product \([\text{Ru(bpy)}^+, \text{HA}^-]\), would generate generous amounts of reduced sensitizer to further reduce the positively charged Co(II) catalyst. This suggested hypothesis would result in a higher amount of hydrogen production and enhanced quantum yields of H\(_2\). However, as will be further discussed in this chapter, the effect of solute on photocatalysis was limited to the presence of salt in solution.
involvement of an anation-based pathway to reduce Co(II) to Co(I), and not by the cage-escape yields.

Using the benchmark photocatalytic compositions that were previously described in chapter 2, Figure 3.1 demonstrates the hydrogen production generated in a mixture

\[
\text{Ru(bpy)}_3^{2+} (67 \mu\text{M}) + \text{Salt (0.3 M)}
\]

\[
\text{Ru(BPS)}_3^{4-} (67 \mu\text{M}) + \text{Salt (0.3 M)}
\]

**Figure 3.1** Hydrogen production as a function of different salts added with a) Ru(bpy)$_3^{2+}$ and b) Ru(BPS)$_3^{4-}$ sensitizer upon photoexcitation at 452 ± 10 nm. Conditions: 6.7 x 10$^{-5}$ M Ru(II) sensitizer, 2 x 10$^{-5}$ M Co$^{I}$bpyPY2Me, 0.3 M of salt, and 0.3 M H$_2$A/HA$^-$ (ascorbic acid) at pH 4. c) Mass spec of the final amount of hydrogen gas accumulated in headspace.
containing Ru (II) sensitizer, Co$^{II}$(bpyPY2Me) catalyst, and ascorbic acid/ascorbate electron donor in the presence of different salts.

Interestingly, the addition of sodium trifluoromethanesulfonate (NaOTf) to the already-established compositions achieved higher amounts of hydrogen production in the headspace vial. This build-up pressure of hydrogen gas (~ 0.3 to 0.5 mmole) was generated from the typical 10 ml solution upon photoexcitation, inspiring further research in the solar-to-fuel photocatalysis.

The amount of hydrogen evolution was highest in the order of supplement of NaOTf > Na$_2$SO$_4$ > NaC$_2$H$_5$O$_2$ > no salt > EDTA. This reproducible data illustrated the unique effect of each solute on photocatalysis, As such, when potassium nitrate (KNO$_3$) was added to the mixture, no hydrogen gas was produced in the headspace vial, as seen in Figure 3.S1.

The turnover numbers (TON) of Co$^{II}$(bpyPY2Me) determined at the end of the experiment in the presence and absence of salt were considerably different quantities. At equivalent concentration of molecular compositions, the solution containing 0.3 M of NaOTf achieved TON ~ 1,500 H$_2$/Co higher than that without salt, data presented in Figure 3.S2 and Figure 3.S3.

### 3.3 Stern-Volmer Quenching

Using the Stern-Volmer relationship, the quenching rate constants and bimolecular rate constants were determined according to Eq 3.1.

$$\frac{\tau_0}{\tau} = \frac{I_0}{I} = k_q[Q] + 1$$

Eq 3.1
Here, $\tau_0$ is the sensitizer lifetime in the absence of a quencher. $\tau$ is the sensitizer lifetime when a quencher is present in solution. $I_0$ and $I$ are the integrated emission profiles for the unquenched and quenched sensitizer emission respectively. $[Q]$ is the concentration of quencher. The Stern-Volmer quenching rate constant ($k_{sv}$ in units of M$^{-1}$) is equal to the bimolecular rate constant ($k_q$ in units of M$^{-1}$s$^{-1}$) multiplied by the unquenched sensitizer lifetime ($\tau_0$ in units of s).

When NaOTf was added to a solution of [Ru(bpy)$_3$]$^{2+}$ and ascorbic acid/ascorbate at pH 4, the rate of quenching constant measured using Stern-Volmer equation was significantly lower than that without salt present in the sample, as seen in Figure 3.2. The quenching rate constant ($k_{sv}$) went from 20.26 M$^{-1}$ to 6.47 M$^{-1}$ in degassed aqueous solution, Figure 3.S4. A similar trend was observed between excited state *[Ru(phen)$_3$]$^{2+}$ and ascorbic acid/ascorbate quencher when solute was present, as $k_{sv}$ decreased from 217.56 M$^{-1}$ of no salt.

**Figure 3.2** Dynamic photoluminescence quenching of the excited state a) [Ru(bpy)$_3$]$^{2+}$ and b) [Ru(phen)$_3$]$^{2+}$ with quencher ascorbic acid/ascorbate (H$_2$A/HA) at pH 4 in degassed water with 0.3 M of NaOTf (red) vs no salt (black).
solution to 42.84 M$^{-1}$ of 0.3 M NaOTf.

The collisional quenching occurring between the positively charged excited-state Ru(II) sensitizer and the radical ascorbate was lowered due to the charges being stabilized when the sodium salt was present in solution. The addition of NaOTf to the charged mixture limited the rate of collision between the sensitizer and quencher, resulting in a slower rate of electron transfer. However, since the optimized concentration of ascorbic acid (quencher) used in photocatalysis was as high as 0.3 M, the amount of excited-state sensitizer quenched was above 85 % for both salt and no-salt samples, suggesting that the enhanced hydrogen production evolution for salt solution was not limited by the slower rate of electron transfer.

From Figure 3.3, slight changes of quenching rate constants were measured when NaOTf was added to the sample containing [Ru(dpbbpyS)$_3$]$^{3+}$ or [Ru(BPS)$_3$]$^{3+}$ in ascorbic acid/ascorbate at pH 4. Since the negatively charged Ru(II) sensitizers were already made in

![Figure 3.3](image_url)

**Figure 3.3** Dynamic photoluminescence quenching of the excited state a) [Ru(dpbbpyS)$_3$]$^{3+}$ and b) [Ru(BPS)$_3$]$^{3+}$ with quencher ascorbic acid/ascorbate (H$_2$A/HA) at pH 4 in degassed water with 0.3 M of NaOTf (red) vs no salt (black).
in excess sodium sulfate to functionalize the (SO$_3^-$) on the moiety of the ligands, no difference in collisional quenching rate was measured when additional salt (NaOTf) was added to the mix. The Stern-Volmer quenching rate constant between the $[\text{Ru(dp bpyS)}_3]^+$ and HA was ($k_{sv} = 52$ M$^{-1}$) and the bimolecular quenching rate constant was ($k_q = 6.77 \times 10^7$ M$^{-1}$s$^{-1}$). For $[\text{Ru(BPS)}_3]^+$ and HA in degassed water had rates of ($k_{sv} = 303$ M$^{-1}$) and ($k_q = 8.02 \times 10^7$ M$^{-1}$s$^{-1}$).

### 3.4 Rate of Electron Transfer from Ru(I) to Co(II)

Subsequent to forming reduced sensitizer through quenching with ascorbic acid/ascorbate, a second thermodynamically favorable electron transfer process occurred from the reduced Ru(I) to the positively charged Co(II) catalyst, thus regenerating the initial ground-state Ru(II) in this reductive quenching pathway. In this step, Co(II) gets reduced to Co(I).

The rate of electron transfer from Ru(I) to Co(II) was measured using transient absorption by fitting the kinetic decay of the reduced sensitizer as a bi-exponential fit under pseudo first-order conditions, a description of which was enclosed in chapter 2. Since the amount of hydrogen production was enhanced when NaOTf was coexisting in solution, it was postulated that the electron transfer would yield a higher rate constant. However, Figure 3.4 clearly reveals that identical kinetics of electron transfer were achieved for the photocatalytic solution containing NaOTf salt versus that with no additives.

In addition, the cage-escape yields for the termed products of samples having NaOTf were measured to be almost equivalent to the typical no-salt photocatalytic mixture. The
The rate of electron transfer from \([\text{Ru(bpy)}]^{+}\) to \(\text{Co}^{\text{II}}\) catalyst in the presence of NaOTf salt was measured at \(1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}\), values almost equivalent to the no-salt sample.

3.5 Decomposition Rates of Molecular Compositions with Salt vs No-Salt

Under optimized photocatalytic conditions, the cage-escape yields and kinetic rates of electron transfer had little to do with the improved hydrogen production for the solution containing salt. Therefore, we looked into investigating the stability of the molecular compositions during photoexcitation.

The relative rates of decomposition were examined using real-time absorption
experiment as a function of 442 nm He/Cd laser irradiation. Figure 3.5 demonstrates that the absorption spectra for the solution containing [Ru(bpy)_3]^{2+}, Co^{II}(bpyPY2Me), and ascorbic acid at pH4 was decreasing at the same rate of decomposition as the sample that had an

![Graph](image-url)

**Figure 3.5** Absorption spectra showing the stability of the sensitizer as a function of irradiation time under 443 nm laser (He/Cd) at 68 mW incident power. Conditions: optically matched [Ru(bpy)_3]^{2+} solution at identical concentration of Co^{II}(bpyPY2Me) (2 x 10^{-5} M) and H_2A/HA^- (0.3 M, pH 4) with a) no salt added and b) 0.3 M of NaOTf was added.
additional 0.3 M of NaOTf. These results indicated that the photostability of the sensitizer was not affected by the presence of salt in the mixture that led to higher amount of hydrogen production.

To investigate the stability of the Co(II) catalyst during photocatalysis, an HPLC experiment was performed for the reaction mixture before and after irradiation. The mobile phase used was a gradient of methanol-water eluent over a 40-minute period of retention time. Both Ru(II) sensitizer and Co^{II}(bpyPY2Me) were separated from the mixture and an absorption spectra was collected using a PDA detector equipped with the HPLC instrument. The results obtained in Figure 3.S5 indicate that the robust Co(II) catalyst remained active up to 90 % after 1.5 hours of photocatalysis, and the benchmark [Ru(bpy)_3]^{2+} decomposed to other degradation products. Identical results were obtained when NaOTf was added to the photocatalytic solution, illustrating that the durability of either sensitizer or catalyst stayed the same upon the supplement of NaOTf.

