Synthetic Tuning of the Properties of Transition Metal Complexes Toward Solar Energy Conversion Applications

by

Isaac N. Mills

Submitted in partial fulfillment of the requirements for the degree Doctorate of Philosophy in Chemistry

Committee Members

Professor Stefan Bernhard, Advisor Professor Danith Ly, Chair Assistant Professor Kevin Noonan Associate Professor Jill Millstone, University of Pittsburgh

> Departments of Chemistry, Carnegie Mellon University Pittsburgh, PA 2017

© Copyright by Isaac N. Mills, 2017

All Rights Reserved

Abstract

The conversion of sunlight into useful forms of energy is a much-researched topic with many successful means to effect such transformations. Modern solar conversion devices operate by direct production of electricity *via* photovoltaic conversion, with DSSCs being a highly-attractive low-cost option. While direct solar conversion to electricity will have a place in an integrated renewable energy economy, production of solar fuels is still a necessity for transportation and to supply power after the sun sets. Many solar fuels exist, with hydrogen being a prime target and zinc metal being a relatively new, but attractive option.

This work reports the design of DSSC dyes which address two shortcomings of current dyes: photodegradation *via* ligand dissociation and the use of rare metals. Iron (II)-based dyes were synthesized using hemicaging ligands with a ruthenium(II) dye being synthesized as a comparator to current dyes. These dye candidates were assessed through electrochemical and spectroscopic techniques where they were found to be promising candidates. The dyes await implementation in a device to assess real-world performance.

This work also reports on the tuning of bis-cyclometalated iridium(III) photosensitizers *via* the inclusion of nitriles on the cyclometalating and diimine ligands. Properties of the complexes were interrogated *via* electrochemical and photophysical

methods which were correlated to results from density functional theory calculations. Photophysically, the nitriles lower luminescence quantum yield and excited state lifetime when placed on the diimine ligand, but strongly enhance these properties when placed on the cyclometalating ligand. Extreme cases of this produced complexes with excited state lifetimes as low as 27 ns and as high as 8 μ s; similarly, luminescence quantum yields varied between 0.09% and 63% for these complexes.

This work also reports on the assessment of the bis-cyclometalated complexes ability to photosensitize water reduction catalysis using a variety of catalysts and solvents. Inclusion of nitriles on the diimine ligands was found to facilitate direct coordination of the photosensitizers to platinum colloids during water reduction photocatalysis. Systems achieved up to 1300 photosensitizer turnovers and functioned without degradation for over 75 hours under optimized conditions. Inclusion of nitriles on the cyclometalating ligand produced complexes with much greater solvent tolerance; these complexes were able to achieve over 2000 photosensitizer turnovers and function in more environmentally-benign solvents such as alcohols and acetone.

Finally, this work reports on the assessment of the bis-cyclometalated iridium (III) complexes as catalysts for the photoreduction of zinc salts to zinc metal as a solar fuel. All complexes synthesized were competent photocatalysts for this reaction, where they achieved between 154 to 237 photocatalyst turnovers. Though the newly-synthesized complexes worked, they did not outperform existing photocatalysts and could not replace the need for acetonitrile.

Acknowledgements

First and foremost, I'd like to thank my amazing wife, Amanda for being the perfect partner on this wild journey. You put up with more craziness from me than you should, and you've always been there to keep me grounded and focused when I get off on some tangent. I'm amazed that your patience has endured through seven years of graduate school, when I'm pretty sure we never thought I'd actually go for a PhD. I'm looking forward to finally being done saying, "just a couple more years" and settling down for our life together.

I'd also like to thank my wonderful daughters Maria, Sophia, and (baby) Helena. Watching them grow has been a constant source of joy and reminder that I have others who depend on me. Their adorable imitations of me "sciencing" have provided some much-needed comic relief during stressful times. I'm pretty sure they think I read about planets and look at pictures of animals all day; it's comforting to know that I can at least keep up with their expectations.

My advisor, Stefan, also deserves credit for his efforts. He took a carbohydrate chemist from a bad part of town (and a fraternity man, nonetheless) and saw a student who could be a doctor someday, if not the kind that helps people. He taught me (literally) everything I know about photochemistry, and he's always eager to do-it-himself and build me crazy devices whenever I need them. I've never seen a professor so involved in their students' lives, and I hope to emulate his earnest interest with my future students.

My family, apart from those I live with, has also played a critical role in my completion of this task. My in-laws, particularly my father- and mother-in-law James and Barbara, have been a safe port during the storms these past few years. They've been unimaginably helpful with watching the children, taking us on vacations we could never afford, and praying for us every step of the way. I'm being literal when I say we couldn't have done it without you. My brother, Benjamin, has been my inspiration from Youngstown these years. Truth be told, one of the reasons I stuck to this program was because I didn't want to let you down. My father and mother, Rick and Patty, have also been supportive of me these years. I think the proudest moment they've had was that initial time I told them I got into CMU. I hope I've lived up to your expectations.

Finally, I'd like to thank my second family: the people I've worked with for the past five years. Husain, Jon and Dani-C, you have been great labmates and much-needed distractions I could always try out a few dad jokes on, play tennis with, or raid the buffet with when I didn't want ramen. I've enjoyed learning from and with all of you very much, and I hope we get the chance to collaborate in the future. I've had the opportunity to work with some wonderful undergraduates as well, namely Jacqueline/J'quell'in, Maegha, and Mike. Mo and Yogesh, I've enjoyed our discussion/complaints about labwork. Sometimes we need to vent and I've always enjoyed our talks. Last and certainly not least, I'd like to thank the wonderful teaching staff here at CMU: Susan, Gloria, Carolyn, Gizelle, and Mark. I miss working those teaching labs with you all, and I'm certain (I've been told directly) that those letters of recommendation greatly helped during my interviews. Thank you for showing me passion for teaching excellence and for putting up with me when I distracted the students with my terrible humor.

Table of Contents

Title Page	i
Abstract	iii
Acknowledgements	v
Lists of Figures	X
Lists of Tables	xix
Chapter 1 Introduction	1
1.1 World Energy Consumption and How to Meet the Demand	1
1.2 Solar Energy Conversion Strategies	4
1.2.1 Direct Solar Energy Conversion through DSSCs	4
1.2.2 Solar Energy Conversion via Hydrogen Generation	7
1.2.3 Photoreduction of Zinc Metal as a Solar Fuel	11
1.3 Development of Bis-cyclometalated Ir(III) Complexes	15
1.3.1 Initial Synthesis of Bis-cyclometalated Ir(III) Complexes	15
1.3.2 Tuning of Bis-cyclometalated $[Ir(C^N)_2(L^L)]^+$ Complexes and Use in OLEDs	17
1.3.3 Development of Water Reduction Photocatalysis Systems	22
1.3.4 Tailoring Photosensitizers to Specific Water Reduction Catalysts	28
1.3.5 Current State of Bis-cyclometalated $[Ir(C^N)_2(N^N)]^+$ Photosensitizers	31
References	33

Chapter 2 Hemicaging Iron Complexes for Dye-Sensitized Solar Cells	
2.1 Introduction	38
2.2 Experimental Section	40
2.2.1 Materials and Methods	40
2.2.2 Physical Characterization	40
2.2.3 Electrochemical Characterization	40
2.2.4 Photophysical Characterization	41
2.2.5 Preparation of Ligands and Complexes	41
2.3 Results and Discussion	46
2.3.1 Synthetic Strategies	46
2.3.2 Electrochemical Properties	47
2.3.3 UV-Visible Spectra	50
2.4 Conclusions and Future Directions	51
References	52

Chapter 3 4,4'-Dicyano-2,2'-bbipyridine Complexes for Solar Fuel Generation	53
3.1 Introduction	53
3.2 Experimental Section	56
3.2.1. Materials	56
3.2.2. Physical measurements	57
3.2.3. Preparation of complexes	59
3.3 Results and Discussion	61
3.3.1 Alternate Synthetic Route Rationale	61
3.3.2 Density Functional Theory Results	62
3.3.3 Electrochemical Properties	63
3.3.4 Photophysical Properties	66
3.3.5 Water Reduction Catalysis Studies	68
3.3.6. Photocatalytic Zinc Reduction	72
3.4 Conclusions and Future Directions	73
References	75

0	Chapter 4 CNmppy Complexes as Alternatives to Fmppy Complexes for Solar Fuel	
	Generation and Oxygen Sensing	78
	4.1 Introduction	78
	4.2 Experimental Section	80
	4.2.1 Materials and Methods	80
	4.2.2 Synthesis	81
	4.2.3 Computational Methods	85
	4.2.3 Electrochemical Characterization	85
	4.2.4 Photophysical Characterization	86
	4.2.5 Water Reduction Photosensitization Protocol	86
	4.2.6 Zinc Photoreduction Studies	87
	4.3 Results and Discussion	88
	4.3.1 Density Functional Theory Results	88
	4.3.2 Electrochemical Properties	90
	4.3.3 TD-DFT and Photophysical Characterization	92
	4.3.4 Photosensitization Studies	98
	4.3.5 Zinc Photoreduction Results	102
	4.4 Conclusions and Future Directions	103
	References	105

Lists of Figures

Figure 1-1. US energy consumption by source
Figure 1-2. Mechanism of energy conversion for a typical DSSC5
Figure 1-3. Ru(II) polypyridine dyes commonly used in DSSCs
Figure 1-4. Successful ligand-assisted acceptorless alcohol dehydrogenation catalysts 8
Figure 1-5. Water splitting half-reactions
Figure 1-6. Successful cp* iridium water oxidation complexes
Figure 1-7. Anode and cathode reactions for a zinc-air fuel cell
Figure 1-8: Maximum Ir turnovers (TON) for various photocatalysts with $ZnCl_2$ in
MeCN using TEA as a sacrificial donor13
Figure 1-9: Maximum PS TON achieved using [Ir(ppy) ₂ (dtbbpy)] ⁺ in various solvents
both neat and with 10% v/v MeCN added

Figure 1-10. Photoreduced Zn yields following 68 h illumination with 3 µmol ligand, 3 mmol ZnCl₂, and 1 mL triethylamine (sacrificial reductant) in 9 mL acetonitrile. .. 14

Figure 1-11: Cyclometalated dimer and cationic mixed-ligand complex......16

Figure 1-14: Slinker complex for use in OLEDs.	18
--	----

Figure 1-15: Ligands evaluated in the combinatorial study by Lowry et al...... 19

Figure 1-16: Emission energy (A), luminescence quantum yield (B), and log[excited state lifetime] in nanoseconds (C) for the complexes [Ir(C^N)₂(L^L)]⁺. For all graphs, (C^N) is enumerated as (1) ppy, (2) dtbppy, (3) bhq, (4) thpy, (5) Fmppy, (6) Clmppy, (7) Brmppy, (8) MeOmppy, (9) Phmppy, and (10) Hmppy; (L^L) is

indicated as (a) dppz, (b) dppe, (c) Me4-phen, (d) 5-MePhen, (e) 4-MePhen, (f)
phen, (g) 5,5'-dmbpy, (h) 4,4'-dmbpy, (i) 4,4'-dtbbpy, (j) bpy20
Figure 1-17: Extremely electron-rich bipyridine complexes based on the Slinker complex
Figure 1-18: Reductive quenching mechanism observed in systems without an electron relay using Pt colloids formed <i>in situ</i> from a K ₂ PtCl ₄ precursor
Figure 1-19: Rh(bpy) ₃ ³⁺ complexes evaluated as molecular catalysts for water reduction photocatalysis
Figure 1-20: Effects of different sacrificial donors, solvents on water photoreduction catalysis with Rh(dtbbpy) ₃ (PF ₆) ₃ as catalyst and [Ir(Fmppy) ₂ (dtbbpy)](PF ₆) as photosensitizer
Figure 1-21: New nickel thiolate hexamer (Left) used as a water reducing catalyst with [Ir(Fmppy) ₂ (dtbbpy)](PF ₆) (Right) as a photosensitizer
Figure 1-22: Effects of varying the cyclometalating and chelating ligands on photosensitizer performance in a water reduction system using colloidal platinum as a catalyst

Figure 1-23: Effect of solvent on selected photosensitizers using colloidal palladium
water reducing catalysts
Figure 1-24: [Ir(ppy) ₂ (bpy)](PF ₆) derivatives with pendant pyridyl moieties
Figure 1-25: PS turnovers for complexes with and without pendant coordinating pyridyls.
Figure 1-26: Photosensitizer (Left) and catalyst (Right) combination employed in
toluene/water/1-octylamine microemulsion study
Figure 1-27: Mechanism of photosensitizer degradation following excitation and
subsequent dissociation and replacement of bipyridine ligand
Figure 2-1. Synthesized hemicage complexes 1, 4, and 5 40
Figure 2-2. Synthesis of Fe(TEMBM)(BF ₄) ₂ 1
Figure 2-3. Synthesis of methyl ester hemicage 5,5-TEMABM 3
Figure 2-4. Synthesis of hemicage complexes $Fe(5,5'-TEMABM)(BF_4)_2$ 4 and $Ru(5,5'-TEMABM)(BF_4)_2$ 4
TEMABM)(PF ₆) ₂ 5

Figure 2-8. UV-Vis spectra of hemicage complexes 1 (blue) 4 (orange) and 5 (red). 50

Figure 3-1. Mechansim of bipyridine dissociation leading to photoinactive species. 55

Figure 3-	7. Ir turnovers obtained for different photosensitizers in THF and N	IeOH, using
K ₂ Pt	tCl_4 and $[Rh(dtbbpy)_3]^{3+}$ as water reduction catalysts. Reprinted with	h permission
from	n ref 1. Copyright 2014 Elsevier Ltd.	

Figure 4-1. S	Synthesized com	plexes 3a and 3b)	
0	2	1		

Figure 4-3.	Synthesis	of [Ir(CNmppy) ₂ Cl]	2 dimer,	2	\$2
0		· Ľ 、 · · · · · · · · · · · · · · · · ·	,		

- Figure 4-7. Experimental spectra (blue), calculated spectra (red), and predicted oscillators (black) for 3a (A) and 3b (B). The numbered transitions correspond to transitions highlighted in Figure 1. Experimental spectra were obtained from 10 μM solutions in Ar-degassed methanol. Calculated spectra and oscillator strengths were obtained from Gaussian TD-DFT calculations with methanol specified as the solvent. Figure reprinted with permission from ref 1. Copyright The Royal Society of Chemistry 2016.

Figure 4-12. A) H_2 evolution traces and corresponding Ir turnovers for 3a (solid lines) and 3b (dotted lines), using alcohols as solvents (0.1 mM photosensitizer, 30 μ M K₂PtCl₄ and 0.7 M TEA). B) Photosensitizer concentration study using EtOH and

Lists of Tables

Table 1-1. Electrochemical data for several bis-cyclometalated complexes. Cyclic
voltammograms were collected at 100 mV/s in 0.1 M TBAH in acetonitrile utilizing
a Pt working electrode, Pt counter electrode, and Ag wire as a pseudoreference.
Ferrocene was used as an internal standard and all values are reported with respect to
SCE
Table 2-1. Electrochemical data for 1, 4, 5, and comparators. 49
Table 3-1. Electrochemical data for 1,2 and comparators. 65
Table 3-2. Emission maxima, quantum yields, and excited state lifetimes of
$[Ir(ppy)_2(dCNbpy)]PF_6$ and $[Ir(Fmppy)_2(dCNbpy)]PF_6$
Table 3-3. Ir turnovers in THF and MeOH using $Co(bpy)_3^{2+}$ as the water reduction
catalyst71
Table 3-4. Production of zinc metal by photocatalytic Ir(III) complexes over 72 h. Each
reaction vial contained 110 μ M Ir(III) photosensitizer, 420 mg ZnCl ₂ , 9 ml solvent,
and 1 ml TEA under argon73

Table 4-3. Photoreduction catalysis turnovers for ZnCl₂ under standard conditions.^a... 102

Chapter 1

Introduction

1.1 World Energy Consumption and How to Meet the Demand

1.1.1 Trends and Background of World Energy Demand

One of the most pressing societal needs in the United States, and the world in general, is the need to fulfill our ever-increasing demand for energy. While domestic energy usage has tapered off with our decrease in industrial output and manufacturing, energy consumption remains high in the United States. Total annual energy consumption has remained just short of 100 quadrillion british thermal units (Quad BTU) since the year 2000, and is projected to remain at that level until approximately 2040.¹ To fill this need, the US relies heavily on fossil fuels with over 80% of its consumption coming from these sources (**Figure 1-1**).¹ All renewable energy sources account for just over 10% of consumption, though this number has been rising steadily for the past decade.