3.6 The Involvement of an Anation-Based Pathway for Co(II) Catalyst

Our collaborators, the Chang and Long groups at the University of California, Berkley have performed computational and electrochemical methods to understand the structure/activity relationship of the Co(II) catalyst. Several mechanisms have been proposed in the literature to illustrate the hydrogen evolution chemistry that involves the reduction of Co(II) to Co(I).^5–7 In the homolytic mechanism, Co(II) gets reduced to Co(I) followed by proton coordination to yield Co(III)-Hydride to then generate hydrogen gas through a bimolecular reaction of the latter. Alternatively, in the heterolytic mechanism, two electrons and two protons
are delivered to the same cobalt complex and undergo a “dihydrogen- σ cleavage” to produce hydrogen. Because the rate-determining intermediate Co(III)-Hydride cannot be isolated and studied kinetically and spectroscopically, it was difficult to distinguish between the bimolecular interactions of two Co(III)-Hydride and the reduction of Co(III)-Hydride.6,8–12

Our investigations of salt effect on hydrogen photocatalysis suggested that a catalyzed anation-based pathway by the cobalt complex was involved in the reaction. Peters and Hu have demonstrated the anation process with specific examples of hydrochloric acid using diglyoximate cobalt catalysts.5,13 Also, Gray and colleagues have reported tosylate anation that has operated under catalytic conditions.14 These findings lay important groundwork for the catalyzed anation process in aqueous photocatalysis.

The process occurring after the Co(III)-Hydride formation remains unclear, but the anation pathway can be demonstrated through examining cyclic voltammetry, as this mechanism precedes the Co(III)-Hydride. The anation mechanism involves the coordination chemistry of specific substrates to the metal cobalt center happening before the production of Co(III)-Hydride. First, the use of NaOTf with a triflate anion (OTf–) was capable of producing triflate-ligated species bound to the cobalt center. The original acetonitrile ligand coordinated to the CoII(bpyPY2Me) was shown to be labile and easily substituted with OTf– before Co(II) gets reduced to Co(I). Chang and colleagues demonstrated similar findings using CoII(PY5Me2) and acetate salt through electrochemical measurements (Chem. Sci., 2013, 4, 1578-1587).1 The triflate-ligated species of CoII(bpyPY2Me)-OTf displayed a higher proton reduction current at more negative potentials than the typical acetonitrile-bound complex with no salt added (E0.1/2 = -1.1 V vs Ag/AgNO3), as seen in Figure 3.6. Plotting the current obtained at -1.2 V as a function of salt concentration [NaOTf] suggested an increase in catalytic activity,
Figure 3.6 Electrochemical measurement for Co(bpyPY2Me)²⁺ catalyst as a function of salt concentration of NaOTf. The data show the reduction a) cyclic voltammogram (CV), b) differential pulse-voltammogram (DPV), and c) plot of maximum current of catalyst versus [NaOTf]. The inset in b) shows the maximum current at more negative potentials with increased concentration of NaOTf. The solvent was ACN and the scan rate was 100 mV/s.

developed through anation process. The enhanced activity of the catalyst that resulted in better performance of hydrogen photocatalysis still remains under mechanistic investigation by our collaborators.
The ultimate goal of this research was to discover and evaluate new approaches for solar hydrogen production from water. In the Castellano group, we aim to thoroughly understand and optimize each step in the sequence from sensitizer excited state electron transfer through H₂ release from the catalyst. Our expertise lies in the fundamentals of chromophore design, excited state chemistry, as well as static and transient (kinetic) spectroscopy, and our collaborators will examine catalytic activity through anation-based pathways.

3.7 Unprecedented Hydrogen Production for [Ru(phen)₃]²⁺ Photosensitizer

The low cage-escape yield for [Ru(phen)₃⁺, HA⁻] was as low as 2 %, where an insufficient transfer of electrons to the Co(II) catalyst were limiting the proton-reduction. In the typical solution of [Ru(phen)₃]²⁺, CoІІ(bpyPY2Me), and ascorbic acid/ascorbate, the photocatalysis experiment failed to produce hydrogen production. However, when NaOTf was coexisting in solution, the Co(II) catalyst went through an anation-based pathway, resulting in a higher catalytic activity as was previously demonstrated in this chapter. The current for CoІІ(bpyPY2Me) became higher with more negative potentials.

Here, we demonstrate the first example of solar hydrogen production observed with [Ru(phen)₃]²⁺ sensitizer when NaOTf was present in the mixture, as seen in Figure 3.7. These results inspire further investigations for studying the structure/activity of the Co(II) catalyst in the company of anation-based salts.
3.8 Conclusion

Upon the addition of NaOTf salt in the photocatalytic mixture, we have demonstrated improved hydrogen production through the involvement of an anation-based process for the catalyzed Co$^{II}$(bpyPY2Me), as was previously illustrated by Chang and coworkers. The effect of salt on photocatalysis was salt-specific as each solute had a significant effect on catalytic activity, as shown by electrochemistry. The TON achieved for hydrogen production in the presence of NaOTf was 1,500 $\text{H}_2$/Co higher than the no-salt solution during photocatalysis.

The Stern-Volmer kinetics suggested that the quenching rate of electron transfer at the optimized concentration of 0.3 M of ascorbic acid/ascorbate did not limit the overall hydrogen production for the salt sample versus no-salt sample, as the fraction quenched

Figure 3.7 Hydrogen production plot. Conditions: $6.7 \times 10^{-5}$ M Ru(phen)$_3^{2+}$ sensitizer, $2 \times 10^{-5}$ M Co(bpyPY2Me), and 0.3 M H$_2$A/H$^+$ (ascorbic acid) at pH 4 with 0.3 M NaOTf. The excitation source was from blue LED’s irradiated at 452 ± 10 nm (540 mW).
remained above 85 %. The bimolecular rate constants ranged from $k_q 10^7$ - $10^8 \text{ M}^{-1}\text{s}^{-1}$. Using transient absorption spectroscopy, the cage-escape yields were not influenced by the addition of salt in solution; neither of the decomposition rates of the molecular compositions were affected when NaOTf was present in the mixture. Also, the rate of electron transfer from the reduced Ru(I) to the positively charged Co(II) catalyst was about $1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ under pseudo first-order conditions. Equivalent rate was observed for the sample containing salt.

Sodium trifluoromethanesulfonate (NaOTf) resulted in an increase in catalytic current of the cobalt catalyst, enhancing its photocatalytic activity through an anation process. When [Ru(phen)$_3$]$^{2+}$ sensitizer was used in conjunction with the Co$^{II}$(bpyPY2Me), ascorbic acid/ascorbate, and 0.3 M of NaOTf, hydrogen production was accumulating in the headspace. These findings inspire further investigations into homogeneous photocatalytic systems to drive the photochemical water reduction to hydrogen using solar photons.
3.9 References


15127–15131.


3.10 Supporting Information

**Figure 3.S1** Hydrogen production was not generated when 0.3 M of KNO₃ salt was added to the reaction mixture. A) H₂ plot. b) MS collected at the end of photocatalysis. Conditions: 6.7 x 10⁻⁵ M Ru(II) Sensitizer, 2 x 10⁻⁵ M Co(II)(bpyPY2Me), and 1 M H₂A/H₂A⁻ (ascorbic acid) at pH 4 irradiated using blue LEDs at 452 ± 10 nm (540 mW).
**Figure 3.S2**

a) H₂ production as a function of Co^{II}(bpyPY2Me) catalyst concentration. Conditions: 1 x 10⁻⁴ M [Ru(bpy)₃]²⁺ in 0.3 M ascorbic acid/ascorbate buffer at pH 4 irradiated using blue LEDs at 452 ± 10 nm (540 mW). b) Turnover numbers as a function of catalyst. c) Final amount of hydrogen production accumulated in the headspace vial. d) Initial rates of H₂ as a function of catalyst concentration.
Figure 3.S3 a) H₂ production as a function of Co^{II}(bpyPY2Me) catalyst concentration. Conditions: 1 x 10⁻³ M [Ru(bpy)₃]²⁺ with 0.3 M of NaOTf in 0.3 M ascorbic acid/ascorbate buffer at pH 4 irradiated using blue LEDs at 452 ± 10 nm (540 mW). b) Turnover numbers as a function of catalyst. c) Final amount of hydrogen production accumulated in the headspace vial. d) Initial rates of H₂ as a function of catalyst concentration.
Figure 3.S4 Dynamic photoluminescence quenching of the excited state Ru(bpy)$_3^{2+}$ and quencher ascorbate in degased water with salt vs no salt. Excited state lifetime decay a) No salt added. b) with 0.3 M NaOTf.
**Figure 3.S5** HPLC study experiment demonstrating the stability of the Ru(II) sensitizer and Co (II) catalyst during photocatalysis. This experiment was performed in a solution of 2.5 x 10^{-5} M of [Ru(bpy)_3]^{2+}, 4 x 10^{-5} M of Co^{II}(bpyPY2Me), in 0.3 M ascorbic acid/ascorbate buffer with 0.3 M NaOTf at pH4 before and after 1.5 hrs of irradiation at 452 nm (540 mW). HPLC has a UV-vis PDA detector to monitor the absorption spectra of the compositions, and the instrument is equipped with a C-18 Column to separate the mixture. The mobile phase H_2O and Methanol.  

a) The LC chromatograph of the photocatalytic solution. The absorption spectra collected from the PDA for a) [Ru(bpy)_3]^{2+} and b) Co^{II}(bpyPY2Me).
Figure 3.6 a) Cyclic voltammetry of the Co(I)(bpyPY2Me) catalyst with NaOTf (red line) and without salt (black line). b) The differential pulse voltammetry. The solvent was ACN and the scan rate was 100 mV/s.
CHAPTER 4. TRIPLET-TRIPLET ANNIHILATION IN WATER USING BENCHMARK RU (II) SENSITIZERS AND CARBOXYLATE ACCEPTORS

4.1 Abstract

A major challenge remaining in photochemical upconversion lies in identifying appropriate chromophore combinations that function in pure water in the absence of hydrophobic or surfactant additives. Using molecular donor and acceptor pairs in water, fast kinetic rates of triplet-triplet annihilation (TTA) led to the population of higher energy singlet excited states, inspiring new approaches to shuttle energy or electrons to other photocatalysts or acceptors. This phenomenon opens the door for further development in the aqueous solar photocatalysis and photobiology.

In this chapter, we demonstrate upconverted blue light (high-energy) emission detected in water in the absence of any molecular self-assembly patterns or surfactant mediums when excited with a green light (low-energy) excitation source. Four representative donor and acceptor pairs generalizing this concept were examined, namely 9-anthracenecarboxylate (AnCO$_2^-$) and 1-pyrenecarboxylate (PyCO$_2^-$) serving as acceptors/annihilators along with the water-soluble Ru(II) MLCT triplet photosensitizers [Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2′-bipyridine) and [Ru(BPS)$_3$]$^{4+}$ (BPS = bathophenanthroline disulfonate).

Using dynamic Stern-Volmer analyses, the bimolecular quenching rate between [Ru(bpy)$_3$]$^{2+}$ and the carboxylate acceptors yielded efficient quenching rate constants of $k_q \equiv 7 \times 10^9$ M$^{-1}$s$^{-1}$ with AnCO$_2^-$ and $k_q \equiv 4 \times 10^9$ M$^{-1}$s$^{-1}$ with PyCO$_2^-$ in degassed water, values
that are just below the diffusion limit. Using pump-probe transient absorption spectroscopy, long-lived triplet excited state acceptors were populated to proceed through triplet-triplet annihilation (TTA) with a rate constant of \( (k_{TTA} = 10^9 - 10^{10} \text{ M}^{-1}\text{s}^{-1}) \), results extrapolated from kinetic parameters of triplet absorption decay data. The fraction of annihilators, denoted by \( \beta \) values, suggested that 75% of the acceptors were undertaking in TTA. In addition to the successful photochemical upconversion performed in water, heavy water (D\(_2\)O) revealed similar results of direct sensitization of acceptors, producing singlet fluorescent light.

Solutions containing PyCO\(_2^-\) have efficiently generated fluorescent \(^1\text{PyCO}_2^-\) excimers under experimental conditions necessary to observe photochemical upconversion, enabling the conversion of monochromatic absorbed photons to broadband light emission. This also illustrates that the singlet-excited state produced through sensitized triplet-triplet annihilation (TTA) had engaged in bimolecular reactions with ground state molecules. The collective results reported here form a compelling argument for the application of sensitized TTA processes to solar-fuel photochemical transformations in water.

### 4.2 Photochemical Upconversion in Water

Several factors are considered when determining the appropriate combination of donor and acceptor pair for photon upconversion schemes. In Figure 4.1, we present Ru(II) MLCT photosensitizers with large molar absorptivity in the visible spectrum enabled for low energy absorption.

Subsequent to photoexcitation, the benchmark sensitizer [Ru(bpy)\(_3\)]\(^{2+}\) (bpy = 2,2′-bipyridine) and [Ru(BPS)\(_3\)]\(^{4+}\) (BPS = bathophenanthroline disulfonate) quantitatively yield
[Ru(bpy)$_3$]$^{2+}$* and [Ru(BPS)$_3$]$^{4+}$* with triplet excited state lifetimes of 0.6 µs and 3.7 µs in degassed water respectively, rendering them susceptible to energy transfer quenching. The triplet energy potential for Ru(II) sensitizers was previously reported at ($E_T \sim 2.10$ eV) and the triplet energy potential for the carboxylate acceptors was estimated at $E_T \sim 1.83$ eV.$^{1-4}$

As such, the excited state was oxidatively quenched by the triplet acceptor AnCO$_2^-$ or PyCO$_2^-$ through triplet-triplet energy transfer (TTET) measured using dynamic Stern-Volmer
relation. Upon populating the long-lived triplet excited state of acceptors (μs), the probability of two triplets colliding together for triplet fusion/annihilation was high enough to generate a singlet fluorescent acceptor. When a high concentration of triplet excited state sensitizer was used, the TTET process became more efficient to populate generous amounts of triplet excited state acceptors, making TTA upconversion more significant.

Our group has recently developed the first example of photochemical upconversion in water through direct energy transfer and triplet-triplet annihilation in the absence of molecular self-assembled aggregations or micelle-accompanied hosts. In this study, Ru(II) photosensitizers were selected for the broad MLCT band absorption that extends to the green visible spectrum. The absorption and prompt photoluminescence spectra of the sensitizers and carboxylate acceptors in H₂O are presented in Figure 4.2.

**Figure 4.2** a) Absorption (solid lines) and normalized photoluminescence (dashed lines) spectra of [Ru(bpy)₃]²⁺ (blue) and [Ru(BPS)₃]⁴⁻ (red) in water. b) Normalized absorption (solid lines) and direct fluorescence (dashed lines) spectra of AnCO₂⁻ (green) and PyCO₂⁻ (pink) in water.
With direct excitation in the UV region at 340 nm, the singlet fluorescence profile of the organic acceptors matched the upconverted emission that resulted from direct sensitization from [Ru(bpy)$_3$]$^{2+}$, as seen in Figure 4.3. These results were consistent with previously reported sensitized-based Anthracene and Pyrene derivatives in organic solvents.\textsuperscript{5-8}

In general, to obtain efficient upconverted emission, the nominated acceptor for photochemical upconversion scheme would have a quantum yield of fluorescence close to unity. But, due to the solubility limitations of the organic acceptors in water, the fluorescence quantum yield of AnCO$_2^-$ and PyCO$_2^-$ was reported at 0.04 upon direct UV excitation.\textsuperscript{9,10} The incorporation of carboxylate functional group on the moiety of the organic compounds was to ensure the solubility of the acceptors in water.

\textbf{Figure 4.3} Upconverted emission spectra sensitized by [Ru(bpy)$_3$]$^{2+}$ ($\lambda_{488}$ nm $\sim$ 0.2) in degassed water for a) 3.2 mM of AnCO$_2^-$ (blue line) and b) 3.6 mM PyCO$_2^-$ (green line). The red line represents the quenched emission of the photosensitizer [Ru(bpy)$_3$]$^{2+}$. The excitation source was from a coherent Ar/Kr laser at 488 nm.
As predicted, photochemical upconversion of AnCO$_2^-$ and PyCO$_2^-$ was detected in degassed water when [Ru(bpy)$_3$]$^{2+}$ was excited using a continuous-beam laser at 488 nm. When a different Ru(II) sensitizer, [Ru(BPS)$_3$]$^{4+}$, was used along with AnCO$_2^-$ or PyCO$_2^-$, upconverted blue light emission was also observed, shown in Figure 4.S1. Also, when replacing H$_2$O with deuterated water, D$_2$O, similar results of higher energy singlet fluorescence were observed, as seen in Figure 4.S2.

The various excited state lifetimes of Ru(II) sensitizers in both H$_2$O and D$_2$O solvents were summarized in Table 4.1. The bimolecular quenching rate constants ($k_q$) and Stern-Volmer rate constants ($k_{sv}$) with carboxylate acceptors were also presented in Figures 4.S3-4.S6. The bimolecular rate constants have reached ~ $10^9$ M$^{-1}$s$^{-1}$, values just one order of magnitude below the diffusion limit. The Stern-Volmer (SV) rate constants ranged between 1746 M$^{-1}$ to 4222 M$^{-1}$ in water. Although these SV values were considerably small compared to Pd(II) porphyrin quenching constants$^{11}$, they were still significant enough to use millimolar concentrations of acceptors to quench at least 90% of sensitizer’s excited state.

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<th>Solvent</th>
<th>Sensitizer</th>
<th>$\tau_0$ (µs)</th>
<th>Acceptor</th>
<th>$k_{sv}$ (M$^{-1}$)</th>
<th>$k_q$ (x 10$^9$ M$^{-1}$s$^{-1}$)</th>
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<tr>
<td>H$_2$O</td>
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<td></td>
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<td>PyCO$_2^-$</td>
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<tr>
<td></td>
<td>$^{4+}$</td>
<td></td>
<td>PyCO$_2^-$</td>
<td>1746</td>
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<tr>
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<td></td>
<td>PyCO$_2^-$</td>
<td>2047</td>
<td>3.55</td>
</tr>
</tbody>
</table>
4.3 Transient Absorption

Using pump-probe nanosecond transient absorption (TA) spectroscopy, the sensitization of triplet acceptors of AnCO$_2^-$ or PyCO$_2^-$ was the result of efficient energy transfer, as suggested from Stern-Volmer studies. The absence of any oxidized or reduced species on the nanosecond TA indicated that no electron transfer was observed under 452 nm excitation in degassed water.$^{12,13}$ However, the TA experiments revealed that the oxidatively quenched photosensitizer through triplet-triplet energy transfer (TTET) was the only possible outcome to generate triplet excited state acceptor, as seen in Figure 4.4.

The negative absorbance data at 450 nm was designated to the ground-state bleach of [Ru(bpy)$_3$]$^{2+}$ sensitizer. The positive feature bands centered at 420 nm were assigned for the triplet-excited state of the acceptors, a result of direct sensitization from Ru(II) sensitizer. At

Figure 4.4 Transient absorption data of [Ru(bpy)$_3$]$^{2+}$ with AnCO$_2^-$ and PyCO$_2^-$ respectively in H$_2$O solvent. Transient absorption difference spectra of [Ru(bpy)$_3$]$^{2+}$ ($A_{452 \text{ nm}} \sim 0.35$) with a) 0.5 mM of AnCO$_2^-$ and b) 0.5 mM of PyCO$_2^-$ respectively measured as a function of delay time in H$_2$O solvent. Samples were bubbled degassed and excited at 452 nm (~3 mJ/pulse).
moderate concentration of quencher with 0.5 mM, the kinetic traces of formation of triplet acceptors at 420 nm matched spectroscopically the rate decay of emission sensitizer at 620 nm. The TA experiments were also performed with [Ru(BPS)$_3$]$^{2+}$ photosensitizer in both degassed H$_2$O and D$_2$O solvent, as shown in Figures 4.S7 – 4.S11.