Globally the trend of increased output from renewables continues with oil subsidies falling from \$500 billion in 2014 to \$325 billion in 2015, while renewable energy sources become the focus of international agreements like the Paris Accord.² High energy-consumption countries are focusing on the goal of meeting 60% of their energy needs through renewable sources by 2040, when these technologies, particularly solar photovoltaics, are expected to compete with oil on a cost-per-watt basis without subsidy.²



Figure 1-1. US energy consumption by source.

There are several factors driving the increase in consumption of renewable energy. Political instability of traditional fossil fuel producers and the falling cost of renewable energy technologies only tell part of the story. Recent environmental disasters have brought environmental concerns to the forefront of the public perception. These environmental disasters are associated not just with the combustion of fossil fuels, but with their production, like the Deep Water Horizon oil spill, or their refinement as was the case in the Elk River chemical spill, or even their transportation like the Mosier Oregon train derailment and fire. Even disregarding the emissions from fossil fuel combustion, their preparation, storage, and transportation can have devastating effects.

1.1.2 Evaluation of Common Renewable Energy Systems

The push to supplement our energy portfolio with more renewable options has been realized through a variety of resources. Popular options have included energy production from wind, solar, geothermal, hydroelectric generation, reforming of biofuels, and tidal power. Each of these methods has its own inherent attractive features and drawbacks, and several have emerged as front-runners for a variety of reasons. Tidal power and geothermal generation, for example, are very attractive options only for small geographically rigid populations; the same can be said for hydroelectric power albeit to a less restrictive geographical area. Wind, solar, and biofuel power generation can be implemented almost everywhere and thus are the most broadly accessible forms of renewable power generation.

These forms of renewable energy are used to generate power in different ways. Wind and solar can be used to directly generate electricity through the use of turbines or photovoltaic devices. These approaches can be tied into existing power grids, or used to set up remote power grids. Unfortunately, power generation by these means is inconsistent due to fluctuating weather conditions and the natural diurnal cycle. Storage of generated power requires costly and often immobile battery banks. Compounding this, transportation relies on the consumption of high-energy density fuels, and will continue to do so until high-capacity batteries can be produced on a larger scale and at a lower cost than current iterations. Generation of portable fuels is therefore needed in addition to grid-based approaches.

Biofuel generation meets this need by directly generating fuels such as ethanol or methanol which can be used in fuel cells or traditional combustion engines. Widespread application of this method is largely hampered by economic factors including existing subsidy of fossil fuels, which makes presents a barrier to entry for new technologies, and cost-benefit inefficiency of current fuel reforming processes.³ An alternative to this approach which involves direct capture and reforming of atmospheric CO_2 has attracted attention recently, though large-scale operations require input of energy, usually as electricity, to drive these the thermodynamically uphill fuel-forming reactions.⁴

Among the popular renewable energy strategies, solar power has the unique advantage of being able to either generate electricity directly, or directly generate energy-added fuelstocks which can be used later. Though solar alone is not economically viable, a mixed renewable energy system deriving the majority of its energy from a mixed solar/wind approach through photovoltaics, solar thermal generation, turbines, and hydrogen could become a viable means of providing clean, reliable, and economically feasible power.⁵

1.2 Solar Energy Conversion Strategies

1.2.1 Direct Solar Energy Conversion through DSSCs

One way to meet solar energy production goals is through the use of dyesensitized solar cells (DSSCs). These devices, originally published by Grätzel in 1991, are comprised of a sensitized semiconductor, a dye molecule, an electrolyte, and a counter electrode.⁶ Titanium dioxide is typically the semiconductor, platinum or platinized graphite is the counter electrode, and a suitable dye/electrolyte combination, typically a Ru(II) polypyridine dye and Γ/I_3^- electrolyte, is employed to facilitate electron transport between the electrodes. A typical mechanism (**Figure 1-2**) for these cells can be seen below.⁷ Briefly, light is absorbed by a dye molecule adsorbed onto the titania, promoting one of its electrons to a high-energy orbital. This electron is then injected into the titania conduction band leaving the dye oxidized. The dye molecule is regenerated by an electrolyte, often the Γ/I_3^- redox couple. Triiodide is then reduced back to iodide at the counter electrode surface by the conduction band electron, completing the cycle.



Figure 1-2. Mechanism of energy conversion for a typical DSSC.

This relatively simple device has been the subject of intense research owing to several key advantages: the cell is typically low-cost, functions across a wide temperature range, functions with diffuse light, can be flexible, and unlike silicon-based cells has a short energy payback timeframe. Additionally, since the dye is the photoactive component, the absorption can be greatly tuned to take advantage of visible, IR, and/or UV light depending on application. Because light is only converted into energy following absorption by the dye, dye candidates must possess high molar absorptivity across the solar spectrum, while resisting photobleaching, and must possess excited orbitals of sufficient potential to transfer electrons into the conduction band of titania. Though these criteria seem restrictive, many dyes have been successful including metal-porphyrins⁸,

coumarin⁹, and most notably ruthenium-based^{10–12} polypyridine dyes. Among these dyes, ruthenium polypyridine dyes have emerged as the most effective, particularly N3, N719, N749, and Z907 (**Figure 1-3**).¹²



Figure 1-3. Ru(II) polypyridine dyes commonly used in DSSCs.

Moving forward with the DSSC, several challenges must be addressed. First, the dyes employed often degrade under illumination or if the cell operates at high temperatures. For Ru(II) polypyridines, the ³MLCT is able to be thermally populated; such a state may also lead to loss of a bipyridine ligand and subsequent deactivation of the dye molecule. This degradation pathway could be addressed by employing ligands which anneal back to the metal center, or by using terpyridine or quarterpyridine as ligands as they are less likely to dissociate from the metal center than bipyridine analogues. Another problem is the use of rare materials, particularly the ruthenium metal

center. Replacing this with more abundant metals, like iron or copper could help make these cells economically viable, even at lower power conversion efficiencies. Switching to metal-free dyes may also be a viable approach, though no long-term stability studies have been conducted on such cells.¹³

1.2.2 Solar Energy Conversion via Hydrogen Generation

Among solar fuels, hydrogen has emerged as the fuel of choice owing to its high specific energy density and its ability to be used in existing fuel cell technology or in combustion engines.¹⁴ Already present is a small, but scalable infrastructure dedicated to hydrogen fuel cells; since this system already exists, this fuel could rapidly and conveniently replace existing infrastructure for gasoline and diesel. Several ways of producing this fuel *via* solar illumination exist, with prime candidates being alcohol oxidation and water splitting.

Alcohol oxidation is attractive owing to its less thermodynamically up-hill process compared to water splitting, as well as the recent discovery of successful acceptorless dehydrogenation systems which would be suitable for generation of gaseous hydrogen.^{15–19} Though promising, this avenue also has several shortcomings. Most of the successful alcohol oxidation catalysts, like those in **Figure 1-4**, feature rare earth metals and complex architectures with assisting ligands. Because both of these are needed, the feasibility of scaling this to commercial processes is economically daunting. In addition one must also consider that the alcohols being oxidized have a fuel value themselves, and they currently require feedstocks which are commonly derived from non-renewable fuels

(e.g. methane, ethane), or they require timely and/or expensive processing (e.g. fermentation-produced alcohols).



Figure 1-4. Successful ligand-assisted acceptorless alcohol dehydrogenation catalysts.

Water splitting has attracted considerable attention for a variety of reasons. Unlike alcohol dehydrogenation, the feedstock for water splitting is an abundant, environmentally benign oxide. As concerns over the emissions from fossil fuel consumption rise, the combustion of hydrogen and oxygen is attractive since it yields only water. The process is also attractive since the hydrogen fuel generated can be used in many modern fuel cell vehicles; infrastructure to support the use of hydrogen as a fuel for transportation already exists, facilitating immediate implementation.

On paper, the process also seems rather straightforward. As seen in **Figure 1-5**, the process is divided into two half-reactions. The water oxidation half reaction involves the oxidation of water into molecular oxygen and the liberation of four electrons and protons. The water reduction half-reaction involves the reduction of these four protons with the released electrons to yield molecular hydrogen. Overall, it seems that the process is simply the splitting of water into hydrogen and oxygen, with the back-reaction again producing water.

Oxidation: Reduction:	$2H_2O \rightarrow O_2 + 4H^+ + 4H^+ + 4e^- \rightarrow 2H_2$	- 4e ⁻	
Overall:	$2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{O}_2 + 2\mathrm{H}_2$	$\Delta E^{o} =$	-1.23 V

Figure 1-5. Water splitting half-reactions.

Unfortunately, reality is more complicated than the apparent simplicity of overall water splitting. Because each half reaction requires catalysts to be driven at a reasonable rate, each reaction is typically studied independently with sacrificial agents used *in lieu* of the missing half-reaction. For water reduction, triethylamine (TEA) and triethanolamine (TEOA), as well as oxalic acid and ascorbic acid are commonly employed as sacrificial agents; for water oxidation ceric ammonium nitrate (CAN) is typically employed. This splitting allows for optimization of each half reaction, but integration of the two half reactions into a total solar water splitting system will have complications such as potential back-reaction of the activated water oxidation catalyst (WRC).

The oxidation half-reaction currently serves as the bottleneck to integrated water splitting systesms. Heterogeneous systems, such as those employing nanoparticle and semiconductor based systems suffer from poor per-site activity, and inefficiencies from hole recombination and collection.^{20,21} Molecular systems offer the advantages of being synthetically tunable and minimizing factors which obscure insights into structure-performance relationships. As a result, homogeneous systems have been heavily studied.^{22–32} Unfortunately, the strongly-oxidizing conditions employed often lead to destruction of the organometallic catalysts.³³ Nevertheless, iridium catalysts, particularly

those with cyclopentadienyl (cp*) ligands show remarkable promise for further development as water oxidation catalysts (**Figure 1-6**).



Figure 1-6. Successful cp* Iridium water oxidation complexes.

Compared to the water oxidation half-reaction, the reduction half-reaction has seen fewer bottlenecks to commercial realization. As this is the fuel-forming half-reaction in a solar hydrogen system, this reaction has been studied extensively. Like water oxidation, water reduction catalysts are often molecular in nature, such as popular $Rh(bpy)_3(PF_6)_3$ (bpy = 2,2'-bipyridine) derivatives; colloidal catalysts, particularly platinum colloids, have seen extensive use as well. Unfortunately, these catalysts have poor absorption in the visible range, necessitating the use of a photosensitizer to drive the reaction. As with water oxidation, iridium complexes, particularly bis-cyclometalated Ir(III) complexes, have emerged as some of the most-studied and successful candidates.

1.2.3 Photoreduction of Zinc Metal as a Solar Fuel

As a more easily handled, transported, and stored fuel than hydrogen gas, the production of reducing metals has recently attracted considerable interest in the field of renewable energy storage. Unfortunately, most of the commonly-available reducing metals (Li, Na, Mg, etc.) have reduction potentials that place them out of the reach of many visible-light driven photocatalytic processes. Zinc metal, however, has a more modest reduction potential (~-0.76 V vs SCE), is air-stable, and is a common component of current battery technologies.³⁴

These already-proven technologies could be realized in a zinc-air fuel cell system where zinc metal is used *in lieu* of gasoline or diesel for transportation. The concept has already been tested with vehicles making trips between 400-600 km.³⁵ Since the fuel is an air-stable metal, the fuel cells would be mechanically recharged, minimizing flammability risks commonly associated with liquid or gaseous fuels. To operate the cell, the zinc anode is placed in contact with a basic electrolyte to form $Zn(OH)_4^{2-}$ which decomposes into ZnO, water and hydroxide ions; at the cathode, atmospheric oxygen is reduced with water to form more hydroxide ions, regenerating those lost during oxidation of the zinc anode. Overall, a water-impermeable cell is established which oxidizes zinc into zinc oxide with no loss of electrolyte (**Figure 1-7**).³⁶ Though the theoretical output of the cell should be around 1.65 V, real-world systems typically realize operating potentials slightly below 1.50 V.³⁷

 $\begin{array}{ll} \underline{\text{Anode:}} & \underline{\text{Cathode:}} \\ & Zn \rightarrow Zn^{2+} + 2e^{-} & O_2 + H_2O + 4e^{-} \rightarrow 4(OH)^{-} \\ Zn^{2+} + 4(OH)^{-} \rightarrow Zn(OH)_4^{2-} & \\ & Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2(OH)^{-} \end{array}$

$$\frac{\text{Overall Reaction:}}{2 \text{ Zn} + \text{O}_2 \rightarrow 2 \text{ ZnO}} \Delta \text{E}^\circ = 1.65 \text{ V}$$

Figure 1-7. Anode and cathode reactions for a zinc-air fuel cell.

Though zinc is currently produced through either electrowinning of zinc oxide in alkaline media or smelting, recent work by Anthony Brooks developed a zinc photoreduction system comprised of a bis-cyclometalated Ir(III) photocatalyst, sacrificial reductant, and Zn^{2+} ions as an acceptor.³⁸ This three-component system functions analogously to the water reduction photolysis systems, producing metallic zinc for use as a solar fuel. A representative mixture of the best-performing photosensitizers and OLED materials were assessed as zinc photoreduction catalysts (**Figure 1-8**). The effect of different anions on Zn^{2+} reduction was also evaluated, with zinc halides, especially zinc chloride, being the most efficient. Finally, a solvent study was performed which indicated that acetonitrile is the best solvent for zinc reduction photocatalysis; even mixed solvent systems featuring 10% added acetonitrile typically saw an increase in maximum turnover numbers (**Figure 1-9**). A fully-optimized system reducing zinc chloride in pure acetonitrile achieved over 400 Ir turnovers using triethylamine as a sacrificial reductant.



Figure 1-8: Maximum Ir turnovers (TON) for various photocatalysts with $ZnCl_2$ in MeCN using TEA as a sacrificial donor.



Figure 1-9: Maximum PS TON achieved using $[Ir(ppy)_2(dtbbpy)]^+$ in various solvents both neat and with 10% v/v MeCN added.

This work was further improved upon in 2014 by replacing the Ir(III) photocatalyst with a zinc-quinoline complex.³⁹ The system again required the use of acetonitrile as a solvent, and zinc halides were the only salt found to be reduced in the study. Regardless, the use of the hydroxyquinoline-zinc complex represented a major step forward with regard to commercial viability. Luminescence quenching studies elucidated that the active photocatlalyst was the zinc monohydroxyquinolate; this result was supported by ¹H NMR. Various hydroxyquinolines were assessed with the trend being more electron-poor ligands producing more active photocatlalysts (**Figure 1-10**).



Figure 1-10. Photoreduced Zn yields following 68 h illumination with 3 μ mol ligand, 3 mmol ZnCl₂, and 1 mL triethylamine (sacrificial reductant) in 9 mL acetonitrile.

Currently, zinc photoreduction is in its infancy. To develop the system for use in a solar fuel system, several challenges need to be overcome. First, acetonitrile needs to be replaced as the solvent; this solvent is very expensive and supply often fluctuates year to year. Second, the catalysts employed need to achieve higher turnover numbers; employed

catalysts need to drastically increase turnovers before they can compete on with the cost of zinc electrowinning and smelting. Though these challenges seem daunting, zinc photoreduction nevertheless represents another interesting and promising way to advance the use of solar fuels.

1.3 Development of Bis-cyclometalated Ir(III) Complexes

1.3.1 Initial Synthesis of Bis-cyclometalated Ir(III) Complexes

The use of photo-active cationic transition metal complexes in electronics, photocatalysis, and sensory applications has long been a topic of great interest. Exemplary complexes, such as $Ru(bpy)_3^{2+}$, garnered great interest due to its modest photoreducing and strong photooxidizing ability, as well as its oxygen-sensitive and longlived triplet excited state. Use of this complex in industrially-relevant applications, such as in the fabrication of OLEDs or as a photocatalyst/photosensitizer, was unfortunately hampered by the lack of electronic and color tunability. This lack of tunability arises from the complex's low-lying ³MC state; the complex's ability to thermally depopulate from the ³MLCT exited state through this metal-centered state can also result in ligand dissociation. Nevertheless, the complex was extensively researched and this deactivation pathway was mitigated by switching to a 5d metal to synthesize $Ir(bpy)_3^{3+}$ and its derivatives. These Ir(III) complexes have also been shown to be potent photooxidants, though they still lack color tunability; they are also very difficult to synthesize as the temperatures required often result in a mix of cyclometalated and non-cyclometalated isomers owing to ring rotation about the 2,2'-bond.