### 4.4 Power Dependence Experiment on Photon Upconversion

The quantitative explanation for the population of singlet excited state acceptor and the resulting upconverted emission revealed two competing kinetic processes of quadratic and first order dependence on laser intensity. From Figure 4.5, the double logarithmic plot of the upconverted emission as a function of incident power showed a slope of 2 at low power densities, and slope of ~ 1 (blue line) implies a linear dependence at high power densities.

![Photoluminescence upconverted emission spectra](image)

**Figure 4.5** Photoluminescence upconverted emission spectra of a) 3 mM of AnCO$_2^-$ and b) 3.2 mM of PyCO$_2^-$ respectively sensitized by [Ru(bpy)$_3$]$^{2+}$ (A$_{488}$ nm ~ 1) in degassed H$_2$O using an Ar/Kr laser at 488 nm excitation at different power intensities. Insets represent a double logarithmic plot of upconverted emission for AnCO$_2^-$ and PyCO$_2^-$ respectively as a function of power densities, where slope of ~ 2 (red line) indicates a quadratic dependence at low power densities, and slope of ~ 1 (blue line) implies a linear dependence at high power densities.

101
densities and a slope of 1 at high power densities. At low incident power, the slope of 2 represented a quadratic dependence kinetic that is limited by the weak annihilation and the two absorbed photons. Upon increasing the excitation power density, the slope deviated until it reached a slope of 1 at high power, an indication of a first-order linear dependence kinetic with excitation intensity. At high laser power, the upconverted sample reached the maximum quantum yield of upconversion rendering the strong annihilation. This result clearly demonstrated the importance of utilizing high-flux incident power excitation on the donor and acceptor sample to achieve high emission intensity of upconversion.

4.5 Excimer Formation

Shuttling energy from that higher energy singlet was demonstrated through excimer formation, a product that was a result of photon upconversion phenomenon. Figure 4.6 summarized the generalized scheme of photochemical upconversion conducted in this study in degassed water in the absence of any molecular self-assembly. In the outlined energetic scheme below, the process of upconversion showed the possible emission pathways produced when the carboxylate acceptors were used. In all instances, excimer formation was observed all over the visible spectrum, but it was more prominent with the PyCO$_2^-$ annihilator.$^{14}$ An excimer product was conceived when a singlet exited state acceptor reacted with a singlet ground state acceptor.

In the Ru(II) sensitizer and PyCO$_2^-$ acceptor scenario, the sensitization of both singlet pyrenecarboxylate and singlet pyrenecarboxylate excimer, $^{1}[\text{PyPy}]^*$, yielded
the upconverted emission profile at 380 nm and a broad emission centered around 470 nm, indicating excimer formation.\textsuperscript{15,16}

Previously, our group has depicted the sensitization of singlet excimer of pyrene through TTA following selective excitation of Ir(III) complexes.\textsuperscript{17} In this particular case, the singlet excimer collected some of the stored energy of the upconverted singlet acceptor, resulting in an additional characteristic band emission and lower quantum yield of primary singlet upconversion. However, this excimer construction clearly confirms the general conclusion of this study, which is to inspire the utilization of higher energy singlet and perform photochemistry in homogenous water.
Figure 4.7 a) Stability of the upconverted emission of 3 mM of AnCO$_2^-$ sensitized by 3 x 10$^{-4}$ M of [Ru(bpy)$_3$]$_{2}^{2+}$ in degassed H$_2$O under continuous-laser beam excitation at 488 nm for 3.5 hour. Inset displays the upconverted intensity monitored at 410 nm as a function of irradiation time. b) Photolysis of a degassed sample of 5.5 x 10$^{-5}$ M of [Ru(bpy)$_3$]$_{2}^{2+}$ and 0.3 mM AnCO$_2^-$ in H$_2$O showing the decomposition of AnCO$_2^-$ in solution upon photoexcitation at 488 nm.

Figure 4.7 shows the upconverted emission of AnCO$_2^-$ monitored as a function of irradiation time, while stirring, under a continuous laser beam excitation at 488 nm. As observed, the emission intensity of AnCO$_2^-$ resulting from sensitization decreased significantly after 3.5 hours of constant laser excitation. In addition, the photolysis experiment provided the static UV-vis absorption spectra of the upconverted solution of [Ru(bpy)$_3$]$_{2}^{2+}$ and AnCO$_2^-$ in relatively dilute concentrations in degassed water upon photoexcitation$^{18,19}$ It was evident that the absorbance of AnCO$_2^-$ between 325 nm and 390 nm was reduced, which predicted the instability of the organic acceptor during photosensitization, a sign of excimer formation. However, the MLCT band of [Ru(bpy)$_3$]$_{2}^{2+}$ shown in the absorption spectra remained stable at the chosen concentrations, indicating that
the photochemical upconversion was limited by the stability of AnCO$_2^-$ acceptor and not by
the sensitizer. It was previously reported that anthracene undergoes [4+4] photocycloaddition
that yields dimerization products, which could anticipate the decrease of upconverted
emission as a function of photoexcitation.$^{20,21}$

From Figure 4.S12, the upconverted emission of PyCO$_2^-$ dropped significantly after
only one and a half hours of irradiation time due to the competing emission pathways. Also,
yany dimerization or excimer product containing the carboxylate functional groups would
retain the product’s solubility in water and avoid precipitation from solution.

4.6 Quantum Yield of Photon Upconversion

In general, the quantum yield of upconversion is the product of each quantum
encounter leading to the upconverted photoluminescence. A representation of this
phenomenon is demonstrated in Eq 4.1.

$$
\Phi_{UC} = \Phi_{ISC} \times \Phi_{TTET} \times \Phi_{TTA} \times \Phi_f
$$

Eq 4.1

Ideally, to maximize the overall quantum yield of upconversion ($\Phi_{UC}$), improvement
of each efficiency step was necessary: intersystem-crossing ($\Phi_{ISC}$), triplet-triplet energy
transfer ($\Phi_{TTET}$), triplet-triplet annihilation ($\Phi_{TTA}$), and the fluorescence of the acceptor ($\Phi_f$).

Several factors have limited the calculation of quantum yield of photon upconversion
in water. First, the reabsorption of upconverted emission by the Ru(II) MLCT, due to the
inner-filter effect, has made it difficult to obtain an accurate yield for upconversion. Second,
the spin-allowed singlet-singlet transition that extracted the energy from the higher singlet
and led to excimer products made it more challenging to find a quantum yield. Third, the nature of the carboxylate acceptors/annihilators contributing with low efficiency of prompt fluorescence ($\Phi_f$) played an additional role in limiting the quantum yield of TTA and upconversion. In this study, the acquired numbers were only pessimistic calculations that did not quite represent the “actual” efficiency of photon upconversion in water.

In both solvents, the quantum yield of upconversion was roughly approximated to be less than 0.1% in water, but the novelty of this study demonstrated fast kinetic rates of triplet-triplet annihilation, inspiring new approaches to transfer energy from that higher energy singlet excited state. The quantum yield of upconversion in D$_2$O solvent was slightly higher than that in H$_2$O, which could be attributed to the longer-lived triplet excited states of sensitizer, as well as the effect of vibrational modes of the solvent on the excited states in solution.

4.7 Kinetic Parameters of Triplet Absorption Decay Data

After populating the triplet-excited state acceptors, the triplet decay rate ($k_T$) and the triplet-triplet annihilation rate constant ($k_{TTA}$) of the acceptors/annihilators were determined from kinetic absorption decay data at 420 nm as a function of time, according to Eq 4.2.

$$\frac{d[^3M^*]}{dt} = -k_T[^3M^*] - k_{TTA}[^3M^*]^2$$

Eq 4.2

Here, $[^3M^*]$ is the concentration of triplet excited state acceptor, $k_T$ is the first-order triplet decay rate constant, and $k_{TTA}$ is the second-order triplet-triplet annihilation rate constant. Fitting the transient absorption decay data of the triplet AnCO$_2^-$ or PyCO$_2^-$ at 420
nm required the integration of Eq 4.2 to yield Eq 4.3, which further translates to a simplified three unknown parameters $P_1$, $P_2$, and $P_3$, as shown in Eq 4.4.\textsuperscript{11,22–25}

The parameters used in Eq 4.4 were fitted in Origin 9.1. The terms were defined as $y = [^3M^*]$, $t =$ time, and $P_1 = \Delta A_0$. Using the extinction coefficient of the triplet excited state of $\text{AnCO}_2^-$ ($\varepsilon_T = 39,000$ M$^{-1}$s$^{-1}$) or $\text{PyCO}_2^-$ ($\varepsilon_T = 21,200$ M$^{-1}$s$^{-1}$) (data in Figure 4.S13)\textsuperscript{24,26–28}, the first- and second- order kinetic rates were readily calculated to give $k_{TTA}$ (M$^{-1}$s$^{-1}$) = $P_2 \times \varepsilon_T \times 10^6$ and $k_T$ (s$^{-1}$) = $P_3 \times 10^6$.

To determine the fraction of acceptors/annihilators undertaking TTA, a series of kinetic absorption decays were collected at the maximum triplet excited state of acceptors at

\[
[^3M^*] = \frac{[^3M^*]_0 e^{-k_T t}}{1 + [^3M^*]_0 \frac{k_{TTA}}{k_T} (1 - e^{-k_T t})} \quad \text{Eq 4.3}
\]

\[
y = \frac{P_1}{1 + \left( \frac{P_1 \cdot P_2}{P_3} \right) \exp(P_3 \cdot t) - \left( \frac{P_1 \cdot P_2}{P_3} \right)} \quad \text{Eq 4.4}
\]

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<tr>
<th>Pulsed Energy (mJ)</th>
<th>$\Delta A_0$</th>
<th>$k_T$ (x10$^4$ s$^{-1}$)</th>
<th>$k_{TTA}$ (x10$^9$ M$^{-1}$s$^{-1}$)</th>
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<th>$\beta$</th>
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Table 4.2 Parameters Obtained from the Fits of the Transient Absorption Decay Data
420 nm as a function of pulsed energy. Table 4.2 summarizes the parameters obtained from fitting the kinetic decays using Eq 4.4 to give $\Delta A_0$, $k_T$, and $k_{TTA}$ as discussed above.

As such, when increasing the pulsed energy, the amount of triplet-excited state of acceptors/annihilators would rise as signified by $\Delta A_0$, shown in Figure 4.8. The concentration of sensitizer was chosen to sufficiently generate generous amounts of excited states of triplet sensitizer, and the concentration of acceptor was sufficient enough to quench at least 90% of triplet sensitizer. The analytical solution to equate for the fraction of acceptors occurring through the bimolecular TTA channel was designated by $\beta$, where $\alpha = k_{TTA} [^3\text{M*}]_0$ and $\beta = \alpha/(k_T + \alpha)$. These values are also reported in Table 4.2.

By extrapolating the fitted data of Figure 4.8, the $\beta$ values approached a maximum of 0.75 at saturated conditions of donor and acceptor pair as the pulsed laser reached high flux.

![Figure 4.8](image)

**Figure 4.8** a) Transient absorption decay at 420 nm of 3.4 x 10^{-5} M [Ru(bpy)_3]^{2+} and 3.78 mM AnCO_2^- in degassed water measured as a function of pulsed energy. ($\lambda_{exc} = 452$ nm). b) Representative kinetic fit (4.9 mJ/ pulse data) to eq. 4 (red line) and the residual of the fit is represented by green line.
power. At these high-pulsed energies, the quantum efficiency of TTA had already reached its highest yield, rendering the strong annihilation on. These kinetic calculations suggested that 75\% of the acceptors/annihilators were colliding through the TTA. As such, most of the acceptors/annihilators present in solution had resulted in producing a higher energy singlet through TTA.

With this information in hand, the triplet-triplet annihilation rate constant calculated from the transient absorption decays gave $k_{TTA} \sim 10^9 \text{ - } 10^{10} \text{ M}^{-1}\text{s}^{-1}$, which are values approximately close to the diffusion limit. These results suggested that the uncommon triplet fusion occurring in degassed water would yield a high efficiency of higher energy singlet excited states, rendering them susceptible for further transfer of energy or electrons to other third party scavengers.

### 4.8 Conclusion

In this study, we demonstrated new approaches for photochemical upconversion schemes that were executed homogenously in water. Triplet-triplet sensitization from Ru (II) sensitizers to carboxylate acceptors/annihilators ($\text{AnCO}_2^-$ or $\text{PyCO}_2^-$) has led to blue light (high-energy) emission when green light (low-energy) was absorbed. The delayed fluorescence of the upconverted sample had the same emission profile, resulting from direct UV excitation at 350 nm.

Subsequent to light absorption, the water soluble carboxylate acceptors quenched the excited state Ru(II) sensitizers with Stern-Volmer rate constants ranging from $k_{sv} \sim 2,000 \text{ M}^{-1}$
to 5,700 M⁻¹, and bimolecular rate constants ranging from \( k_q \sim 4 \times 10^9 \text{M}^{-1}\text{s}^{-1} \) to \( 7 \times 10^9 \text{M}^{-1}\text{s}^{-1} \) in both degassed H₂O and D₂O. These values were just below the diffusion limit in water.

Using pump-probe nanosecond transient absorption (TA) spectroscopy, long-lived triplet excited state acceptors (μs) were the result of triplet-triplet energy transfer (TTET). The rate of formation of the triplet acceptors at 420 nm matched spectroscopically the emission decay rate of the Ru(II) sensitizers at 620 nm.

The decay of the triplet excited state acceptors/annihilators was a function of two competing kinetic pathways: first-order triplet decay (\( k_T \)) and second-order triplet-triplet annihilation (\( k_{TTA} \)) rate constants. The second order \( k_{TTA} \) reached values as high as \( 10^9 -10^{10} \text{M}^{-1} \) for AnCO₂⁻ and PyCO₂⁻, which were calculated by fitting the transient absorption decay data at 420 nm as a function of pulsed energy. Based on these fast kinetic rates, 75% of the triplet acceptors were contributing in triplet fusion/annihilation, as suggested by the β values to yield higher energy singlet fluorescence.

At high laser flux intensity, the quantum yield of photon upconversion has reached its maximum, rendering the strong annihilation that resulted in a linear kinetic dependency as a function of power density. On the other hand, at low power densities, the weak annihilation was responsible for the quadratic dependence versus incident power.

In conclusion, the excimer products that were formed subsequent to triplet–triplet annihilation were concrete evidence that this higher energy singlet can be used in further photochemistry. Both sensitized AnCO₂⁻ and PyCO₂⁻ exhibited excimer formation when low energy photons were absorbed. The concept of shuttling energy or electrons from this higher
energy singlet will inspire further advancement in solar aqueous research especially in photocatalysis and photobiology.

4.9 Future Direction

In order to increase the quantum yield of upconversion in water, several factors that were discussed in section 4.5 need to be reduced. Ideally, water-soluble metalloporphyrins acting as sensitizers with low energy absorption would be promising candidates for photon upconversion. Their absorption spectra would not overlap with the upconverted emission of the acceptors, eliminating the inner-filter effect from the equation.

The use of other water-soluble acceptors with high quantum yield of fluorescence would result in a higher quantum yield of upconverted emission. Derivatives of diphenylanthracene (DPA) with functionalized groups, to insure the solubility of the organic compounds in water, would have higher energy fluorescence with singlet quantum yield close to near unity. In addition, DPA has been one of the most commonly used acceptors in photon upconversion because of its inability to produce excimers, hence increasing the upconverted photoluminescence.

The higher energy singlet resulting from triplet-triplet annihilation will inspire further transfer of energy/electrons to other Co(II) photocatalysts to produce hydrogen gas, as discussed in previous chapters in this dissertation. This will also allow us to explore a variety of other water reduction catalysts with higher reduction energetics to produce hydrogen gas, a high-energy feedstock chemical.
4.10 References


No. 5, 423–424.


4.11 Supporting Information

**Figure 4.S1** Upconverted emission spectra of 3.1 mM of AnCO₂⁻ sensitized by [Ru(BPS)]^{4+} (λ₅₁₄ nm ~ 0.2) in degassed D₂O (blue line) as a function of 514 nm excitation. [Ru(BPS)]^{4+} quenched emission intensity in D₂O is represented with red line.

**Figure 4.S2** Upconverted emission spectra of 2.8 mM of AnCO₂⁻ sensitized by [Ru(bpy)]^{2+} (λ₅₁₄ nm ~ 0.1) in degassed D₂O (black line) and H₂O (blue line) at 514 nm excitation wavelength. [Ru(bpy)]^{2+} quenched emission intensity for the corresponding samples in D₂O and H₂O are represented with red and pink lines respectively.
Figure 4.53 Dynamic photoluminescence quenching of Ru(II) photosensitizers monitored at 625 nm. Ruthenium(II) samples were prepared optically dilute in degassed D$_2$O. a) [Ru(bpy)$_3$]$^{2+}$ quenched by AnCO$_2^-$ b) [Ru(BPS)$_3$]$^{4+}$ quenched by AnCO$_2^-$ c) [Ru(bpy)$_3$]$^{2+}$ quenched by PyCO$_2^-$ d) [Ru(BPS)$_3$]$^{4+}$ quenched by PyCO$_2^-$. 
Figure 4.S4 Dynamic photoluminescence quenching of Ru(II) photosensitizers monitored at 625 nm. Ruthenium(II) samples were prepared optically dilute in degassed H₂O. 
a) [Ru(bpy)₃]²⁺ quenched by AnCO₂⁻ b) [Ru(BPS)₃]⁴⁺ quenched by AnCO₂⁻ c) [Ru(bpy)₃]²⁺ quenched by PyCO₂⁻ d) [Ru(BPS)₃]⁴⁺ quenched by PyCO₂⁻.
Figure 4.S5 Stern-Vomer plots of samples prepared in degassed H₂O solvent. a) [Ru(bpy)₃]²⁺ quenched by AnCO₂⁻ (black square) and PyCO₂⁻ (red circles). b) [Ru(BPS)₃]⁴⁻ quenched by AnCO₂⁻ (black square) and PyCO₂⁻ (red circles).