A major advancement in this field was achieved through deliberate cylcometalation by replacing the electron-poor bipyridine ligand with phenylpyridine ligands to synthesize the dichloro-bridged [Ir(ppy)₂Cl]₂ dimer (**Figure 1-11**).^{40,41} Color and redox tunability was subsequently observed with the synthesis of the mixed-ligand [Ir(ppy)₂(bpy)]PF₆ complex (**Figure 1-11**) and its derivatives.⁴² Analysis of the excited states of the mixed-ligand complex indicated that the dominant emission is the result of a mixed ³ILCT-³MLCT transition, with partitioning of the HSOMO on the bipyridine and LSOMO on the metal and the phenylpyridine ligands (**Figure 1-12**).^{43,44} The result is a complex with substantial metal character in the excited states, strong spin-orbit coupling, and readily partitioned and therefore synthetically tunable photoexcited states; additionally, the triplet state creates a complex which is both powerfully oxidizing *and* reducing allowing the complex to be used in a variety of redox processes.



Figure 1-11: Cyclometalated dimer and cationic mixed-ligand complex.


Figure 1-12. HSOMO and LSOMO of $\text{Ru}(\text{bpy})_3^{2+}$ (Left) and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ (Right) showing pure ³MLCT character in the $\text{Ru}(\text{bpy})_3^{2+}$ orbitals and mixed ³ILCT-³MLCT character in the $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ orbitals.

1.3.2 Tuning of Bis-cyclometalated $[Ir(C^N)_2(L^L)]^+$ Complexes and Use in OLEDs

One of the first groups to successfully realize the applications of this family of luminophores was Kenneth Lo, who first used the complexes as luminescent probes for biological applications. In this work, biotin was attached to the diimine ligand (**Figure 1-13**), which was not found to disturb the luminescence properties of the complexes.⁴⁵ Variation of the cyclometalating ligands, however, produced a modest variation in the emission maxima of the complexes, with complexes emitting between 554 - 587 nm in degassed acetonitrile at room temperature.



Figure 1-13: Bis-cyclometalated Ir^{3+} complex with pendant biotin moiety synthesized by Lo *et al*.

Around the same time as Lo's work on iridium-based luminescent dyes, investigations into the use of cationic bis-cyclometalated iridium complexes in organic light-emitting devices (OLEDs) were being conducted. In work by Slinker et al, a vastly-improved variant of the traditional $[Ir(ppy)_2(bpy)]^+$ complex was made by substituting the 4 and 4' positions of the bipyridine ligand with *tert*-butyl groups (**Figure 1-14**). These groups led to a three-fold increase in the luminescence quantum yield along with an approximate doubling of the excited state lifetime. The complex was found to be an efficient luminophore in a single layer OLED with a light output of 10 Lm/W as well as being a bright emitter at 300 cd/m², both at 3 V.⁴⁶



Figure 1-14: Slinker complex for use in OLEDs.

Following this, Lowry synthesized a library of 76 new bis-cyclometalated Ir³⁺ complexes in a combinatorial effort to probe the limits of the motif's tunability. 100 complexes were synthesized, including previously studied controls, by step-wise synthesis of the dimer with one of 10 cyclometalating ligands followed by dimer cleavage with one of the 10 neutral, bidentate ligands (**Figure 1-15**). The controls were in excellent agreement with previous results, while the new complexes proved these complexes' emission maxima, excited state lifetime, and quantum yield can be dramatically affected by variation of the ligands employed (**Figure 1-16**).⁴⁷



Figure 1-15: Ligands evaluated in the combinatorial study by Lowry et al.



Figure 1-16: Emission energy (A), luminescence quantum yield (B), and log[excited state lifetime] in nanoseconds (C) for the complexes $[Ir(C^N)_2(L^L)]^+$. For all graphs, (C^N) is enumerated as (1) ppy, (2) dtbppy, (3) bhq, (4) thpy, (5) Fmppy, (6) Clmppy, (7) Brmppy, (8) MeOmppy, (9) Phmppy, and (10) Hmppy; (L^L) is indicated as (a) dppz, (b) dppe, (c) Me4-phen, (d) 5-MePhen, (e) 4-MePhen, (f) phen, (g) 5,5'-dmbpy, (h) 4,4'-dmbpy, (i) 4,4'-dtbbpy, (j) bpy.

Following the success of the Slinker complex, computational insights into the mechanism of luminescence were sought to inform future OLED luminophore design. These computational studies confirmed that for $[Ir(ppy)_2(bpy)]^+$ complexes, the dominant emissive pathway is from the $T_1 \rightarrow S_0$ transition.⁴⁸ In addition to computational investigation of successful luminophores like the Slinker complex, a more electron-rich modification of the dtbbpy ligand was evaluated utilizing di-methylamino groups in place of the di-*tert*-butyl groups. Two new complexes (**Figure 1-17**) were synthesized by Nazeeruddin *et al.* and found to be highly-efficient emitters with quantum yields of 80 and 85 %, respectively; the complexes also possessed excited-state lifetimes of 2.4 and 4.1 μ s.⁴⁹ These results are unexpected, as modification of the bipyridine ligand had not

thus far drastically altered the photophysical properties of this class of luminophores; investigation of the mechanism of luminescence, however revealed that the complexes had strong $\pi \rightarrow \pi^*$ character in addition to the typical ³MLCT, accounting for the changes observed in this extreme case.



Figure 1-17: Extremely electron-rich bipyridine complexes based on the Slinker complex

As a consequence of the partitioning of the frontier orbitals to separate ligands in these complexes, the oxidation and reduction potentials may be directly targeted *via* ligand modification. The basic strategy follows that with the HOMO and LSOMO residing on the cyclometalating ligand, they may be stabilized by the inclusion of electron-withdrawing groups there; this would increase the oxidation potential of the complex. The LUMO and HSOMO may be targeted in a similar manner by incorporation of electron-donating groups to the diimine ligand; this would be expected to produce a destabilizing effect on those orbitals and hence produce a complex with a more negative 1st reduction potential. In practice, modification of the cyclometalating ligand is the preferred strategy to produce dramatic tuning effects. Indeed, substitution of the diimine ligand with bipyridine, phenanthroline, or modified phenanthrolines produces only a

small effect on the reduction potential of these complexes (**Table 1-1**). Substitution of the cyclometalating ligand, however, produces a much more dramatic shift in the electrochemical behavior of the complexes.⁵⁰

Table 1-1. Electrochemical data for several bis-cyclometalated complexes. Cyclic voltammograms were collected at 100 mV/s in 0.1 M TBAH in acetonitrile utilizing a Pt working electrode, Pt counter electrode, and Ag wire as a pseudoreference. Ferrocene was used as an internal standard and all values are reported with respect to SCE.

Photosensitizer	$E^{0'} M^{n+}/M^{(n+1)+b}$	ΔE_p	<u>E^{0'} L/L⁻</u>	ΔE_p	
	(V vs SCE)	<u>(mV)</u>	<u>(V vs SCE)</u>	<u>(mV)</u>	
$[Ir(ppy)_2(bpy)]^+$	+1.25	65	-1.42	70	
$[Ir(ppy)_2(phen)]^+$	+1.24	65	-1.42	80	
$[Ir(ppy)_2(dphphen)]^+$	+1.23	75	-1.38	70	
[Ir(Fmppy) ₂ (bpy)] ⁺	+1.38	75	-1.39	60	
[Ir(Fmppy) ₂ (phen)] ⁺	+1.36	60	-1.39	80	
[Ir(Fmppy) ₂ (dphphen)] ⁺	+1.36	75	-1.35	70	

1.3.3 Development of Water Reduction Photocatalysis Systems

Based on prior success tuning and utilizing bis-cyclometalated Ir³⁺ complexes as luminophores for OLEDs, work also began on using these complexes to drive water

reduction and generate hydrogen. Previous systems realized photocatalytic water reduction with $\text{Ru}(\text{bpy})_3^{2+}$ derivatives as a photosensitizer and $\text{Co}(\text{bpy})_3^{2+}$ as the water reduction catalyst.⁵¹ This system was adapted using promising candidates from the combinatorial screening in place of $\text{Ru}(\text{bpy})_3^{2+}$. Despite the lower molar extinction coefficients of the iridium complexes compared to the ruthenium complexes, the iridium-based photosensitizers achieved much higher turnovers, up to a maximum of 920 for $[\text{Ir}(\text{Fmppy})_2(\text{bpy})]^+$ compared to 580 for an optimized $\text{Ru}(\text{phen})_3^{2+}$ system.⁵⁰ Compared to $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{dmphen})_3^{2+}$, these complexes are 4-20 times more efficient when accounting for the difference in molar absorptivity.

These efforts to further improve upon the above photocatalytic water reduction system were again realized in 2007 with the replacement of $Co(bpy)_3^{2+}$ by K₂PtCl₄ as a catalyst. This catalyst allowed photocatalytic hydrogen generation *via* reductive quenching without the use of an electron relay (**Figure 1-18**), simplifying future studies on efficient photosensitizer and catalyst designs. Initially, this system was only capable of 63 PS turnovers, but a photon-to-hydrogen conversion efficiency of 26% was achieved.⁴⁴ Subsequent studies of the post-illumination reaction mixture confirmed that loss of the bipyridine ligand was responsible for photosensitizer degradation and subsequent system failure.



Figure 1-18: Reductive quenching mechanism observed in systems without an electron relay using Pt colloids formed *in situ* from a K₂PtCl₄ precursor.

Again in 2008, advances in the photogeneration of H_2 were made with the realization of a fully homogeneous system for photoinduced water reduction. Modifications were again made to the catalyst, this time featuring modified $Rh(bpy)_3^{3+}$ complexes (**Figure 1-19**).⁵² Replacing K₂PtCl₄, which is known to form colloids *in situ*, with a truly molecular catalyst allowed a maximum of 5000 PS turnovers using $[Ir(Fmppy)_2(dtbbpy)](PF_6)$ and $Rh(dtbbpy)_3(PF_6)_3$. As before, triethylamine proved to be an effective sacrificial reductant, and solvents with less coordinating ability proved more effective (**Figure 1-20**). These two choices, while seeming trivial, must be carefully made as the solvent controls electron transfer rates between the PS and the catalyst. The ligating power of the solvent may stabilize or destabilize key intermediates, while the sacrificial reductant plays a vital role in efficient quenching of the excited photosensitizer and prevention of unwanted side reactions.



Figure 1-19: $Rh(bpy)_3^{3+}$ complexes evaluated as molecular catalysts for water reduction photocatalysis.



Figure 1-20: Effects of different sacrificial donors, solvents on water photoreduction catalysis with $Rh(dtbbpy)_3(PF_6)_3$ as catalyst and $[Ir(Fmppy)_2(dtbbpy)](PF_6)$ as photosensitizer.

In 2013, Kagalwala and Gottlieb developed a successful photocatalytic water reduction system using a new catalyst featuring a nickel thiolate hexamer (**Figure 1-21**) *in lieu* of K₂PtCl₄ or Rh(bpy)₃³⁺ derivatives.⁵³ As before, [Ir(Fmppy)₂(dtbbpy)](PF₆) was employed as the photosensitizer, triethylamine was the sacrificial reductant, and a

THF/H₂O mixture was the solvent. The new catalyst was shown, like $Rh(dtbbpy)_3^{3+}$, to proceed *via* a reductive quenching mechanism. Mercury poisoning tests confirmed the active species are molecular. At optimal concentrations of both the catalyst and photosensitizer, a maximum of over 3700 PS turnovers at a turnover frequency of 970 h⁻¹ were observed; lower concentrations of the photosensitizer yielded up to 30,000 catalyst turnovers.



Figure 1-21: New nickel thiolate hexamer (Left) used as a water reducing catalyst with [Ir(Fmppy)₂(dtbbpy)](PF₆) (Right) as a photosensitizer.

While the $[Ir(ppy)_2(bpy)]^+$ photosensitizers have been demonstrated to work with a variety of water reduction catalysts and under a variety of conditions, it is difficult to discern clear patterns from separate studies that would inform future sensitizer design. In 2009, studies were conducted by varying the cyclometalating ligands and the bipyridine ligands on the photosensitizer, and their effect the overall evolution of H₂ from water photolysis. From the results below (**Figure 1-22**), it is unclear how modification of the cyclometalating ligand can improve performance; placement of electron-rich stericallyblocking groups in the 4- and 4'- or 5- and 5'- positions of the bipyridine, however, drastically improves performance of the complexes.⁵⁴ While this is counter to the strategy seen before in the OLED tuning efforts, it can be rationalized in terms of preventing dissociation of the bipyridine ligand; groups which make the coordinating nitrogens more basic, and hence more strongly coordinating, or groups which block the coordination of other ligands to the metal center during bipyridine dissociation will improve sensitizer longevity. This is most realized in the 5,5'-di-*iso*-propyl bipyridine ligand, which achieved the highest number of turnovers.



Figure 1-22: Effects of varying the cyclometalating and chelating ligands on photosensitizer performance in a water reduction system using colloidal platinum as a catalyst.

Variation of the solvent was also found to play a strong role in the performance of the system. While keeping the catalyst the same, three selected photosensitizers demonstrated a notable difference in performance across mixtures of water with tetrahydrofuran, N,N-dimethylformamide, and acetonitrile. Based on the turnover numbers achieved, it is clear that increased ligating power of the solvent favors degradation of the photoactive species in solution (**Figure 1-23**). Since previous studies had indicated bis-cyclometalated Ir(III) photosensitizers can work with Pt or Pd colloids and with either triethylamine or triethanolamine, an additional sequence was run testing all of the reductant/catalyst combinations; triethylamine with Pt colloids was shown to have the greatest turnover frequency while triethanolamine with Pd colloids was shown to be a longer-lived pair.



Figure 1-23: Effect of solvent on selected photosensitizers using colloidal palladium water reducing catalysts.

1.3.4 Tailoring Photosensitizers to Specific Water Reduction Catalysts

Though $[Ir(ppy)_2(bpy)](PF_6)$ derivatives possess incredible versatility of working solvent, catalyst, and donor conditions, they all suffer the same eventual fate: displacement of the bipyridine upon photoexcitation leads to loss of activity. One way to counter this is to design photosensitizers which are able to rapidly transfer photoexcited electrons to the catalyst. This has been achieved in two ways: first by tethering of the

photosensitizer to a catalyst and second by formation of microemulsions which promote PS-catalyst aggregation.

In the first work on this strategy, DiSalle synthesized iridium complexes with pendent pyridyl moieties (**Figure 1-24**).⁵⁵ These moieties were placed at the 4- and 4'- positions of the bipyridine *in lieu* of the traditional *tert*-butyl moieties. The pyridyl moieties were intended to coordinate to colloidal platinum catalysts formed *in situ*, resulting in rapid transfer of electrons from the π^* orbitals of the bipyridine served as a control. Of the photosensitizer groups evaluated, those containing qpy were consistently strong performers, typically achieving 7000-8000 PS turnovers; similar results were obtained using detqpy. Comparators with non-coordinating methyl and phenyl groups evolved less hydrogen, with maximum turnovers reaching around 2000 (**Figure 1-25**).



Figure 1-24: [Ir(ppy)₂(bpy)](PF₆) derivatives with pendant pyridyl moieties.



Figure 1-25: PS turnovers for complexes with and without pendant coordinating pyridyls.

A second attempt at tethering photosensitizers was again made by Stefan Metz using pendant vinyl groups in place of the pyridines featuring in DiSalle's work.⁵⁶ The use of vinyl groups on the bipyridine ligand was justified as vinyl groups had previously been used to stabilize platinum colloids. Under optimized conditions, the new complexes achieved 8500 turnovers, though the inclusion of vinyl groups sharply decreased the complexes' luminescence quantum yields.