Figure 4.S6 Stern-Vomer plots of samples prepared in degassed D₂O solvent. a) [Ru(bpy)₃]²⁺ quenched by AnCO₂⁻ (black square) and PyCO₂⁻ (red circles). b) [Ru(BPS)₃]⁴⁻ quenched by AnCO₂⁻ (black square) and PyCO₂⁻ (red circles).
Figure 4.57 Nanosecond transient absorption spectroscopy of \([\text{Ru(bpy)}_3]^{2+}\) \((\lambda_{452 \text{ nm}} \sim 0.35)\) excited at 452 nm (~3 mJ/pulse) in D$_2$O vs H$_2$O solvent. Samples were bubble degassed for 40 min each. a) Transient absorption spectra of \([\text{Ru(bpy)}_3]^{2+}\) in D$_2$O at zero delay time. b) Excited state kinetic decay at 370 nm in D$_2$O (black line) vs in H$_2$O (blue line). c) Ground state bleach recovery measured at 470 nm in D$_2$O (black line) vs in H$_2$O (blue line). The red and pink lines represent single exponential decay fits, and the green data represents the residual of the single exponential decay fit.
Figure 4.S8 Transient absorption data of [Ru(bpy)₃]^{2+} with AnCO₂⁻ and PyCO₂⁻ respectively in D₂O solvent. Transient absorption difference spectra of [Ru(bpy)₃]^{2+} (A₄₅₂ nm ~ 0.35) with A) 0.5 mM of AnCO₂⁻ and A') 0.5 mM of PyCO₂⁻ respectively measured as a function of delay time in D₂O solvent. B) and B') show the kinetic growth (blue line) of the sensitized triplet acceptor of AnCO₂⁻ and PyCO₂⁻ respectively measured at 420 nm and the quenched emission decay (black line) of [Ru(bpy)₃]^{2+} at 625 nm with each acceptor; the red and pink lines represent single exponential decay fits. C) and C') are kinetic decay (black line) of triplet acceptor monitored at 420 nm for AnCO₂⁻ and PyCO₂⁻ respectively; the red line represent a exponential decay fit according to eq.3. The green data represents the residual of the exponential decay. Samples were bubble degassed and excited at 452 nm (~ 3 mJ/pulse).
Figure 4.89 Nanosecond transient absorption spectroscopy of [Ru(BPS)$_3$]$^+$ ($A_{452 \text{ nm}} \sim 0.35$) excited at 452 nm (~3 mJ/pulse) in D$_2$O vs H$_2$O solvent. Samples were bubble degassed for 40 min each. a) Transient absorption spectra of [Ru(BPS)$_3$]$^+$ in D$_2$O (black line) and in H$_2$O (red line) at zero delay time. b) Excited state kinetic decay at 340 nm in D$_2$O (black line) vs in H$_2$O (blue line). c) Ground state bleach recovery measured at 470 nm in D$_2$O (black line) vs in H$_2$O (blue line). The red and pink lines in b) and c) represent single exponential decay fits, and the green data represents the residual of the single exponential decay fit.
Figure 4.S10 Transient absorption data of [Ru(BPS)$_3$]$^{4-}$ with AnCO$_2^-$ and PyCO$_2^-$ respectively in H$_2$O solvent. Transient absorption difference spectra of [Ru(BPS)$_3$]$^{4+}$ (A$_452$ nm $\sim$ 0.35) with A) 0.5 mM of AnCO$_2^-$ and A') 0.5 mM of PyCO$_2^-$ respectively measured as a function of delay time in H$_2$O solvent. B) and B') show the kinetic growth (blue line) of the sensitized triplet acceptor of AnCO$_2^-$ and PyCO$_2^-$ respectively measured at 420 nm and the quenched emission decay (black line) of [Ru(BPS)$_3$]$^{4+}$ at 625 nm with each acceptor; the red and pink lines represent single exponential decay fits. C) and C') are kinetic decay (black line) of triplet acceptor monitored at 420 nm for AnCO$_2^-$ and PyCO$_2^-$ respectively; the red line represents the exponential decay fit according to eq.3.
Figure 4. S11 Transient absorption data of [Ru(BPS)₃]⁺⁺ with AnCO₂⁻ and PyCO₂⁻ respectively in D₂O solvent. Transient absorption difference spectra of [Ru(BPS)₃]⁺⁺ (λ₄52 nm ~ 0.35) with A) 0.5 mM of AnCO₂⁻ and A’) 0.5 mM of PyCO₂⁻ respectively measured as a function of delay time in D₂O solvent. B) and B’) show the kinetic growth (blue line) of the sensitized triplet acceptor of AnCO₂⁻ and PyCO₂⁻ respectively measured at 420 nm and the quenched emission decay (black line) of [Ru(BPS)₃]⁺⁺ at 625 nm with each acceptor; the red and pink lines represent single exponential decay fits. C) and C’) are kinetic decay (black line) of triplet acceptor monitored at 420 nm for AnCO₂⁻ and PyCO₂⁻ respectively; the red line represents the exponential decay fit according to eq.3. The green data represents the residual of the exponential de
Figure 4. S12 Stability of the upconverted emission of 3 mM of PyCO$_2^-$ sensitized by 0.3 mM of [Ru(bpy)$_3$]$^{2+}$ in degassed H$_2$O upon 488 nm excitation for 1.5 hour. Inset displays the upconverted intensity monitored at 383 nm as a function of irradiation time.
Figure 4.S13 Time resolved absorption kinetic decay of the triplet excited state of AnCO$_2^-$ (black line) and PyCO$_2^-$ (red line) in degassed H$_2$O monitored at 420 nm upon 452 nm excitation. The conditions were Ru(bpy)$_3^{2+}$ (3.5 x 10$^{-5}$ M) with AnCO$_2^-$ (3.7 mM) and PyCO$_2^-$ (3.9 mM) respectively. The triplet extinction coefficient of AnCO$_2^-$ ($^3\varepsilon = 39,000$ M$^{-1}$cm$^{-1}$) and PyCO$_2^-$ ($^3\varepsilon = 21,200$ M$^{-1}$cm$^{-1}$) were averaged as a function of pulsed energy and calculated using Eq 4.S1.$^{23,24,27,28}$ Ru(bpy)$_3^{2+}$ in water was used as the donor for the excited state absorption maximum at 370 nm ($^3\varepsilon_{\text{Donor}} = 22,000$ M$^{-1}$cm$^{-1}$).$^{26}$ The inset shows the single exponential fit (magenta line) and the residual (green line) of Ru(bpy)$_3^{2+}$ in water monitored at 370 nm.

\[
\frac{^3\varepsilon_{\text{Accepter}}}{^3\varepsilon_{\text{Donor}}} = \frac{\Delta A_{\text{Accepter}}}{\Delta A_{\text{Donor}}}
\]  

(Eq 4.S1)
CHAPTER 5. EXPERIMENTAL SECTION: SYNTHESIS, INSTRUMENTATION, 
AND MOLECULAR CHARACTERIZATION

5.1 Synthesis

General: All reagents and solvents were purchased from commercially available sources and used without any further purification unless otherwise specified. [Ru(bpy)₃]Cl₂ and [Ru(phen)₃]Cl₂ were purchased from Sigma Aldrich and used without further purification. Na₄[Ru(BPS)₃], Na₄[Ru(dpbpyS)₃], and Co¹¹(bpyPY2Me), were synthesized as specified in this chapter of the dissertation. The water used for photocatalysis was deionized using a Barntead nanopure system (~18MΩ-cm). Deuterated water (D₂O, 99.9% of D) was purchased from Sigma Aldrich. Several other Ru(II) sensitizers with heteroleptic ligands have been synthesized according to literature precedent (some of which involved microwave synthesis) but will not be reported in this dissertation.¹

Synthesis of ligand 4,4’-diphenyl-2,2’-bipyridine disulfonated. Na₂[dpbpyS]. The synthesis of dpbpyS was carried out using a reported literature procedure.² Using commercially available starting material 4,4’-diphenyl-2,2’-bipyridine (dpbpy), 500 mg (1.62 mmole) of dpbpy was placed in a 50 ml round bottom flask. The flask was placed in an ice bath. Using a pipet, add 10 ml of chlorosulfonic acid (excess) drop-wise to the solid material. The reaction was vigorously stirred overnight at room temperature. After the reaction mixture cooled down, it was added drop-wise to a 100
ml cold-water beaker. Precipitate was obtained then it was filtered. The solid product was then placed in a beaker and 30 ml of fresh water was added. Under vigorous stirring, 6 M of NaOH was titrated to the beaker where the solid dissolved in solution. The pH of the mixture was adjusted to pH 7 using 1 M of HCl, and then the solvent was evaporated and washed with ether to yield white solid. Yield 80 %. $^1$H NMR (400 MHz, D$_2$O): 8.2 (d, 2H), 7.82 (s, 2H), 7.65 (m, 4H), 7.45 (m, 3H), 7.3 (m, 3H)

**Synthesis of Tetrasodium Tris(4,4'-diphenyl-2,2'-bipyridine disulfonated ruthenium(II).** Na$_4$[Ru(dpbyS)$_3$]. The synthesis of [Ru(dpbyS)$_3$]$^{4-}$ was carried out using a similar approach to a reported literature procedure.$^{34}$ 200 mg of Na$_2$[dpbyS] (0.655 mmole) was mixed with 51.3 mg of RuCl$_3$.x3H$_2$O (0.196 mmole) in a 3 neck round bottom flask in 10 ml ethylene glycol. The mixture was bubble-degassed for 30 minutes. Then, the red reaction mixture was refluxed at 200$^0$C for 5 hours and under nitrogen inert atmosphere. After cooling to room temperature, 20 ml of ethanol was used to quench the reaction. The orange solution was then added to 150 ml ethyl ether where it remained stirring for 2 hours. Red solid have precipitated out of solution. It was filtered. To purify the compound, LH-20 sephadex column was used with methanol as an eluent solvent. Yield 72%. $^1$H NMR (400 MHz, MeOD): 9.1 (d, 2H), 7.92 (m, 3H), 7.77 (dd, 2H), 7.4 (m, 7H). NMR and MALDI were shown in supporting information Figure 5.S1 and 5.S2.
Synthesis of Tetrasodium Tris(bathophenanthroline disulfonate) ruthenium (II). 

$\text{Na}_4[\text{Ru(BPS)}_3]$. The synthesis of $[\text{Ru(BPS)}_3]^{4+}$ was carried out as previously reported in the literature.$^3,^4$

Synthesis of Co$^{II}$($\text{bpyPY2Me}$). The water reduction Co (II) catalyst, Co$^{II}$($\text{bpyPY2Me}$) was synthesized according to a previously reported literature procedure.$^5$
5.2 Hydrogen Production

5.2.1 Photocatalytic Experiment

Hydrogen production experiments were performed using a home-built 16 well setup. This apparatus contained IKA shaker, starboard, LEDs, lenses, aluminum blocks, EPA vials, Teflon spacers, pressure transducers, and capillary tubes connected to a Mass Spectrometer as seen in Figure 5.1.

Typically, 10 mL of the photocatalytic solutions were prepared in a 40 mL airtight EPA vial (VWR Scientific). The solution vials were irradiated from the bottom using Blue LEDs ($\lambda = 452 \pm 10$ nm, 540 mW) whose output was passed through a Fraen narrow beam lens (12° beam angle, FLP-N4-RE-HRF) that was positioned on top of the starboard (LXMS-PM01-0425-CT). The current passing through the LEDs was controlled by a custom-built circuit board and could be adjusted between 450 mA to 850 mA.

Figure 5.1 High-throughput screening apparatus for rapid optimization of hydrogen production compositions.
All experiments were done at a constant speed of 150 rpm using an IKA orbital shaker. The apparatus was temperature controlled at 20 °C using a circulating chiller that passes through the starboard and aluminum blocks. Before running the experiment, all reaction vials were headspace-degassed using a series of ten pressurizing cycles of vacuum/argon, and then finished by equilibrating to atmospheric pressure.

Each vial was connected to Pressure Transducers (SSI technologies, P51 pressure sensors) through Teflon spacers using stainless steel fittings to monitor the headspace pressure during the course of the reaction. Using a data acquisition box (National Instruments, NI-USB-6210), the data was logged into LabVIEW SignalExpress software generating a plot of voltage (V) versus time (s) corresponding to pressure change during the reaction in real time. The standard atmospheric pressure (1 atm) was equivalent to 1.67 V. A Universal Gas Analyzer (Stanford Research Systems, UGA-Hydrogen) was separately connected to the Teflon spacer through capillary tubes.

Before analyzing the headspace volume by Mass spectrometry at the end of the experiment, the pressurized vials containing the build-up evolved hydrogen gas were equilibrated to atmospheric pressure again. Certified 10% H₂/Ar standard was used as a calibration tank when quantifying the relative amount of hydrogen produced with respect to argon in each vial. And using the molar volume at 1 atm and room temperature, the number of mole of hydrogen evolved was calculated. The pressurized data was normalized to the amount of hydrogen produced showing the rate of the reaction as the number of moles of hydrogen (μmole) as a function of time (h).5–8
Another technique used to quantify the amount of hydrogen gas was through Gas Chromatography (GC) instrument (Shimadzu). At the end of the experiment, 0.1 ml headspace volume was pulled-out from the reactor vial through a Hamilton syringe and injected straight into the GC, with a thermal conductivity detector (TCD). The carrier gas was Argon. The temperature of the column (5 Å molecular sieves) was 50\(^0\) C. Calibration for the hydrogen gas produced was conducted accordingly for the instrument. Quantitative results of hydrogen gas were typically averaged between the GC and MS methods.

### 5.2.2 Quantum Yield of Hydrogen Production

Quantum yield calculations were determined from the initial rates of hydrogen production by measuring the output power of the photons being absorbed according to Eq 5.1.

\[
\Phi_{H_2} = \frac{2 \times n_{H_2}}{n_{\text{photons absorbed}}} \quad \text{Eq 5.1}
\]

\(n_{H_2}\) is the number of moles of hydrogen gas produced, and \(n_{\text{photons}}\) is the number of photons absorbed by the photocatalytic sample. Since two photons are absorbed to produce two electrons and generate hydrogen, a factor of 2 was included in the numerator.\(^6\) Here, the amount of hydrogen produced was back-calculated from the total volume of the headspace, utilizing the ideal gas law and molar volume at room temperature and 1 atmosphere.
The quantum yield of H$_2$ for each composition was averaged at three different power densities (30 mW, 45mW, 68 mW) of He/Cd laser 442 nm excitation source. The irradiation time was about 30 to 60 minutes. Identical results of quantum yield of hydrogen were obtained when blue LED 452 ± 10 nm (540 mW) was used.

5.2.3 Deuterated Experiment for Photocatalysis

When H$_2$O was replaced with D$_2$O, the gases produced were D$_2$, HD, and H$_2$. To calibrate the MS for the evolved gases, Li metal was used following the reaction in D$_2$O, H$_2$O/D$_2$O mixture (1:1), and H$_2$O. The percentages of each gas evolved when Li was added to the sample were calculated from the pressure build-up and the MS signals. Identical calibration results were found when certified gas standard (D$_2$) was used relative to the reaction of Li with water.

5.2.4 Steady-State Measurements

The absorption spectra were acquired using Agilent 845 diode array spectrophotometer or Cary 50. The spectrofluorometer FL/FLS920 (Edinburgh Instruments) equipped with a 450 W Xe arc lamp and PMT (R2658P, Hamamatsu) was used to collect the static emission spectra. All emission spectra were corrected for detector response.

The samples were optically dilute (O.D. = 0.1- 0.2). Solutions were excited into the lowest energy absorption band. Before photoexcitation, the aqueous solutions were
bubbles-degassed with Argon for at least 30 minutes and kept under positive pressure during the data acquisition.

5.2.5 Transient Absorption Measurements for Photocatalytic Compositions

Pump-probe nanosecond transient absorption (TA) spectroscopy was acquired using a Vibrant 355 LD-UVM Nd:YAG/OPO system (OPOTEK). The transient absorption data collected was from an LP920 laser flash photolysis (Edinburgh Instruments) with an iStar ICCD Camera (Andor), and the kinetic traces were acquired using a PMT (R928 Hamamatsu). Samples were prepared with an optical density of 0.1 – 0.2 for photoluminescence and 0.3 – 0.6 at the excitation wavelength for transient absorption measurements. The aqueous solutions were bubbles-degassed with Argon for at least 30 minutes, and any samples contained in an organic solvent were freeze-pump-thawed before the start of the experiment.

5.2.6 Fraction Quenched

Using Stern-Volmer relation, the Stern-Volmer constants (k_{sv}) and the bimolecular quenching rates (k_q) were extrapolated from photoluminescence lifetime or Intensity experiments according to the Stern-Volmer equation, \( \frac{\tau_0}{\tau} = \frac{I_0}{I} = 1 + k_{sv}[Q] \). \( \tau_0 \) and \( \tau \) are the sensitizer lifetimes of the unquenched and quenched emission respectively. \( I_0 \) and \( I \) are the integrated emission of the sensitizer measured using FL/FL920 spectrofluorometer (Edinburgh Instruments) for the unquenched and quenched samples respectively. The absorbance of the sensitizers was chosen to be optically
dilute at the excitation wavelength (0.1 - 0.2). All samples were bubbled degassed for 40 min before the start of the experiment. The fraction quenched was represented in Eq 5.2

\[
\text{fraction quenched} = 1 - \frac{\tau}{\tau_0} = \frac{\tau_0 - \tau}{\tau_0} = \frac{k_v [Q]}{k_{sv} [Q] + 1}
\]

Eq 5.2

5.2.7 Cage-Escape Calculations

The cage-escape yields (Φ_{CE}) for the reduced Ru(II) sensitizers and the oxidized ascorbate (HA⁺) were determined using a series of experiments of transient absorption spectroscopy, spectroelectrochemistry, and Stern-Volmer quenching. The yields were calculated relative to an actinometer, [Ru(bpy)₃]²⁺ in water, according to Eq 5.3.⁠¹⁰⁻¹³

\[
\Phi_{CE} = \frac{\Delta A_{\text{sample}}}{\Delta A_{\text{actinometer}}} \frac{\Delta \varepsilon_{\text{sample}}}{\Delta \varepsilon_{\text{actinometer}}} \times (1 - 10^{A_{\text{actinometer}}}) \times (1 - 10^{A_{\text{sample}}}) \times \text{fraction quenched}
\]

Eq 5.3

Where ΔA_{sample} represents the maximum of the decay of the radical anion. Δε_{sample} corresponds to the maximum extinction coefficient of that radical anion at the same wavelength for ΔA_{sample}, data estimated from spectroelectrochemistry. ΔA_{actinometer} is the maximum transient observed for the [Ru(bpy)₃]²⁺ actinometer under identical excitation conditions. Δε_{actinometer} was previously reported as ~ 22,000 M⁻¹cm⁻¹ at 370 nm.⁠¹³⁻¹⁴ The fraction quenched was extrapolated from the Stern-Volmer relation.
5.2.8 Electrochemistry

Cyclic voltammetry and differential pulse voltammetry experiments were carried out using a BAS Potentiostat in an oxygen-free glovebox (Nitrogen flow). The working electrode was a Platinum (Pt) disc, and the counter electrode was a Pt wire. A glass electrode containing Ag wire and Ag/AgNO$_3$ solution (0.01 M) was the reference electrode. Ferrocene (Fc) was used as an internal standard. Reduction and oxidation potentials were measured in acetonitrile (ACN) solvent with 0.1 M of tetrabutylammonium hexafluorophosphate as a supporting electrolyte.

5.2.9 Spectroelectrochemistry

Spectroelectrochemistry experiments were performed using an Ocean Optics (HR2000+ Spectrometer) and Fiber optics with a BAS Potentiostat for potential control. The experiment was carried out in an oxygen-free glovebox (Nitrogen flow). A Pine Instruments Honeycomb electrode was used as a working and counter electrode. A glass electrode containing Ag wire and Ag/AgNO$_3$ solution (0.01 M) was the reference electrode. The controlled potential bulk-electrolysis was 50-100 mV more negative than the reduction potentials of the corresponding Ru(II) compounds. The samples were measured with 0.1 M of tetrabutylammonium hexafluorophosphate as a supporting electrolyte in acetonitrile (ACN) solvent. The change in absorption due to the reduction of the compound was monitored by the ocean optic spectrophotometer described above.
5.2.10 Real-Time Absorption Measurements for Decomposition Rates

Real-time absorbance of the photocatalytic composition was measured in a home-built apparatus whereby a 1 cm pathlength air-tight cuvette (Starna Cells) was placed in a cuvette holder and irradiated from the front side with a He/Cd laser (442 nm) whose intensity was varied using neutral density filters. A representation of the experiment was shown in Figure 5.2

![Figure 5.2](image)

**Figure 5.2** A representation of the home-built real-time absorption experiment to monitor the absorption spectra for the photocatalytic solution under He/Cd laser (452 nm; 68 mW) irradiation.

The photocatalytic solution in the cuvette was constantly stirred using a magnetic stirrer-bar and absorbance was taken as a function of irradiation time using an Ocean Optic spectrophotometer (HR2000+ Spectrometer). The spectrophotometer was equipped with both deuterium and halogen light sources (DT-MINI-2GS, Ocean Optics) which are both coupled to fiber optic cords placed perpendicular to the laser beam (He/Cd laser).
5.2.11 HPLC Study

The HPLC (Shimadzu) instrument equipped with a PDA detector was used to demonstrate the percentage/ratio of degradation species in solution after photocatalysis by separating the compositions using a C18 column and monitoring their respective absorbance spectra. The solution contained Ru(II) sensitizer, Co(II)(bpyPY2Me), and ascorbic acid at pH 4. Measurements were taken before and after 1.5 hours of irradiation at 452 ± 10 nm (540 mW) and at room temperature. The compositions were separated in gradient solvents of HPLC grade water and methanol over a period of 40 minutes (10-90% methanol). The flow rate was 0.1 ml/min. Trifluoroacetic acid (0.1%) was added to the HPLC solvents. The LC traces were monitored at 280 nm wavelength.