The second method employed to facilitate rapid transfer of electrons from photosensitizer to the catalyst was by formation of microemulsions. Recently, Kagalwala developed a new photosensitizer/water reduction catalyst system (**Figure 1-26**) with oxalic acid as a sacrificial reductant.⁵⁷ The system relied on the formation of an emulsion of toluene and water, aided by an *in-situ* generated ion pair between 1-octylamine and the oxalic acid sacrificial donor. This system, unlike previous water reduction photolysis systems utilizing $[Ir(ppy)_2(bpy)]^+$ complexes, is driven by an oxidative quenching mechanism. One key advantage of this system is that it takes place in a biphasic system;

integrated water splitting systems would require some method of separating the oxidation and reduction half-reactions and a biphasic system would be a great first step toward linking these two processes. Under optimal conditions, the system produced 240 PS turnovers and 400 catalyst turnovers; the system was still able to produce hydrogen from oxalic acid after 95 hours of illumination.



Figure 1-26: Photosensitizer (Left) and catalyst (Right) combination employed in toluene/water/1-octylamine microemulsion study.

<u>1.3.5 Current State of Bis-cyclometalated $[Ir(C^N)_2(N^N)]^+$ Photosensitizers</u>

Since the development of bis-cyclometalated Ir(III) complexes for OLEDs and solar fuel applications, they have found application in the recently-emerging field of photoredox catalysis. Chief among cited Ir(III) photoredox catalysts is $[Ir(dFCF_3ppy)_2(dtbbpy)](PF_6)$, which has seen extensive use by the MacMillan group and others.^{58–61} Unfortunately, like other $[Ir(ppy)_2(bpy)]^+$ complexes, solvent stability, especially in acetonitrile, proves to be a weak point for these catalysts. This necessitates loading as much as 1 mol% photocatalyst and extended reaction times under typical photoredox conditions. Additionally, while the electronic properties of highly-fluorinated

Ir(III) complexes remain attractive, their molar absorptivity in the visible spectrum decreases with increasing fluorination, decreasing their utility in such applications.

While photochemical systems utilizing [Ir(ppy)₂(bpy)]⁺ derivatives seem at first glance akin to other three-component systems, in practice they behave more like a fourcomponent system. Other three component systems can focus on modification of the photosensitizer, catalyst, and sacrificial donor with clear trends in individual components' properties affecting the system at large; because the dissociation of the diimine ligand (**Figure 1-27**) greatly influences system performance and longevity, [Ir(ppy)₂(bpy)]⁺ systems must also take into account the coordinating power of the solvent environment. Some of these systems have been able to successfully "tune" the photosensitizer to resist dissociation of the diimine either through steric bulk, coordination to the catalyst species, or by increasing the electron density at the coordinating nitrogen which in turn produces a stronger N-Ir bond. Further work is needed to produce complexes with greater solvent tolerances, or complexes which function under more environmentally-benign solvents to produce a viable hydrogen photogeneration system.



Figure 1-27: Mechanism of photosensitizer degradation following excitation and subsequent dissociation and replacement of bipyridine ligand.

References

- (1) U.S. Energy Information Administration, Annual Energy Outlook 2017.
- (2) International Energy Agency, World Energy Outlook **2015**.
- McLaughlin, S. B., De La Torre Ugarte, D. G., Garten, C. T., Lynd, L. R.,
 Sanderson, M. A., Tolbert, V. R., Wolf, D. D., *Environ. Sci. Technol.* 2002, 36, 2122–2129.
- Kauffman, D. R.; Thakkar, J.; Siva, R.; Matranga, C.; Ohodnicki, P. R.; Zeng, C.; Jin, R. ACS Appl. Mater. Interfaces 2015, 7, 15626–15632.
- (5) Grossmann, W. D.; Grossmann, I.; Steininger, K. *Environ. Sci. Technol.* 2010, 44, 4849–4855.
- (6) Gratzel, M.; O'Regan, B. *Nature* **1991**, *353*, 737–740.
- (7) Clifford, J. N.; Palomares, E.; Nazeeruddin, M. K.; Thampi, R.; Grätzel, M.; Durrant, J. R. J. Am. Chem. Soc. 2004, 126, 5670–5671.
- Milot, R. L.; Moore, G. F.; Crabtree, R. H.; Brudvig, G. W.; Schmuttenmaer, C. A. J. Phys. Chem. C 2013, 117, 21662–21670.
- (9) Hara, K.; Miyamoto, K.; Abe, Y.; Yanagida, M. J. Phys. Chem. B 2005, 23776–23778.
- (10) Benko, G.; Myllyperkio, P.; Pan, J.; Yartsev, A. P.; Sundstro, V. J. Am. Chem. Soc
 2003, 2, 1118–1119.
- (11) Thompson, D. W.; Kelly, C. A; Farzad, F.; Meyer, G. J. *Langmuir* 1999, *15*, 650–653.
- (12) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Chem. Rev. 2010, 6595–6663.
- (13) Peter, L. M. J. Phys. Chem. Lett 2011, 1861–1867.
- (14) Balat, M. Int. J. Hydrogen Energy 2008, 33, 4013–4029.

- (15) Fujita, K.; Tanino, N.; Yamaguchi; Ryohei, Y. R. Org. Lett. 2007, 9, 109–111.
- (16) Kawahara, R.; Fujita, K.; Yamaguchi, R. J. Am. Chem. Soc. 2012, 134, 3643– 3646.
- (17) Kawahara, R.; Fujita, K.; Yamaguchi, R. Angew. Chem. Int. Ed. Engl. 2012, 51, 12790–12794.
- (18) Musa, S.; Shaposhnikov, I.; Cohen, S.; Gelman, D. Angew. Chem. Int. Ed. Engl.
 2011, 50, 3533–3537.
- (19) Zeng, G.; Sakaki, S.; Fujita, K.; Sano, H.; Yamaguchi, R. ACS Catal. 2014, 4, 1010–1020.
- (20) Maeda, K.; Domen, K. J. Phys. Chem. Lett. 2010, 1, 2655–2661.
- (21) Zandi, O.; Hamann, T. W. J. Phys. Chem. Lett. 2014, 5, 1522–1526.
- Blakemore, J. D.; Schley, N. D.; Balcells, D.; Hull, J. F.; Olack, G. W.; Incarvito,
 C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H.; Gerhardt, I. C. J. Am. *Chem. Soc.* 2010, 132, 16017–16029.
- Brewster, T. P.; Blakemore, J. D.; Schley, N. D.; Incarvito, C. D.; Hazari, N.;
 Brudvig, G. W.; Crabtree, R. H. *Organometallics* 2011, *30*, 965–973.
- Bucci, A.; Savini, A.; Rocchigiani, L.; Zuccaccia, C.; Rizzato, S.; Albinati, A.;
 Llobet, A.; MacChioni, A. *Organometallics* 2012, *31*, 8071–8074.
- (25) Deng, Z.; Tseng, H.-W.; Zong, R.; Wang, D.; Thummel, R. *Inorg. Chem.* 2008, 47, 1835–1848.
- (26) Gersten, S. W.; Samuels, G. J.; Meyer, T. J. J. Am. Chem. Soc. 1982, 104, 4029–4030.
- (27) Graeupner, J.; Brewster, T. P. Organometallics 2012, 31, 7158–7164.
- (28) Graeupner, J.; Hintermair, U.; Huang, D. L.; Thomsen, J. M.; Takase, M.; Campos, J.; Hashmi, S. M.; Elimelech, M.; Brudvig, G. W.; Crabtree, R. H. *Organometallics* 2013, *32*, 5384–5390.

- Hull, J. F.; Balcells, D.; Blakemore, J. D.; Incarvito, C. D.; Eisenstein, O.;
 Brudvig, G. W.; Crabtree, R. H. J. Am. Chem. Soc. 2009, 131, 8730–8731.
- (30) Mcdaniel, N. D.; Coughlin, F. J.; Tinker, L. L.; Bernhard, S. J. Am. Chem. Soc.
 2008, 130, 210–217.
- Petronilho, A.; Rahman, M.; Woods, J. a; Al-Sayyed, H.; Müller-Bunz, H.; Don MacElroy, J. M.; Bernhard, S.; Albrecht, M. *Dalton Trans.* 2012, *41*, 13074– 13080.
- Woods, J. A.; Lalrempuia, R.; Petronilho, A.; McDaniel, N. D.; Müller-Bunz, H.;
 Albrecht, M.; Bernhard, S. *Energy Environ. Sci.* 2014, *7*, 2316–2328.
- Grotjahn, D. B.; Brown, D. B.; Martin, J. K.; Marelius, D. C.; Abadjian, M.-C.;
 Tran, H. N.; Kalyuzhny, G.; Vecchio, K. S.; Specht, Z. G.; Cortes-Llamas, S. a;
 Miranda-Soto, V.; van Niekerk, C.; Moore, C. E.; Rheingold, A. L. J. Am. Chem.
 Soc. 2011, 133, 19024–19027.
- (34) Neburchilov, V.; Wang, H.; Martin, J. J.; Qu, W. *J. Power Sources* **2010**, *195*, 1271–1291.
- (35) Beck, F.; Rüetschi, P. *Electrochim. Acta* **2000**, *45*, 2467–2482.
- (36) Sapkota, P.; Kim, H. J. Ind. Eng. Chem. 2010, 16, 39-44.
- (37) Sapkota, P.; Kim, H. J. Ind. Eng. Chem. 2009, 15, 445–450.
- (38) Brooks, A. C.; Basore, K.; Bernhard, S. Inorg. Chem. 2013, 52, 5794–5800.
- (39) Brooks, A. C.; Basore, K.; Bernhard, S. Chem. Commun. 2014, 50, 5196–5199.
- (40) Garces, F. O.; King, K. A.; Watts, R. J. Inorg. Chem. 1988, 27, 3464–3471.
- (41) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. J. Am. Chem. Soc. 1984, 106, 6647–6653.
- (42) Ohsawa, Y.; Sprouse, S.; King, K. A.; DeArmond, M. K.; W., H. K.; Watts, R. J. J. Phys. Chem. B 1987, 91, 1047–1054.
- (43) Colombo, M. G.; Hauser, A.; Guedel, H. U. Inorg. Chem. 1993, 32, 3088–3092.

- (44) Tinker, L. L.; McDaniel, N. D.; Curtin, P. N.; Smith, C. K.; Ireland, M. J.;
 Bernhard, S. *Chem. Eur. J.* 2007, *13*, 8726–8732.
- (45) Lo, K. K.; Chan, J. S.; Lui, L.; Chung, C. Organometallics 2004, 23, 3108–3116.
- (46) Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J.; Parker, S.; Rohl, R.;
 Bernhard, S.; Malliaras, G. G. J. Am. Chem. Soc. 2004, 126, 2763–2767.
- (47) Lowry, M. S.; Hudson, W. R.; Pascal, R. A.; Bernhard, S. J. Am. Chem. Soc. 2004, 126, 14129–14135.
- (48) Minaev, B.; Aegren, H.; DeAngelis, F. Chem. Phys. 2009, 358, 245–257.
- (49) DeAngelis, F.; Fantacci, S.; Evans, N.; Klein, C.; Zakeeruddin, S. M.; Moser, J.;
 Kalyanasundaram, K.; Bolink, H. J.; Gratzel, M.; Nazeeruddin, M. K. *Inorg. Chem.* 2007, 46, 5989–6001.
- (50) Goldsmith, J. I.; Hudson, W. R.; Lowry, M. S.; Anderson, T. H.; Bernhard, S. J. Am. Chem. Soc. 2005, 127, 7502–7510.
- (51) Krishnan, C. V.; Brunschwig, B. S.; Creutz, C.; Sutin, N. J. Am. Chem. Soc. 1985, 107, 2005–2014.
- (52) Cline, E. D.; Adamson, S. E.; Bernhard, S. Inorg. Chem. 2008, 47, 10378–10388.
- (53) Kagalwala, H. N.; Gottlieb, E.; Li, G.; Li, T.; Jin, R.; Bernhard, S. *Inorg. Chem.* **2013**, 52, 9094–9101.
- (54) Curtin, P. N.; Tinker, L. L.; Burgess, C. M.; Cline, E. D.; Bernhard, S. *Inorg. Chem.* 2009, 48, 10498–10506.
- (55) Disalle, B. F.; Bernhard, S. J. Am. Chem. Soc. 2011, 133, 11819–11821.
- (56) Metz, S.; Bernhard, S. Chem. Commun. 2010, 46, 7551–7553.
- (57) Kagalwala, H. N.; Chirdon, D. N.; Mills, I. N.; Budwal, N.; Bernhard, S. *Inorg. Chem.* 2017, acs.inorgchem.7b00463.
- (58) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Pascal, R. A; Malliaras, G. G.; Bernhard, S.; Rohl, R. *Chem. Mater.* **2005**, *17*, 5712–5719.

- (59) Zuo, Z.; Ahneman, D. T.; Chu, L.; Terrett, J. A.; Doyle, A. G.; MacMillan, D. W. C. *Science* 2014, *345*, 437–440.
- (60) Noble, A.; McCarver, S. J.; Macmillan, D. W. C. J. Am. Chem. Soc. 2015, 137, 624–627.
- (61) Ventre, S.; Petronijevic, F. R.; Macmillan, D. W. C. J. Am. Chem. Soc. 2015, 137, 5654–5657.

Chapter 2

Hemicaging Iron Complexes for Dye-Sensitized Solar Cells

2.1 Introduction

DSSCs have received significant attention as an attractive option for solar energy conversion. These cells, like silicon cells, directly convert incident photons into useable electricity. Compared to crystalline solar cells, they offer several key advantages in that they work in diffuse lighting, have better heat exchange and tolerance, and can be flexible. Though these devices are attractive as low-cost solar energy convertors, widespread commercial application of these devices is still hampered by several characteristics, especially pertaining to the dye. Chief among these concerns are the use of expensive and rare metals in the dye molecule, and limited stability of the dye to UV irradiation which causes ligand dissociation and renders the dye molecule photochemically inert. Work which successfully replaces the metal center with more earth-abundant materials, or which resists UV degradation would help make these devices more commercially viable.

One way to improve the employed photosensitizers is the use of hemicaging ligands. Rigid caging ligands restrict the degrees of freedom of the ligands in the metal sphere. This serves to decrease non-radiative decay, thus increasing the quantum efficiency of the photosensitizer or catalyst.¹ This added efficiency comes at a price, namely the extra consideration that must be put into the design of the bridging ligands. The extra effort is not unwarranted, as the dissociated portion of the hemicaging ligand

may anneal back to the metal center, ameliorating one method of photodegradation encountered with these dyes.

Prior work in the field of hemicage complexes has seen impressive photophysical effects, particularly with the use of hemicaging polypyridine and poly-8-hydroxyquinoline ligands.^{2–7} The use of these ligand architectures has yielded complexes with markedly enhanced excited state properties, and in some cases, switches from fluorescence to phosphorescence as the dominant emissive pathway have been observed.⁷

In this chapter, a new hemicage complex, $Fe(5,5'-TEMBM)(BF_4)_2$ **1** (5,5'-TEMBM = 1,3,5-tris(5-ethyl,5'-methyl-2,2'-bipyridyl)mesitylene) was synthesized. Additionally, a new hemicaging ligand featuring methyl ester grousps 1,3,5-tris(5ethyl,5'-methylacetoxy-2,2'-bipyridyl)mesitylene **3** (5,5'-TEMABM), was created and used to synthesize two potential dyes for DSSCs, $Fe(5,5'-TEMABM)(BF_4)_2$ **4** and $Ru(5,5'-TEMABM)(PF_6)_2$ **5**. Complexes **1** and **4** were designed to assess both the feasibility of replacing rare Ru(II) with more abundant Fe(II); complexes **4** and **5** were designed to evaluate the ability of methyl esters to facilitate binding to titania during device fabrication. The synthesized complexes were evaluated as potential dyes *via* UV-Vis spectroscopy, and their electrochemistry was probed to determine their suitability as photosensitizers for application in DSSCs.



Figure 2-1. Synthesized hemicage complexes 1, 4, and 5.

2.2 Experimental Section

2.2.1 Materials and Methods

All materials were obtained from Sigma and used without further purification unless otherwise stated. RuCl₃·x H₂O was obtained from Pressure Chemicals and used without further purification. Ru(DMSO)₄Cl₂ was synthesized according to literature procedures.⁸ 5,5'-TEMBM was synthesized according to literature procedures.^{2,9}

2.2.2 Physical Characterization

 1 H NMR and 13 C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at room temperature. Mass-to-charge ratios were determined from 33 μ M methanolic solutions with a Thermo-Fisher Finnigan LCQ instrument using an electrospray ionization (ESI) source.