5.2.12 Dynamic Light Scattering (DLS)

Dynamic Light Scattering experiments were performed using a DynaPro Nanostar (Wyatt Technology) equipped with a 663 nm incident laser light. This experiment demonstrated the absence of nanoparticles present in solution upon photoexcitation, validating the homogenous nature of the photocatalytic studies presented in this dissertation. The scattering angle was 90° relative to the incident light. Measurements were taken before and after irradiation. The samples were filtered using a 0.4 µM pore size filter before each measurement and run at room temperature. The experiment was an average of 50 acquisitions, using a 5 second scan rate. The software used was Wyatt`s Dynamic 7 software.
5.3 Photon Upconversion in Water

General: [Ru(bpy)$_3$](Cl)$_2$ was purchased from Sigma Aldrich and used without further purification. Na$_4$[Ru(BPS)$_3$] was synthesized and purified as previously reported in the literature.$^{4,15}$ 9-Anthracenecarboxylic acid (AnCO$_2$H) and 1-Pyrenecarboxylic acid (PyCO$_2$H) were purchased from Sigma Aldrich. Each carboxylic acid compound was treated with hot sodium hydroxide in water, under vigorous stirring overnight, followed by recrystallization from acetone to yield the sodium salts 9-Anthracenecarboxylate anion (AnCO$_2^-$) and 1-Pyrenecarboxylate anion (PyCO$_2^-$) respectively.$^{13}$ The anionic compounds, AnCO$_2^-$ and PyCO$_2^-$, were water soluble, however their conjugate acid form was insoluble.

Spectroscopic samples were placed in a 1 cm path length Starna cell (quartz) cuvette, bubble-degassed with argon gas for at least 40 min where they remained under positive inert atmosphere during the course of the photospectroscopic experiments. Deuterated water (D$_2$O, 99.9% of D) was purchased from Sigma Aldrich, and HPLC grade water (H$_2$O) was purchased from J.T. Baker. Absorption spectra were measured using Cary 50 or Agilent 845 diode array spectrophotometer. Static emission spectra were collected by FL/FL920 spectrofluorometer (Edinburgh Instruments) and corrected for emission detector response.

5.3.1 Transient Absorption Spectroscopy for Upconversion Compositions

The optical density of the samples at 452 nm excitation wavelength was $\sim$ 0.35. The laser pulse excitation source was from a Vibrant 355 LD-UVM Nd:YAG/OPO system.
(OPOTEK) (∼3 mJ/pulse, 1Hz). The transient absorption data collected was from an LP920 laser flash photolysis (Edinburgh Instruments) with an iStar ICCD Camera (Andor), and the kinetic traces were acquired using a PMT (R928 Hamamatsu) and exponential decays were fitted accordingly using Origin 9.1

5.3.2 Stern-Volmer Kinetics

Using steady state dynamic photophysics, the Stern-Volmer constants ($k_{sv}$) and the bimolecular quenching rates ($k_q$) were extrapolated from photoluminescence lifetime experiments according to the Stern-Volmer relation, $\tau_0/\tau = 1+k_{sv}[Q]$, where $\tau_0$ and $\tau$ are the sensitizer lifetimes of the unquenched and quenched emission respectively. The slope ($k_{sv}$) was linear upon the addition of [Q], molar concentration of quencher/acceptor. The samples were excited using a Nitrogen-pumped dye laser at 442 nm to selectively excite the Ru (II) MLCT band in the absorption spectra. The absorbance of the sensitizers was chosen to be optically dilute at the excitation wavelength (0.1 - 0.2). All samples were bubbled degassed for 40 min before the start of the experiment.

5.3.3 Upconversion Power Dependence Experiment.

The upconverted photoluminescence detected from the FL/FLS 920 spectrofluorometer discussed above was a result of a continuous laser beam excitation from an Argon/Krypton ion laser (Innova 70C Coherent) excited at 488 nm or 514 nm (∼ 1 mm diameter spot). A Nova II/PD300-UV power meter was used to determine the excitation power before reaching the sample.
The appropriate filters were positioned in front of the incident laser to filter-out all wavelengths except the excitation wavelength issued from the laser preventing direct absorption of the acceptor. It is significant to note that no emission was observed when samples were irradiated in the absence of sensitizer. In addition, band pass filters were placed before the PMT detector to avoid light scattering from the laser.\textsuperscript{16}

For the power dependence experiment, neutral density filters were used to adjust the laser power prior to exciting the sample. To gain an improved upconverted emission profile, a spatial geometry adjustment of sample illumination was used to correct for the inner-filter effect. In the formulations examined here, upconversion was detected when the laser beam was incident along the edge square of the cuvette sample (Figure 5.3). Direct excitation from the Xenon arc lamp, which is associated with the PMT detector of the FL/FLS920 mentioned earlier, lead to insignificant upconverted emission due to the non-coherent incident power.

\textbf{Figure 5.3} Illustration of the laser beam irradiated along the edge-geometry square cuvette to correct for the inner filter effect and avoid the reabsorption of the upconverted emission
The concentration of sensitizer was chosen with an absorbance of ~ 1 at the excitation wavelength, whereas the acceptor concentration was selected so that it can quench the excited state of the sensitizer at least up to 90 % as extrapolated from Stern-Volmer kinetics \( (k_{sv}) \). The power dependence data were plotted as a double logarithmic graph showing the integrated upconverted emission as a function of incident power densities.

5.3.4 Quantum Yield of Upconversion

Upconversion quantum yield of acceptor \( \text{AnCO}_2^- \) or \( \text{PyCO}_2^- \) sensitized by Ru(II) sensitizers were calculated relative to \( [\text{Ru(bpy)}_3](\text{PF}_6)_2 \) in aerated spectrophotometric grade acetonitrile with quantum efficiency of \( \Phi_{\text{std}} = 0.018 \).\(^{17,18} \) The conditions used to calculate the quantum yield were selected to have optically-dilute samples of sensitizers (\( A_{514 \text{ nm}} = 0.1 \sim 0.2 \)) with acceptor concentration appropriate for at least 90 % quenching rate. The samples were irradiated using the Ar/Kr laser at 514 nm via the edge-excitation geometry mentioned above, where the laser was focused onto the edge of the 1 cm path length square-cuvette.

Because photochemical upconversion requires a two absorbed photons to yield one upconverted photon emission, the quantum yield of upconversion \( (\Phi_{\text{UC}}) \) is multiplied by a factor of 2 to obtain a maximum conversion of 100% efficiency as seen in Eq 5.4.

\[
\Phi_{\text{UC}} = 2\Phi_{\text{std}} \left( \frac{A_{\text{std}}}{A_{\text{UC}}} \right) \left( \frac{I_{\text{UC}}}{I_{\text{std}}} \right) \left( \frac{\eta_{\text{UC}}}{\eta_{\text{std}}} \right)^2 \tag{5.4}
\]

\( A_{\text{std}} \) and \( A_{\text{UC}} \) are the absorbance of the standard sample and upconverted sample at 514 nm respectively; \( I_{\text{std}} \) and \( I_{\text{UC}} \) are the integrated area of the corrected emission profile for
the standard and upconverted sample. \( \eta_{\text{std}} \) and \( \eta_{\text{UC}} \) are the refractive index of the standard and upconverted solvents respectively.

5.3.5 Triplet Extinction Coefficient of AnCO\(_2\)\(^-\) and PyCO\(_2\)\(^-\) in Water

The molar extinction coefficient of AnCO\(_2\)\(^-\) and PyCO\(_2\)\(^-\) were determined using the energy transfer method as was previously described.\(^{19-22}\) This method involved [Ru(bpy)\(_3\)]\(^{2+}\) donor with a known triplet extinction coefficient (\( ^3\varepsilon_{\text{Donor}} = 22,000 \text{ M}^{-1}\text{cm}^{-1} \)) at 370 nm in the presence of acceptor to quench all the excited state triplet sensitizer.\(^5\) Through Triplet-Triplet energy transfer (TTET) quenching, the transient absorption difference spectrum were measured for the respective triplet donor and triplet acceptor according to Eq 5.5. \( ^3\varepsilon_{\text{Donor}} \) and \( ^3\varepsilon_{\text{Acceptor}} \) are the extinction coefficient of the donor (known) and acceptor (unknown) respectively. \( \Delta A_{\text{Donor}} \) and \( \Delta A_{\text{Acceptor}} \) are the maximum optical densities for the triplet donor (370 nm) and triplet acceptor (420 nm).

\[
\frac{^3\varepsilon_{\text{Acceptor}}}{^3\varepsilon_{\text{Donor}}} = \frac{\Delta A_{\text{Acceptor}}}{\Delta A_{\text{Donor}}} \quad \text{Eq 5.5}
\]

The conditions were [Ru(bpy)\(_3\)]\(^{2+}\) (3.5 x 10\(^{-5}\) M) with AnCO\(_2\)\(^-\) (3.7 mM) and PyCO\(_2\)\(^-\) (3.9 mM) respectively. The triplet extinction coefficient of AnCO\(_2\)\(^-\) (\(^3\varepsilon = 39,000 \text{ M}^{-1}\text{cm}^{-1} \)) and PyCO\(_2\)\(^-\) (\(^3\varepsilon = 21,200 \text{ M}^{-1}\text{cm}^{-1} \)) were averaged as a function of pulsed energy.
5.4 References


Figure A.1 $^1$H NMR of Na$_4$[Ru(dpbyS)$_3$] in MeOD solvent performed on 400 MHz
Figure A.2 MALDI of Na₄[Ru(dpbpyS)₃]
Figure A.3 $^1$HNMR of Na[AnCO$_2$] in D$_2$O solvent performed on 400 MHz.
Figure A.4 IR spectra of 9-Anthracenecarboxylic acid and Sodium 9-Anthracenecarboxylate