2.2.3 Electrochemical Characterization

Cyclic voltammetry was performed using a CH-Instruments Electrochemical Analyzer 600C potentiostat with a three-electrode system comprised of a silver wire pseudo-reference, a platinum coil counter electrode, and a 1 mm² platinum disk working electrode. All potentials were collected under an argon purge in acetonitrile solutions containing 500 μ M analyte and 0.1 M (*t*-Bu)₄NPF₆ as supporting electrolyte. Positive scan polarity was used with a scan rate of 0.10 V/s. Potentials were referenced to SCE using a ferrocene internal standard (fc/fc⁺ = 0.40 V).¹⁰

2.2.4 Photophysical Characterization

UV-Vis spectra were measured at room temperature with a Shimadzu UV-1800 spectrophotometer using 33 μ M methanolic solutions which were purged with argon for 10 min in capped quartz cuvettes.

2.2.5 Preparation of Ligands and Complexes

2.2.5.1 Synthesis of Fe(5,5'-TEMBM)(BF₄)₂ 1



Figure 2-2. Synthesis of Fe(TEMBM)(BF₄)₂ 1.

 $Fe(5,5'-TEMBM)(BF_4)_2$ **1** was synthesized *via* slow addition of $Fe(BF_4)_2$ dihydrate (140 mgs, 0.40 mmol) in 75 mL methanol to 5,5'-TEMBM (325 mgs, 0.46 mmol, 1.15 EQ) in 400 mL methanol. The solution was stirred at room temperature overnight, after which the reaction mixture turned a deep red color. The solvent was then

removed under vacuum, and the sample was dissolved in acetone and passed through a short column of neutral alumina to remove oligomeric and polymeric impurities, followed by vapor diffusion recrystallization from diethyl ether and acetonitrile to afford **1** as red-purple crystals. Overall yield: 112 mg (0.12 mmol, 30%)

¹H NMR ((CD₃)₂CO, 500 MHz): δ 8.66 (1H, d, *J*=8.0 Hz), 8.60 (1H, d, *J*=8.1 Hz), 8.33 (1H, dd, *J*₁=8.2 Hz, *J*₂=2.0 Hz), 8.01 (1H, dd, *J*₁=8.2 Hz, *J*₂=1.8 Hz), 7.57 (1H, d, *J*=1.8 Hz), 6.12 (1H, d, *J*=1.8 Hz), 3.43-3.28 (1H, m), 3.11-3.04 (1H, m), 2.99-2.92 (1H, m), 2.78-2.68 (1H, m), 2.19 (3H,s), 2.01 (3H, s)

MS (ESI) Calculated: m/z: 382.2 (M²⁺), Found: m/z (%): 382.4 (M²⁺, 100%)

2.2.5.2 Synthesis of Methyl-Ester Hemicaging Ligand 3



Figure 2-3. Synthesis of methyl ester hemicage 5,5-TEMABM 3.

In a round-bottom flask 5,5'-TEMBM (33.0 mg, 0.046 mmol) was dissolved in 10 mL anhydrous THF and flushed with Ar for 20 minutes. The solution was then cooled to -78 °C, and LDA (2.0 M in hexanes, 0.07 mL, 0.14 mmol, 3 EQ) was added dropwise. The solution turned brown-black, and was stirred for 90 min after which point dried CO₂

was allowed to bubble through the solution for 60 minutes. The solvent was then removed under vacuum and the solids were dissolved in H_2O . The pH was adjusted to 2, and the resulting white solid **2** was collected.

2 was converted to the methyl ester by dissolving the solids in 6 M H_2SO_4 in MeOH (10 mL) and heating to reflux for 18 hours. The reaction mixture was then neutralized with aqueous NaHCO₃ which caused a yellow solid to precipitate. The crude **3** was then purified by chromatography on a short alumina plug with dichloromethane to yield 1,3,5-tris(5-ethyl,5'-methylacetoxy-2,2'-bipyridyl)mesitylene (5,5'-TEMABM) as an ivory colored solid. Overall yield: 29 mg (0.033 mmol, 71%)

¹H NMR (CD₃Cl, 500 MHz): δ 8.60 (1H, d, *J*=1.8 Hz), 8.56 (1H, d, *J*=1.2 Hz), 8.39 (1H, dd, *J*=8.2 Hz), 8.35 (1H, dd, *J*=7.9 Hz), 7.78 (1H, dd, *J*₁=8.1 Hz, *J*₂=2.3 Hz), 7.68 (1H, dd, *J*₁=7.9 Hz, *J*₂=1.8 Hz), 3.75 (3H, s), 3.72 (2H, s), 3.05-3.08 (2H, m), 2.87-2.84 (2H, m), 2.38 (3H,s)



Figure 2-4. Synthesis of hemicage complexes Fe(5,5)-TEMABM)(BF₄)₂ **4** and Ru(5,5)-TEMABM)(PF₆)₂ **5**.

Fe(5,5'-TEMABM) (BF₄)₂ **4** was synthesized *via* slow addition of Fe(BF₄)₂ dihydrate (70 mg, 0.20 mmol) in 40 mL methanol a solution of 5,5'-TEMABM (200 mg, 0.22 mmol, 1.1 EQ) in 200 mL methanol. The reaction mixture was stirred overnight at room temperature after which it turned a deep red color. The solvent was then removed under vacuum, and the sample was dissolved in acetone and passed through a short column of neutral alumina to remove oligomeric and polymeric impurities, followed by vapor diffusion recrystallization three times from diethyl ether and acetonitrile to afford **4** as deep red crystals. Overall yield: 52 mg (0.047 mmol, 23%)

¹H NMR ((CD₃)₂CO, 500 MHz): δ 8.72 (1H, d, *J*=8.2 Hz), 8.68 (1H, d, *J*=8.2 Hz), 8.36 (1H, dd, *J*₁=8.1 Hz, *J*₂=1.7 Hz), 8.13 (1H, dd, *J*₁=8.1 Hz, *J*₂=1.7 Hz), 7.65 (1H, bs), 6.21

(1H, d, *J*=1.7 Hz), 3.69 (2H, dd, *J*₁=7.0 Hz, *J*₂=17 Hz), 3.59 (3H, s), 3.39-3.33 (1H, m), 3.12-3.08 (1H, m), 2.99-2.96 (1H, m), 2.80-2.74 (1H, m), 2.01 (3H, s)

MS (ESI) Calculated: m/z: 469.2 (M²⁺), Found: m/z (%): 469.5 (M²⁺, 100%)

Ru(5,5'-TEMABM)(PF₆)₂ **5** was synthesized analogously to **4**. Ru(DMSO)₄Cl₂ (99 mg, 0.20 mmol) was dissolved in 50 mL methanol and added to a solution of **3** (200 mg, 0.22 mmol, 1.1 EQ) in 500 mL methanol. The reaction mixture was then heated to reflux overnight until the solution was faintly luminescent orange. The solvent was then removed, and the crude was dissolved in water, washed with dichloromethane to remove excess ligand, and the product was precipitated from the aqueous layer by precipitation with KPF₆ (1.0 g, excess). The precipitate was dissolved in acetone and passed through a short plug of neutral alumina to remove oligomeric and polymeric impurities. The crude was then recrystallized three times *via* vapor diffusion from acetonitrile and diethyl ether to afford **5** as an orange solid. Overall yield: 34 mg (0.027 mmol, 13%)

¹H NMR (CD₃CN, 500 MHz): δ 8.38 (2H, d, *J*=8.4 Hz), 8.09 (1H, dd, *J*₁=8.2 Hz, *J*₂=2.0 Hz), 7.95 (1H, dd, *J*₁=8.4 Hz, *J*₂=1.8 Hz), 7.68 (1H, d, *J*=1.5 Hz), 6.28 (1H, d, *J*=1.8 Hz), 3.61 (2H, d, *J*=2.5 Hz), 3.59 (3H, s), 3.33-3.23 (1H, m), 3.05-2.99 (1H, m), 2.96-2.89 (1H, m), 2.82-2.73 (1H, m), 1.92 (3H, s)

MS (ESI) Calculated: m/z: 492.1 (M²⁺), Found: m/z (%): 491.1 (M²⁺, 100%)

2.3 Results and Discussion

2.3.1 Synthetic Strategies

Initial plans to synthesize the carboxy hemicage ligand started with synthesis of an oxazoline-protected 5,5'-dmbpy. The oxazoline product would then be coupled to the mesitylene cap via standard alkylation protocol. Following coordination of the metal center, the oxazoline could then be removed with an acid wash to yield the carboxylic acid groups for binding to titania. Intended reaction conditions can be seen below in **Figure 2-5**.



Figure 2-5. Attempted synthesis of oxazoline hemicage.

First, 5,5'-dmbpy was oxidized to the mono-carboxylated species *via* alkylation with carbon dioxide and the crude product was precipitated by acidifying the reaction to pH 2, where it was further purified by chromatography on silica. The second step involved the formation of the oxazoline protecting group *via* two subsequent condensations of the carboxylic acid with 2-methyl-2-amino-1-propanol. This part of the reaction did not proceed as intended, and the oxazoline was never isolated.

Since the oxazoline could not be isolated, it was decided to attempt direct carboxylation of the 1,3,5-tris(5-ethyl,5'-methyl-2,2'-bipyridyl)mesitylene (5,5'-TEMBM). This was accomplished by synthesis of 5,5'-TEMBM and subsequent alkylation with carbon dioxide as discussed above. This method proved effective, and the carboxylic acid intermediate was converted to the methyl ester to protect against unintentional coordination of the metal center to the carboxylic acid groups. If the chromophores will not adhere to the titania during device fabrication, the methyl ester can be gently removed to yield the free-acid chromophore.

2.3.2 Electrochemical Properties

Cyclic voltammetry was utilized to probe the frontier orbitals of the new complexes. Both iron hemicage complexes possess similar redox behavior including a quasi-reversible oxidation typical for $Fe(N^{N}N)_{3}^{2+}$ complexes (**Figure 2-6**).^{11,12} The oxidation and reduction potentials of complex **4** are anodically shifted compared to complex **1** (**Table 2-1**). This anodic shift of potentials is likely due to the inductive effect of the electron-poor ester moiety introduced. Both complexes displayed multiple reductions similar to their tris-bipyridine analogue (**Table 2-1**). Complex **1** displayed two resolvable reductions, both reversible, while complex **4** possessed three reversible reductions. It is expected that **1** would also display a third reversible reduction¹², but this event was possibly obscured by the onset of the solvent breakdown. With the exception of this missing reduction, both complexes featured redox chemistry remarkably similar to Fe(bpy)₃²⁺ which is expected as the hemicaging ligand should have more influence on excited state properties than ground state properties.³

47



Figure 2-6. Cyclic voltammograms for $Fe(5,5'-TEMBM)(BF_4)_2$ 1 (blue) and $Fe(5,5'-TEMABM)(BF_4)_2$ 4 (red) in degassed acetonitrile. Cyclic voltammograms were collected at 100 mV/s in 0.1 M TBAPF₆ in acetonitrile utilizing a Pt working electrode, Pt counter electrode, and Ag wire as a pseudoreference. Ferrocene was used as an internal standard and all values are reported with respect to SCE

Complex 5 displayed redox behavior similar to both the iron hemicage complexes 1 and 4 as well as $Ru(bpy)_3^{2+}$ (Figure 2-7,Table 2-1). As expected, the oxidation potential of complex 5 is strongly anodically shifted compared to the iron-bearing complex 4 (Table 2-1). Complex 5 displayed two readily-resolvable reversible reductions with a third reversible reduction discernable when scans were only taken across negative potentials (Figure 2-7, inset). These reduction potentials all coincided with very similar potentials from complex 4, suggesting all of these reduction events primarily take place on the ligand with little involvement from the metal center.



Figure 2-7. Cyclic voltammogram for $Ru(5,5'-TEMABM)(PF_6)_2$ **5** in degassed acetonitrile. Inset depicts observed reduction events when only sweeping negative potentials. Cyclic voltammograms were collected at 100 mV/s in 0.1 M TBAPF₆ in acetonitrile utilizing a Pt working electrode, Pt counter electrode, and Ag wire as a pseudoreference. Ferrocene was used as an internal standard and all values are reported with respect to SCE

Table 2-1. Electrochemical data for 1, 4, 5, and comparators.

Dhotogongitizon	<u>E_{1/20x}</u>	<u>ΔΕ</u>	E _{1/2red}	<u>ΔΕ</u>
<u>r notosensitizer</u>	(V vs SCE)	(mV)	(V vs SCE)	(mV)
Fe(5,5'-TEMBM)(BF ₄) ₂ , 1	1.05	90	-1.43,-1.64	60,80
Fe(5,5'-TEMABM)(BF ₄) ₂ , 4	1.07	90	-1.39,-1.59,-1.85	60,60,70
Ru(5,5'-TEMABM)(PF ₆) ₂ , 5	1.28	70	-1.40,-1.59,-1.88 ^a	70,80,90
$\mathrm{Fe}(\mathrm{bpy})_{3}(\mathrm{BF}_{4})_{2}^{12}$	1.06		-1.36,-1.54,-1.78	
$Ru(bpy)_{3}(PF_{6})_{2}^{13}$	1.34	80	-1.28,-1.45,-1.68	60,70,70

2.3.3 UV-Visible Spectra

Complexes **1** and **4** showed strong absorption in the UV-region around 260 nm and 300 nm with an additional visible absorption around 500 nm accounting for its red color (**Figure 2-8**). The absorption around 260-300 nm arises from π - π * transitions on similar complexes, while the absorptions around 500 nm arise from MLCT transitions.⁶ Complex **5** showed similar features to previous hemicage Ru(II) complexes.⁷ In the UV region strong absorptions from 260-300 nm being again assigned as π - π * transitions; an additional broad absorption around 450 nm is tentatively assigned as an MLCT based on similar complexes.^{14,4} Both complexes can be considered strong chromophores, with visible light absorptions on the order of 10^4 M⁻¹cm⁻¹. The presence of these intense absorptions, along with the complexes readily-driven MLCT transitions, supports the use of these chromophores as potential dye sensitizers for solar energy harvesting.



Figure 2-8. UV-Vis spectra of hemicage complexes 1 (blue) 4 (orange) and 5 (red).

2.4 Conclusions and Future Directions

In summary, this chapter presents the synthesis and characterization of three hemicage complexes for use as dyes in DSSCs. The new complexes feature either an iron metal center, as in complexes 1 and 4, or a ruthenium center as in 5. The ligand architecture is capped with mesitylene on top and features methyl groups in complex 1 methyl ester groups in 4 and 5. The esters were chosen to directly facilitate binding to the titania, but can be converted to carboxylic acids if the dyes don't bind.

All complexes feature comparable electrochemical potentials to both each other and to their free tris-bipyridine analogues. Both iron complexes feature quasi-reversible oxidations and a series of reversible reductions; all electrochemical events are reversible for the ruthenium complex. The complexes also feature strong, broad visible absorption bands around 500 nm for the iron complexes and 450 nm for the ruthenium complex. Their strong visible light absorption and quasi- or fully-reversible redox events initially bode well for application as dyes for DSSCs.

The purified complexes have been shipped to a cooperating lab for device fabrication where they will be tested for sensitization of solar cells. Sensitization of titania with iron-based complexes would be a significant achievement, though it is likely these complexes will require careful tuning of the electrolyte to function as intended. Future work should include DFT modeling of the excited states to better understand the dyes' orbital structures and inform future modifications and improvement. Alteration of the ligand architecture to better facilitate binding to titania and electron transfer from the electrolyte should be pursued as well.

References

- Beeston, R. F.; Aldridge, W. S.; Treadway, J. A.; Fitzgerald, M. C.; Degraff, B. A.; Stitzel, S. E.; College, D.; Carolina, N. *Inorg. Chem.* **1998**, 4368–4379.
- (2) Beeston, R. F.; Larson, S. L.; Fitzgerald, M. C. Inorg. Chem. 1989, 4187–4190.
- Barigelletti, F.; Cola, L. De; Balzani, V.; Belser, P.; Zelewsky, A. Von; Vogtle, F.;
 Ebmeyer, F.; Grammenudild, S. J. Am. Chem. Soc. 1989, 111, 4662–4668.
- (4) Sohna Sohna, J. E.; Carrier, V.; Fages, F.; Amouyal, E. *Inorg. Chem.* 2001, 40, 6061–6063.
- (5) Wang, J.; Oyler, K. D.; Bernhard, S. Inorg. Chem. 2007, 46, 5700–5706.
- (6) Coughlin, F. J.; Oyler, K. D.; Pascal, R. A.; Bernhard, S. *Inorg. Chem.* 2008, 47, 974–979.
- (7) Oyler, K. D.; Coughlin, F. J.; Bernhard, S. J. Am. Chem. Soc 2007, 210–217.
- (8) Evans, I. P.; Spencer, A.; Wilkinson, G. Dalt. Trans. 1973, 204–209.
- (9) Bernhard, S.; Takada, K.; Jenkins, D.; Abruña, H. D. *Inorg. Chem.* 2002, *41*, 765–772.
- (10) Connelly, N. G.; Geiger, W. E. Chem. Rev. 1996, 96, 877–910.
- (11) Sawyer, D. T. J. Mol. Catal. 2003, 194, 53-67.
- (12) Richert, S. A.; Tsang, P. K. S.; Sawyer, D. T. Inorg. Chem. 1989, 28, 2471–2475.
- (13) Bernhard, S.; Barron, J. A.; Houston, P. L.; Abruna, H. D.; Ruglovksy, J. L.; Gao, X.; Malliaras, G. G. J. Am. Chem. Soc 2002, 13624–13628.
- (14) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. Inorg. Chem. 1978, 17, 3334–3341.
Chapter 3

4,4'-Dicyano-2,2'-bipyridine Complexes for Solar Fuel Generation

This chapter has been adapted from a 2014 article in Polyhedron.¹ The article represents the collaborate efforts of several people within the Bernhard group as described in the experimental section.

3.1 Introduction

Producing the ever-increasing amount of energy the world needs is a challenging problem in modern society. Additional worries over the future availability and environmental impact of currently-employed fuels have spurred research into alternative means of energy production and storage. One possible alternative to current non-renewable fuels is the use of sunlight for direct energy conversion and the production of solar fuels, as the earth receives more energy from sunlight in a day than the global population consumes each year.^{2,3} Many solar fuels exist, with hydrogen being a particularly promising fuel due to the possibility for production from abundant water resources via reduction. Current water reduction catalyst (WRC) systems typically suffer from poor absorptivity in the visible range which constitutes the majority of the solar spectrum at 1.5 atmospheres.⁴ These problems may be ameliorated by the use of photosensitizers (PS) which absorb strongly in the visible range.

Among current art, bis-cyclometalated Ir(III) photosensitizers have been extensively researched due to their facile synthesis, long-lived triplet excited state, and high degree of tunability.^{5–9} Conveniently, the HOMO lies on the cyclometalating ligands as well as the metal center, while the LUMO and LUMO+1 lie on the auxiliary 1,2-diimine ligand, allowing for synthetic control of frontier orbitals via substituent control.¹⁰

In addition to water reduction, iridium photosensitizers have been found to be useful for photo-reduction of zinc(II) salts.¹¹ This system precipitates zinc metal from dissolved zinc salts; the generated zinc metal can then be used as fuel in systems such as zinc–air batteries while avoiding some of the problems and hazards associated with gaseous hydrogen. Initial work with zinc reduction shows that the presence of nitriles improves performance of these systems.¹² Nitriles are also of interest because they can bind to colloids in solution.¹³

Unfortunately, the partitioning of the frontier orbitals which makes these complexes so attractive also represents their greatest shortcoming. Upon excitation from the HOMO, an electron will populate the π^* orbital on the diimine ligand.¹⁴ This may lead to subsequent dissociation of the ligand and eventual replacement of the diimine with other ligands, particularly in coordinating environments (**Figure 3-1**). Loss of the diimine ligand is irreversible and renders the complex photochemically inert. As many of the systems involving photoreduction of zinc salts and water involve the use of coordinating solvents, rapid removal of the electron from the diimine π^* orbital by coordination of the photosensitizer to the catalyst represents a viable strategy to enhance the longevity of the photoactive species.



Figure 3-1. Mechansim of bipyridine dissociation leading to photoinactive species.

Work in this area was pioneered by DiSalle and Metz in the Bernhard group. DiSalle began work in this field with the incorporation of pendant pyridyl moieties which were intended to bind to colloidal Pt catalysts in solution. The complexes synthesized by DiSalle were shown to have a dramatic effect on the maximum photosensitizer turnovers (PS TON) of the system; comparable complexes with phenyl moieties in lieu of the pyridyls produced no such effect.¹⁵ Metz observed a similar effect when incorporating vinyl groups onto the diimine ligand of the photosensitizers; water reduction photosystems employing colloidal Pt catalysts were shown to have a 5-fold increase in maximum PS TON achieved over their comparators.¹⁶ Work by both DiSalle and Metz did not show any effect when employing molecular catalysts such as [Rh(bpy)₂Cl₂]Cl.

In this chapter, two new bis-cyclometalated Ir(III) complexes with 4,4'-dicyano-2,2'-bipyridine (dCNbpy), [Ir(Fmppy)₂(dCNbpy)]PF₆ and [Ir(ppy)₂(dCNbpy)]PF₆ (**Figure 3-2**) (Fmppy = 2-(4-fluorophenyl)-5-methylpyridine), are synthesized and evaluated as photosensitizers in water reduction and photocatalysts in and zinc reduction. For water reduction studies, both K₂PtCl₄ and Rh(dtbbpy)₃(PF₆)₃ (dtbbpy = 4,4'-di-*tert*butyl-2,2'-bipyridine) are used as water-reduction catalysts. K₂PtCl₄ forms colloids *in situ*, while Rh(dtbbpy)₃(PF₆)₃ is a molecular catalyst; these are chosen to evaluate the bridging ability of the cyano groups incorporated on the bipyridine ligand. In the zinc photoreduction studies, the dicyano-bipyridine complexes are evaluated against di*-tert*-butyl comparators to evaluate the cyano ligand's ability to eliminate the need for acetonitrile.



Figure 3-2. Structures of $[Ir(C^N)_2(dCNbpy)]^+$ photosensitizers containing dicyano bipyridine ligands. Reprinted with permission from ref 1. Copyright 2014 Elsevier Ltd.

3.2 Experimental Section

3.2.1. Materials

All materials were obtained from Sigma and used without further purification unless otherwise stated. IrCl₃·4 H₂O was obtained from Pressure Chemicals and used without further purification. 2-Phenylpyridine (ppy) was obtained from Alfa and used without further purification. 2-(4-Fluorophenyl)-5-methylpyridine (Fmppy) was synthesized via previously established procedures.¹⁷ 4,4'-Dicyano-2,2'-bipyridine (dCNbpy) was synthesized according to literature procedures reported elsewhere.¹⁸ [Ir(Fmppy)₂(dtbbpy)]PF₆ and [Ir(ppy)₂(dtbbpy)]PF₆ complexes were synthesized according to standard procedures.¹⁹

3.2.2. Physical measurements

3.2.2.1. Physical characterization

¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at room temperature. Mass-to-charge ratios were determined from 100 mM acetonitrile solutions with a Thermo-Fisher Finnigan LCQ instrument using an electrospray ionization (ESI) source.

3.2.2.2. DFT computations

Ground state geometries and frontier orbital energies were predicted via DFT using gaussian 09.²⁰ The B3LYP functional was employed with the LANL2DZ basis set applied to all atoms. No solvent or symmetry conditions were specified. Frequency calculations were performed with each geometry optimization to ensure that no imaginary frequencies were obtained. Orbitals were visualized using Ampac software.²¹

3.2.2.3. Electrochemistry

Cyclic voltammetry was performed by Danielle Chirdon in the Bernhard group using a CH-Instruments Electrochemical Analyzer 600C potentiostat with a threeelectrode system comprised of a silver wire pseudo-reference, a platinum coil counter electrode, and a 1 mm² platinum disk working electrode. All potentials were collected under an argon purge in acetonitrile solutions containing 1 mM analyte and 0.1 M (*t*-Bu)₄NPF₆ as supporting electrolyte. Positive scan polarity was used with a scan rate of 0.10 V/s. Potentials were referenced to SCE using a ferrocene internal standard (fc/fc⁺ = 0.40 V).²²

3.2.2.4. Photophysical characterization

Photophysical measurements were carried out at room temperature on 100 μ M acetonitrile solutions which were purged with argon for 10 min in capped quartz cuvettes. UV–Vis absorption spectra were then obtained with a Shimadzu UV-1800 spectrophotometer. Photoluminescence was measured using a Fluorolog-3 spectrophotometer equipped with dual monochromators and a photomultiplier tube at right angle geometry. All compounds were excited at 450 nm. Samples were pulsed at 337 nm with a Stanford Research Systems NL 100 N₂ laser to determine excited state lifetimes. Quantum yields were determined relative to a 10 μ M [Ru(bpy)₃](PF₆)₂ solution in acetonitrile.

3.2.2.5. Hydrogen generation studies

Photocatalytic hydrogen generation was carried out by Husain Kagalwala in the Bernhard group following previous protocols.⁵ Solutions containing 0.020 mM photosensitizer and 300 nmol of K₂PtCl₄ or 750 nmol Rh(dtbbpy)₃(PF₆)₃ were made in 40 mL screw top vials (VWR) with 10 mL of solvent composed of 8 mL of tetrahydrofuran (THF), 1 mL of water, and 1 mL of triethylamine (TEA). Control vials were prepared with photosensitizers, but without any catalyst. All vials were placed in a 16 well, water-cooled photoreactor mounted on an orbital shaker and equipped with pressure transducers as well as bottom LED illumination (Luxeon V Dental Blue LEDs, LXHL-LRD5 with collimating optics Fraen FHS-HNB1-LL01-H). Solutions were vacuum degassed and argon flushed 7 times before being brought to atmospheric pressure. H₂ generation was monitored by conversion of pressure transducer readings into pressure traces using a LabView PC interface. Analysis of the reaction headspace of each vial was performed

after illumination using a residual gas analyzer which was calibrated using 10% and 30% H_2 /Ar standards.

3.2.2.6 Zinc photoreduction studies

Zinc photoreduction studies were performed by Anthony Brooks according to previous literature.¹¹ Briefly, samples were prepared in 40 mL EPA vials with open top caps containing PTFE/silicone septa (ICHEM SB36-0040). Photoreaction mixtures contained 9 mL of solvent, 1 mL of TEA, 1.1 µmol of Ir(III) photocatalyst, and 420 mg ZnCl₂. The mixture was sealed and purges with 6 consecutive cycles of vacuum and argon. Following degassing, the samples were illuminated under argon with magnetic stirring in a custom designed photoreactor comprised of a 5 m long 24 W 460 nm LED strip with 300 diodes (Solid Apollo SA-LS-BL-3528-300-24 V) mounted inside an 8" galvanized steel tube in a uniform, spiral pattern. Following illumination, photoreduced zinc metal was measured by injecting an aliquot of concentrated hydrochloric acid and measuring the headspace for hydrogen content.

3.2.3. Preparation of complexes

3.2.3.1. Synthesis of [Ir(Fmppy)2(dCNbpy)]PF61

To a 25 mL round-bottom flask were added $[Ir(Fmppy)_2Cl]_2$ (86.5 mg, 72.1 µmol, 1.0 eq), dCNbpy (32.0 mg, 155 µmol, 2.2 eq), and 15 mL 95% ethanol. The flask was fitted with a condenser, and the headspace was purged with Ar for 5 min. Following this, the reaction mixture was heated to 75 °C for 36 h, at which point the mixture turned a transparent orange color. The mixture was then cooled to room temperature and added to 100 mL H₂O. The crude product was isolated *via* precipitation following addition of KPF₆ (1 g, excess) and subsequent vacuum filtration. The collected solid was washed with diethyl ether (3×15 mL) to remove excess dCNbpy and subsequently triturated with 10 mL diethyl ether under sonication. The solid product was collected by vacuum filtration and purified *via* vapor diffusion recrystallization from acetonitrile and diethyl ether to afford **1** as a red-orange crystalline solid (77.1 mg, 84. µmol). Overall yield: 58%.

¹H NMR (CD₃CN, 300 MHz): δ 2.15(6H, s), 5.86 (2H, dd, $J_1 = 2.6$ Hz, $J_2 = 9.5$ Hz), 6.85 (2H, dt, $J_1 = 2.7$ Hz, $J_2 = 8.9$ Hz), 7.32 (2H, dd, $J_1 = 0.7$ Hz, $J_2 = 1.8$ Hz), 7.75 (2H, ddd, $J_1 = 0.7$ Hz, $J_2 = 1.8$ Hz, $J_3 = 8.4$ Hz), 7.84 (2H, dd, $J_1 = 5.9$ Hz, $J_2 = 8.8$ Hz), 7.85 (2H, d, J = 5.9 Hz), 7.95 (2H, d, J = 8.1 Hz), 8.21 (2H, dd, $J_1 = 0.7$ Hz, $J_2 = 5.9$ Hz), 8.90 (2H, dd, $J_1 = J_2 = 0.7$ Hz); ¹³C NMR (CD₃CN, 75 MHz): δ 17.00, 109.88, 110.19, 115.20, 117.53, 119.77, 122.76, 126.63, 126.76, 128.02, 131.15, 134.47, 134.49, 140.11, 140.45, 140.48, 148.94, 150.59, 152.20, 155.82, 161.64, 163.20, 164.98; MS (ESI) Calculated: m/z: 771.17 (M⁺), Found: m/z (%): 771.0 (M⁺, 100%) Elem. Anal. Calc. for C₃₆H₂₄F₈IrN₆P·½ H₂O: C, 46.75; H, 2.72; N, 9.09. Found: C, 46.30; H, 2.84; N, 8.96%.

3.2.3.2. Synthesis of [Ir(ppy)2(dCNbpy)]PF6 2

The complex was prepared analogously to **1** above using $[Ir(ppy)_2Cl]_2$ (83.4 mg, 78 µmol, 1.0 eq), dCNbpy (33.1 mg, 161 µmol, 2.1 eq), and 15 mL 95% ethanol. The reaction completed in 18 h, during which time the solution turned a deep red color. The crude was purified *via* vapor diffusion recrystallization from acetonitrile and diethyl ether to afford **2** as a deep red crystalline solid (91.1 mg, 107 µmol). Overall yield: 68%.

¹H NMR (CD₃CN, 300 MHz): δ 6.25 (2H, dd, $J_1 = 0.9$ Hz, $J_2 = 7.5$ Hz), 6.97 (2H, td, $J_1 = 1.5$ Hz, $J_2 = 7.5$ Hz), 7.08 (4H, m), 7.58 (2H, ddd, $J_1 = 0.7$ Hz, $J_2 = 1.5$ Hz, $J_3 = 5.9$ Hz), 7.84 (4H, m), 7.90 (2H, ddd, $J_1 = 1.5$ Hz, $J_2 = J_3 = 7.3$ Hz), 8.10 (2H, d, J = 8.1 Hz), 8.20 (2H, dd, $J_1 = 0.7$ Hz, $J_2 = 5.9$ Hz), 8.88 (2H, dd, $J_1 = 0.7$ Hz, $J_2 = 1.5$ Hz); ¹³C NMR (CD₃CN, 75 MHz): δ 115.22, 120.14, 122.60, 123.17, 123.69, 125.02, 127.87, 130.59, 131.19, 131.36, 139.00, 148.40, 149.55, 152.04, 155.82, 167.03; MS (ESI) Calculated: m/z: 707.15 (M⁺), Found: m/z (%): 707.1 (M⁺, 100%) Elem. Anal. Calc. for C₃₄H₂₂F₆IrN₆P: C, 47.94; H, 2.60; N, 9.87. Found: C, 48.37; H, 2.46; N, 9.47%.

3.3 Results and Discussion

3.3.1 Alternate Synthetic Route Rationale

A side product was also formed during the initial attempts to synthesize the complexes described. Traditional Ir(III) dimer cleavage is accomplished by heating the dimer and diimine ligand in ethylene glycol at 150 °C overnight. When this method was initially attempted, bright orange crystals were obtained which strongly luminesced. During ¹H NMR analysis of the recrystallized product, two unexplained shifts (CD₃CN, 500 MHz, δ 4.50 ppm (dd, 2H, $J_1 = 1.2$ Hz, $J_2 = 4.6$ Hz) and 3.88 ppm (dd, 2H, $J_1 = 1.3$ Hz, $J_2 = 4.6$ Hz) were observed. These signals are too far downfield to be remnants of the diethyl ether and ethylene glycol used in the preparation and purification of the compounds²³; additionally, these peaks were observed during the synthesis of both Fmppy and ppy derivatives; the integration ratio for these signals is 2:1 against bpy C-H signals in both complexes indicating that both nitriles in each complex are affected

similarly. It is possible these peaks are due to partial alcoholysis of the nitrile bond by ethylene glycol. For this reason, subsequent attempts to synthesize the complexes employed lower reaction temperatures to avoid this degradation.

3.3.2 Density Functional Theory Results

DFT calculations were performed using the B3LYP functional with a LANL2DZ basis set. Generated frontier orbitals are shown in **Figure 3-3** and are representative of the MOs typically predicted for $[Ir(ppy)_2(bpy)]^+$ complexes.^{24,25} The HOMO in both new compounds is a mixture of iridium d and ppy π orbitals whereas the LUMO involves dCNbpy π * orbitals. Notably, the calculations predict that the cyano groups on the bipyridine ligand are included in the LUMO and thus are significant to the electronic structure. This is in agreement with a later study of similar dCNbpy complexes.²⁶



Figure 3-3. Frontier orbital diagrams based on DFT calculations performed using gaussian 09 with the B3LYP functional and LANL2DZ basis set. Reprinted with permission from ref 1. Copyright 2014 Elsevier Ltd.

3.3.3 Electrochemical Properties

Cyclic voltammetry was utilized to probe the frontier orbitals of the new complexes. Both show similar redox behavior including a quasi-reversible oxidation typical for iridium-based HOMOs (**Figure 3-4**). The oxidation potentials are anodically shifted compared to potentials for analogous bis-cyclometalated iridium complexes with di-*tert*-butyl-bipyridine neutral ligands (Table 3-1).^{25,27} This signifies stabilization of the HOMO through the inductive effect of the electron-poor dCNbpy. Further HOMO stabilization occurs with fluorination of the ppy in accordance with DFT predictions that the ppy directly participates in that orbital.



Figure 3-4. Cyclic voltammograms for $[Ir(ppy)_2(dCNbpy)]PF_6$ (red solid line) and $[Ir(Fmppy)_2(dCNbpy)]PF_6$ (blue dashed line) in degassed acetonitrile. Reprinted with permission from ref 1. Copyright 2014 Elsevier Ltd.

Table 3-1. Electrochemical data for **1**,**2** and comparators.

<u>Photosensitizer</u>	<u>E_{1/20x}</u>	<u>ΔΕ</u>	<u>E_{1/2red}</u>	<u>ΔΕ</u>
	(V vs SCE)	(mV)	(V vs SCE)	(mV)
[Ir(ppy) ₂ (dCNbpy)]PF ₆ , 1	1.37	110	-0.80, -1.43	71, 71
$[Ir(Fmppy)_2(dCNbpy)]PF_6^b, 2$	1.50	100	-0.79, -1.42	68, 71
[Ir(ppy) ₂ (dtbbpy)]PF ₆ ^c	1.21	65	-1.51	65
[Ir(Fmppy) ₂ (dtbbpy)]PF ₆ ^c	1.33	85	-1.50	70
$[Ir(ppy)_2(bpy)]PF_6^d$	1.25	65	-1.42	70
$[Ir(Fmppy)_2(bpy)]PF_6^d$	1.38	75	-1.39	60

^{*a*}All potentials were measured in degassed acetonitrile solutions with 0.1mM $(tBu)_4NPF_6$ as electrolyte and 1 mM analyte. Potentials were referenced to SCE *via* a ferrocene internal standard. ^{*b*}This compound also exhibits a third irreversible reduction at -1.79V which is not well-resolved from solvent processes and causes sample degradation during consecutive potential sweeps. ^{*c*}From ref. 24. ^{*d*}From ref. 27. bpy=2,2'-bipyridine.

Beyond oxidation, the dicyano-bipyridine complexes exhibit two reductions. The first reduction occurs on the neutral ligand and is markedly easier than reduction of bipyridine (**Table 3-1**) or electron-poor 4,4'-diethylester-2,2'-bipyridine ($E_{red} \approx -1.00 \text{ V}$ versus SCE) in similar complexes.^{25,27} This shows that cyano groups significantly enhance the neutral ligand's electron deficiency and stabilize the LUMO. The first reduction is not affected by ppy tuning in agreement with its assignment to dCNbpy. Assignment of the second reduction is more ambiguous. Although the process remains largely unchanged by ppy modification, it has previously been assigned to the ppy ligand

in similar complexes and has sometimes shown minimal response to ppy fluorination.^{24,25} In both dicyano-bipyridine complexes, full reversibility of the first two reductions and quasi-reversibility of the oxidation suggests general stability to redox processes. However, the fluorinated derivative also exhibits a poorly resolved, third reduction at highly negative potentials (-1.79 V) and is not stable to that particular process.

3.3.4 Photophysical Properties

UV-Vis [Ir(ppy)₂(dCNbpy)]⁺ absorption spectra for complexes and $[Ir(Fmppy)_2(dCNbpy)]^+$ (Figure 3-5) show agreement with their respective deep red and orange-red appearances. As is typically the case with bis-cyclometalated Ir(III) complexes, the fluoro-substituent on the Fmppy causes a slight blue-shift in the absorption and emission spectra by stabilizing the HOMO. Based on the low intensity of the transitions around 525 and 530 nm, they have been assigned as ³MLCT transitions. The stronger absorptions observed around 360 and 375 nm are assigned as mixed MLCT-ILCT transitions. Absorptions above 300 nm are assigned as ligand π - π * transitions. Excited state emissions, lifetimes, and quantum yields were measured for $[Ir(ppy)_2(dCNbpy)]PF_6$ and $[Ir(Fmppy)_2(dCNbpy)]PF_6$ as seen in **Table 3-2** above. These compounds exhibit short-lived emission with low quantum yields, both of which are unusual for bis-cyclometalated complexes of iridium.



Figure 3-5. UV–Vis absorption (solid lines) and emission (dotted lines) spectra of $[Ir(ppy)_2(dCNbpy)]^+$ (light red) and $[Ir(Fmppy)_2(dCNbpy)]^+$ (dark blue). Reprinted with permission from ref 1. Copyright 2014 Elsevier Ltd.

Table 3-2. Emission maxima, quantum yields, and excited state lifetimes of [Ir(ppy)₂(dCNbpy)]PF₆ and [Ir(Fmppy)₂(dCNbpy)]PF₆.

<u>Sample</u>	<u>Emission λ_{max} (nm)</u>	<u>φ (%)</u>	<u>τ (ns)</u>
[Ir(Fmppy) ₂ (dCNbpy)]PF ₆	694	0.598	66
[Ir(ppy) ₂ (dCNbpy)]PF ₆	750	0.091	27
$Ru(bpy)_3(PF_6)_2^{28}$	610	6.2	855

3.3.5 Water Reduction Catalysis Studies

 $[Ir(ppy)_2(dCNbpy)]^+$ [Ir(Fmppy)₂(dCNbpy)]⁺ employed and were for photocatalytic hydrogen generation from water to evaluate their potential as photosensitizers. The reactions were first carried out in THF using TEA as the sacrificial reductant. K_2PtCl_4 and $[Rh(dtbbpy)_3](PF_6)_3$ were chosen as catalysts because of their high catalytic activity, and pertinent to this case. to study the effect of heterogeneous/homogeneous catalyst on photosensitizer activity. Two state-of-the-art photosensitizers, namely $[Ir(Fmppy)_2(dtbbpy)]PF_6$ and $[Ir(ppy)_2(dtbbpy)]PF_6$, were also tested under similar conditions to serve as comparators. As illustrated by the hydrogen evolution traces and the corresponding Ir turnover numbers (Ir TON) (Figure 3-6A), both dicyano-bipyridine complexes surpass the standard Ir photosensitizers in hydrogen production when used along with Pt. Interestingly, $[Ir(ppy)_2(dCNbpy)]^+$ was found to have enhanced photostability, generating hydrogen even after 75 h and achieving 1300 turnovers in the process. Replacing Pt with Rh led to a drastic decrease in activity for the dicyano-bipyridine photosensitizers, generating lower turnovers in comparison to the standard ones. Control vials without catalysts produced negligible hydrogen. The same experiments were carried out in MeOH to explore the photosensitizers' ability to perform in a benign solvent. Comparable quantities of hydrogen were obtained as compared to THF. More importantly, consistent trends were observed, as depicted in Figure 3-6B. A summary of Ir TONs obtained for all the reactions is presented in Figure 3-7.



Figure 3-6. H₂ evolution traces and corresponding Ir turnovers obtained during photocatalytic water reduction in (A) THF and (B) MeOH, employing the two new $[Ir(C^N)_2(dCNbpy)]^+$ photosensitizers along with state-of-the-art $[Ir(C^N)_2(dtbpy)]^+$ complexes. K₂PtCl₄ and $[Rh(dtbpy)_3]^{3+}$ were used as catalysts. Reprinted with permission from ref 1. Copyright 2014 Elsevier Ltd.



Figure 3-7. Ir turnovers obtained for different photosensitizers in THF and MeOH, using K_2PtCl_4 and $[Rh(dtbbpy)_3]^{3+}$ as water reduction catalysts. Reprinted with permission from ref 1. Copyright 2014 Elsevier Ltd.

The observed activities of the dicyano-bipyridine complexes are likely a direct consequence of the inclusion of cyano groups on the bipyridine ligands. As mentioned earlier, K_2PtCl_4 forms colloids during the photoreactions, which then catalyze proton reduction. The presence of cyano groups creates probable binding sites for the said colloids, facilitating efficient electron transfer and therefore better performance. In the case of $[Rh(dtbbpy)_3]^{3+}$ which is known to be a molecular catalyst, no such binding would be possible, thus leading to reduced hydrogen evolution as compared to the

colloid. Another key aspect which provides supplementary evidence is the photosensitizer lifetime. The short lifetimes of the dicyano-bipyridine complexes would be unfavorable for a homogeneous system which is diffusion-limited but would actually be advantageous in presence of bound Pt colloids. As far as the Ir dtbbpy photosensitizers are concerned, their long lived excited states allow for proficient electron transport in homogeneous conditions and thus they exhibit better activity with the molecular catalyst.

Complexes **1** and **2** were also assessed for water reduction photocatalysis using $Co(bpy)_3^{2+}$, which is another known molecular catalyst. Unsurprisingly, the new photosensitizers performed poorly, only generating approximately 200 PS TON in all trials (**Table 3-3**); other $[Ir(ppy)_2(bpy)]^+$ derivatives generate between 400-900 PS TON.^{24,27} While these results are unimpressive, they do serve to reinforce that the new photosensitizers likely coordinate with colloids which explains their superior performance vs dtbbpy derivatives with K₂PCl₄.

Table 3-3. Ir turnovers in THF and MeOH using $Co(bpy)_3^{2+}$ as the water reduction catalyst.

<u>Photosensitizer</u>	THF	<u>MeOH</u>	
[Ir(ppy) ₂ (dCNbpy)]PF ₆ , 1	243	193	
[Ir(Fmppy) ₂ (dCNbpy)]PF ₆ , 2	198	252	

3.3.6. Photocatalytic Zinc Reduction

[Ir(ppy)₂(dCNbpy)]⁺ and [Ir(Fmppy)₂(dCNbpy)]⁺ were also tested as potential photocatalysts for the reduction of Zn(II) to zinc metal. In acetonitrile, [Ir(Fmppy)₂(dCNbpy)]PF₆ and [Ir(ppy)₂(dCNbpy)]PF₆ produced 154 and 231 TONs respectively, as seen in Table 3-4. Zinc photo-reduction by these complexes was less than that of $[Ir(ppy)_2(dtbbpy)]PF_6$, which remains the strongest Zn(II) reducing photocatalyst.¹¹ This can be attributed to the decreased molar absorptivity of the dicyanobipyridine complexes under the 465 nm blue light employed; future studies should focus on the use of AM 1.5 solar irradiation for a better comparison of photosensitizing ability. In ethyl acetate, the dicyano-bipyridine Ir(III) complexes produced between four and five times less zinc than in acetonitrile, similar to $[Ir(ppy)_2(dtbbpy)]PF_6$. The success of acetonitrile as a solvent has been attributed to its ability to positively shift the onset of Zn(II) reduction to higher potentials, allowing for more facile photo-reduction.¹¹ $[Ir(ppy)_2(dCNbpy)]PF_6$ and $[Ir(Fmppy)_2(dCNbpy)]PF_6$ did not boost performance in the absence of acetonitrile, so the dicyano-bipyridine moiety alone cannot replace the role of acetonitrile in Zn(II) photoreduction. This may result because the cyano of dCNbpy is incorporated into the pi system of the ligand, which reduces its capacity as a pi acceptor for the d10 Zn(II) ion.

Table 3-4. Production of zinc metal by photocatalytic Ir(III) complexes over 72 h. Each reaction vial contained 110 μ M Ir(III) photosensitizer, 420 mg ZnCl₂, 9 ml solvent, and 1 ml TEA under argon.

<u>Photocatalyst</u>	<u>Solvent</u>	<u>µmol Zn⁰</u>	<u>TONs</u>
[Ir(ppy) ₂ (dCNbpy)]PF ₆	MeCN	253.8	230.8
[Ir(ppy) ₂ (dCNbpy)]PF ₆	EtOAc	54.2	49.2
[Ir(Fmppy) ₂ (dCNbpy)]PF ₆	MeCN	169.4	154.0
[Ir(Fmppy) ₂ (dCNbpy)]PF ₆	EtOAc	38.2	34.8
[Ir(ppy) ₂ (dtbbpy)]PF ₆	MeCN	387.5	352.2
[Ir(ppy) ₂ (dtbbpy)]PF ₆	EtOAc	94.1	85.5

3.4 Conclusions and Future Directions

Two new bis-cyclometalated Ir(III) complexes were synthesized featuring dicyano-bipyridine moieties. These dicyano-bipyridine moieties were desired as possible bridging ligands to existing colloidal water reduction catalysts, and as possible bridging ligands to stabilize zinc(II) photo-reduction intermediates. The compounds produced possess very short lifetimes ($<1 \mu$ s) and low quantum yields which make them poor photosensitizers with molecular water reduction catalysts. Their bridging ligands, however, compensate for these shortcomings when used with colloidal water reduction

catalysts; in particular, $[Ir(ppy)_2(dCNbpy)]PF_6$ showed no signs of degradation following irradiation for 75 h and over 1300 PS turnovers.

Under 465 nm irradiation, the dicyano-bipyridine complexes were poorer performers than comparable di-*tert*-butyl complexes in Zn(II) photoreduction; this is likely due to poor absorption of the dicyano-bipyridine complexes in the blue region and could be remedied by studying activities under AM 1.5 solar irradiation. Future studies would still need to incorporate acetonitrile, as the dicyano-bipyridine moiety alone cannot obviate its use.

These complexes, which feature highly-reversible electrochemical reductions, high PS turnovers in water reduction catalysis, and visible-photon-driven ³MLCT transitions are attractive candidates to aid in the production of solar fuels from water. Future work would focus on enhancement of photophysical properties of these complexes *via* tuning of the cyclometalating ligand, and tuning of the bridging ability of the nitrile moieties via addition of electron-rich substituents on the bipyridine or cyclometalating ligands.

While unintentional, the side product observed during initial attempts to synthesize **1** and **2** could merit further investigation. Due to the repeatable nature of the side product formed during both the Fmppy and ppy derivatives, and the observed luminescence of the isolated complex, it is possible that the complex formed could be a useful photosensitizer. Further characterization of the complex to determine its exact identity and properties would be carried out with any interesting candidates being further evaluated in photocatalysis studies.

References

- Mills, I. N.; Kagalwala, H. N.; Chirdon, D. N.; Brooks, A. C.; Bernhard, S. Polyhedron 2014, 82, 104–108.
- (2) Lewis, N. S.; Nocera, D. G. PNAS 2007, 103, 15729–15735.
- Cargnello, M.; Gasparotto, A.; Gombac, V.; Montini, T.; Barreca, D.; Fornasiero,
 P. *Eur. J. Inorg. Chem.* 2011, 4309–4323.
- (4) McDaniel, N. D.; Bernhard, S. Dalt. Trans. 2010, 39, 10021–10030.
- (5) Cline, E. D.; Adamson, S. E.; Bernhard, S. *Inorg. Chem.* **2008**, *47*, 10378–10388.
- (6) Cui, H.; Hu, M.; Wen, H.; Chai, G.; Ma, C.; Chen, H.; Chen, C. Dalt. Trans. 2012, 41, 13899–13907.
- Gärtner, F.; Sundararaju, B.; Surkus, A. E.; Boddien, A.; Loges, B.; Junge, H.;
 Dixneuf, P. H.; Beller, M. Angew. Chemie Int. Ed. 2009, 48, 9962–9965.
- (8) Ma, L.; Guo, H.; Li, Q.; Guo, S.; Zhao, J. Dalt. Trans. 2012, 41, 10680–10689.
- (9) Zhang, P.; Jacques, P. A.; Chavarot-Kerlidou, M.; Wang, M.; Sun, L.; Fontecave,
 M.; Artero, V. *Inorg. Chem.* 2012, *51*, 2115–2120.
- (10) Hay, P. J. J. Phys. Chem. A 2002, 106, 1634–1641.
- (11) Brooks, A. C.; Basore, K.; Bernhard, S. Inorg. Chem. 2013, 52, 5794–5800.
- (12) Brooks, A. C.; Basore, K.; Bernhard, S. Chem. Commun. 2014, 50, 5196–5199.
- (13) Blackbourn, R.; Johnson, C. J. Am. Chem. Soc. 1991, 1, 1060–1062.

- (14) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porhyrin Complexes*;Academic Press: London, 1992.
- (15) Disalle, B. F.; Bernhard, S. J. Am. Chem. Soc. 2011, 133, 11819–11821.
- (16) Metz, S.; Bernhard, S. Chem. Commun. 2010, 46, 7551–7553.
- (17) Xie, H. Z.; Liu, M. W.; Wang, O. Y.; Zhang, X. H.; Lee, C. S.; Hung, L. S.; Lee, S. T.; Teng, P. F.; Kwong, H. L.; Zheng, H.; Che, C. M. Adv. Mater. 2001, 13, 1245–1248.
- (18) Losse, S.; Görls, H.; Groarke, R.; Vos, J. G.; Rau, S. Eur. J. Inorg. Chem. 2008, 2008, 4448–4452.
- (19) Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J.; Parker, S.; Rohl, R.;
 Bernhard, S.; Malliaras, G. G. J. Am. Chem. Soc. 2004, 126, 2763–2767.
- M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J. R. C.; G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. C.; X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M.; Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y.; Honda, O. Kitao, H. Nakai, T. Vreven, J.A.J. Montgomery, J.E. Peralta, F. O.; M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J.; Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M.; Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. A.; J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C.; Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G. A. V.; P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J. B. F.; J.V.

Ortiz, J. Cioslowski, D. J. F. GAUSSIAN 09, revision A.01, Gaussian Inc., Wallingford, CT, 2009.

- (21) AMPAC 10 GUI, 2011.
- (22) Connelly, N. G.; Geiger, W. E. Chem. Rev. 1996, 96, 877-910.
- (23) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. J. Org. Chem. 1997, 62, 7512–7515.
- (24) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Pascal, R. A; Malliaras, G. G.;
 Bernhard, S.; Rohl, R. *Chem. Mater.* 2005, *17*, 5712–5719.
- (25) Chirdon, D. N.; Mccusker, C. E.; Castellano, F. N.; Bernhard, S. *Inorg. Chem.* **2013**, *52*, 8795–8804.
- (26) Skórka, Ł.; Filapek, M.; Zur, L.; Małecki, J. G.; Pisarski, W.; Olejnik, M.;
 Danikiewicz, W.; Krompiec, S. J. Phys. Chem. C 2016, 120, 7284–7294.
- (27) Goldsmith, J. I.; Hudson, W. R.; Lowry, M. S.; Anderson, T. H.; Bernhard, S. J.
 Am. Chem. Soc. 2005, *127*, 7502–7510.
- (28) Caspar, J. V; Meyer, T. J. J. Am. Chem. Soc. 1983, 105, 5583-5590.

Chapter 4

CNmppy Complexes as alternatives to Fmppy Complexes for Solar Fuel Generation and Oxygen Sensing

This chapter has been adapted from a 2016 article in Dalton Transactions.¹ The article represents the collaborate efforts of several people within the Bernhard group as described in the experimental section.

4.1 Introduction

Worldwide consumption of fossil-derived fuels, and environmental concerns related to their production, transportation, and combustion, have driven massive efforts to find more benign substitute fuel stocks. While alternatives such as wind and tidal power are promising parts to a comprehensive renewable-energy solution, there still exists the need to produce fuels for remote and high-power applications. Solar fuels represent an attractive way to directly and renewably produce low-impact fuels such as hydrogen from water-splitting^{2–15}, acid dehydrogenation^{16–19}, and alcohol dehydrogenation^{20–26}; water-splitting is particularly attractive due to the benign nature of its combustion byproducts.

Water splitting is typically studied as separate oxidation- and reduction- halfreactions to optimize catalysts for each component. Water reduction is often photodriven, though catalysts typically require photosensitizers due to poor absorptivity in the visible-light range. Among the most successful photosensitizers are bis-cyclometalated Ir(III) complexes; they are particularly attractive due to their high tunability and very long-lived excited triplet excited states.

Previous work with bis-cyclometalated Ir(III) complexes show strong stabilization of the HOMO *via* electron-withdrawing moieties on the cyclometalating ligands while electron-rich groups on the chelating ligand destabilize the LUMO.²⁷ This allows for both fine-tuning of the HOMO-LUMO gap and the wide range of energy gap values achievable. While fluoro-substituted cyclometalated Ir(III) chromophores are widely studied²⁸⁻³⁴, the incorporation of nitriles may obviate the need for expensive or environmentally problematic fluorinated ligands, which are also more susceptible to nucleophilic attack. Previous literature has also shown the ability of nitrile moieties to interact with Pt catalyst colloids during photosensitization.³⁵ Though minimal tuning of the electrochemical and photophysical properties is traditionally accomplished *via* modification of the bipyridine ligands in bis-cyclometallated Ir complexes, incorporation of nitriles on both the cyclometalating and chelating ligands, is therefore expected to produce compounds with interesting electronic and catalytic properties.

In this chapter, a new cyclometalating ligand, 2-(4-cyanophenyl)-5methylpyridine **1** (CNmppy), was created and used to synthesize the *di*-chloro-bridged Ir(III) dimer, [Ir(CNmppy)₂Cl]₂ **2**. Two new bis-cyclometalated Ir(III) complexes, namely [Ir(CNmppy)₂(dtbbpy)](PF₆) **3a** and [Ir(CNmppy)₂(dCNbpy)](PF₆) **3b** (dtbbpy = 4,4'-di-*tert*-butyl-2,2'bipyridine, dCNbpy = 4,4'-dicyano-2,2'-bipyridine), (**Figure 4-1**) were then produced by cleavage of the dimer and assessed as photosensitizers for waterreduction catalysis. Insight into the electronic properties of these complexes was gained through photophysical, electrochemical, and density functional theory (DFT) analysis. Both complexes synthesized were found to be active photosensitizers and photocatalysts, with one complex demonstrating marked robustness in acetonitrile, which is known to cause ligand dissociation.³⁶ The complexes were assessed for their water reduction photosensitizing ability in a variety of solvents, including alcohols, in an effort to replace expensive and environmentally toxic media. The complexes were also assessed as zinc reduction photocatalysts.



Figure 4-1. Synthesized complexes 3a and 3b

4.2 Experimental Section

4.2.1 Materials and Methods

All materials were obtained from Sigma Aldrich and used without further purification unless otherwise stated. IrCl₃·4H₂O was obtained from Pressure Chemicals and used without further purification. 4-(Bromoacetyl)benzonitrile (98%) was obtained from Alfa Aesar and used without further purification. 4,4'-dicyano-2,2'-bipyridine (dCNbpy) was synthesized according to literature procedures described elsewhere.³⁷ The new cyclometalating ligand 2-(4-Cyanophenyl)-5-methylpyridine (CNmppy) **1** was

synthesized *via* standard procedures.³⁸ Synthesis of $[Ir(CNmppy)_2Cl]_2$ **2**, $[Ir(CNmppy)_2(dtbbpy)]PF_6$ **3a**, and $[Ir(CNppy)_2(dCNbpy)]PF_6$ **3b** were performed according to modified literature procedures³⁹ which employed lower reaction temperatures and longer reaction times to avoid degradation of the nitrile moieties as previously observed.³⁵

4.2.2 Synthesis





To a round-bottom flask was added 50 mL of diethyl ether and 50 mL pyridine. The mixture was cooled to 0 °C and 4-(bromoacetyl)-benzonitrile (5.0 g, 21.9 mmol) was slowly added, immediately producing a bright yellow solid. The reaction was left to warm to room temperature over 1 hour with constant stirring at which point the solid was filtered and washed with ice-cold ethanol to afford approximately 6.5 g of the bromopyridinium precursor as a white powdery solid. The bromo-pyridinium precursor was used without further purification or characterization.

The bromo-pyridinium precursor (7.5 g, 24.8 mmol, 1 eq.) was added to a roundbottom flask along with 2-methacrolein (2.4 mL, 26.2 mmol, 1.05 eq.) and methanol (150 mL). Ammonium acetate (10 g, 130 mmol, 5.25 eq.) was added and the mixture was then heated to reflux with stirring for 18 hours during which time the solution turned dark red. The mixture was then cooled to room temperature and added to a slurry of ice-water and stirred for one minute to precipitate the solid product. The crude solid was then isolated *via* vacuum filtration and subsequently washed with water (250 mL) to afford a light crème-colored solid. Crude **1** was purified *via* flash chromatography (9:1 Hex:EtOAc) on silica gel and the solvent was removed to afford **1** as a white crystalline solid (3.1 g, 16 mmol, 65% overall yield).

¹H NMR (CDCl₃, 300 MHz): δ 2.42 (3H, s), 7.63 (1H, dd, J₁=1.8 Hz, J₂=8.1 Hz), 7.69 (1H, d, J=8.1 Hz), 7.76 (2H, dt, J₁=1.8 Hz, J₂=8.4 Hz), 8.11 (2H, dt, J₁=1.8 Hz, J₂=8.4 Hz), 8.57 (1H, d, J=1.8 Hz); ¹³C NMR (CDCl₃, 75 MHz): δ ; 18.3, 112.1, 118.9, 120.5, 127.2, 132.5, 133.3, 137.8, 143.2, 150.3, 152.4; MS (ESI) Calculated: m/z: 194.1 (M⁺), Found: m/z (%):195.2 ([M+H]⁺, 100%)



Figure 4-3. Synthesis of [Ir(CNmppy)₂Cl]₂ dimer, 2

To a round-bottom flask was added $IrCl_3 \circ 4 H_2O$ (370 mg, 1.0 mmol) and CNmppy **1** (430 mg, 2.2 mmol, 2.2 eq.). To the flask was added 140 mL 5:1 2-MeOEtOH:H₂O and the mixture was sonicated for 10 min. The reaction mixture was purged with argon and heated to reflux with constant stirring for 18 hours during which time the solution turned translucent orange. The solvent was removed under rotary

evaporation to afford a bright orange solid which was washed with CH_2Cl_2 (50 mL) to remove excess CNmppy. **2** was afforded as a bright orange solid (456 mg, 0.37 mmol, 74% yield) which faintly luminesced orange under longwave UV. The isolated solid was verified *via* ESI-MS in acetonitrile, as non-coordinating solvents failed to produce a charged complex under ESI conditions.

MS (ESI) Calculated: m/z: 1226.2 (M+, 100%), 1228.2 (M+, 100%), Found: m/z (%): 660.6 (¹/₂[M-Cl⁻+2MeCN]⁺, 100%), 678.4 (¹/₂[M-Cl⁻+2MeCN+H₂O]⁺, 15%), 736.9 (¹/₂[M-Cl⁻+2MeCN+MeOEtOH]⁺, 15%)



Figure 4-4. Cleavage of [Ir(CNmppy)₂Cl]₂ 2 to yield 3a or 3b

$[Ir(CNmppy)_2(dtbbpy)]PF_6$ **3a**

To a screw-cap EPA vial were added $[Ir(CNmppy)_2Cl]_2 2 (120 \text{ mg}, 100 \mu \text{mol}, 1.0 \text{ eq.}), 4,4'-dtbbpy (60 mg, 220 \mu \text{mol}, 2.2 eq.), and 20 mL 95% ethanol. The vial was sealed, and the headspace was purged with Ar for 5 minutes. Following this, the reaction mixture was heated to 95 °C with stirring for 36 hours, at which point the reaction mixture turned a bright yellow color which luminesced yellow-green under long-wave UV irradiation. The mixture was then cooled to room temperature and added to 100 mL$

H₂O. The solution was filtered through celite and the crude product was isolated from the supernatant *via* precipitation following addition of KPF₆ (1 g, excess) and subsequent vacuum filtration. The collected solid was washed with diethyl ether (3x15 mL) and dried in air. The crude product was purified *via* flash chromatography on ethylated silica⁴⁰ (CH₂Cl₂ to acetone gradient) and vapor diffusion recrystallization from acetonitrile and diethyl ether to afford **3a** as a bright yellow crystalline solid (132 mg, 133 µmol, 67% yield).

¹H NMR (CD₃CN, 500 MHz): δ 1.45 (18H, s), 2.19 (6H, s), 6.52 (2H, d, J=1.2), 7.39 (2H, dd, J₁=0.6 Hz, J₂=1.2 Hz), 7.41 (2H, dd, J₁=1.5 Hz, J₂=7.9 Hz), 7.52 (2H, dd, J₁=1.8 Hz, J₂=5.8 Hz), 7.82 (4H, m), 7.90 (2H, d, J=7.9 Hz), 8.10 (2H, d, J=8.2 Hz), 8.52 (2H, d, J = 1.2 Hz); ¹³C NMR (CD₃CN, 125 MHz): δ 29.5, 35.5, 112.2, 119.0, 121.1, 122.3, 124.4, 125.3, 126.5, 134.5, 136.2, 139.9, 149.2, 149.3, 150.4, 164.4; MS (ESI) Calculated: m/z: 847.3 ([M-PF₆]⁺), Found: m/z (%): 847.3 ([M-PF₆]⁺, 100%)

[*Ir*(*CNmppy*)₂(*dCNbpy*)]*PF*₆ **3b**

The complex was prepared analogously to **3a** above using $[Ir(CNmppy)_2Cl]_2$ (120 mg , 100 µmol, 1.0 eq.), dCNbpy (48 mg, 220 µmol, 2.2 eq.), and 20 mL 95% ethanol. The reaction completed in 36 hours, and the solution turned a deep red color. The crude was purified as described above to afford **3b** as a red crystalline solid (98 mg, 105 µmol, 53% yield).

¹H NMR (CD₃CN, 500 MHz): δ 2.17 (6H, s), 6.56 (2H, d, J=1.5), 7.46 (2H, dd, J₁=1.8 Hz, J₂=8.1 Hz), 7.85 (2H, s), 7.97 (2H, dd, J₁=1.5 Hz, J₂=8.4 Hz), 8.10 (2H, d, J=8.0 Hz), 8.16 (2H, dd, J₁=1.3 Hz, J₂=5.7 Hz), 8.35 (2H, d, J=8.4 Hz), 8.50 (2H, d, J=5.5 Hz), 9.42 (2H, s); ¹³C NMR (CD₃CN, 125 MHz): δ 112.3, 121.4, 123.1, 124.6, 127.2, 128.2, 131.2, 134.5, 136.7, 140.4, 149.8, 152.4, 155.8, 162.1; MS (ESI) Calculated: m/z: 785.2 ([M-PF₆]⁺), Found: m/z (%): 785.1 ([M-PF₆]⁺, 100%)

4.2.3 Computational Methods

Ground state geometries and frontier orbital energies were predicted *via* DFT using Gaussian 09D.⁴¹ The B3LYP functional and LANL2DZ basis sets were applied to all atoms. No solvent or symmetry conditions were specified for static singlet or triplet energy level calculations. Frequency calculations were performed with each geometry optimization to ensure that no imaginary frequencies were obtained. Time-dependent DFT calculations were performed for the first 150 states with methanol as the solvent. Orbitals were visualized using Ampac software.⁴²

4.2.3 Electrochemical Characterization

Cyclic voltammetry was performed using a CH-Instruments Electrochemical Analyzer 600C potentiostat with a three-electrode system comprised of a silver wire pseudo-reference, a platinum coil counter electrode, and a 1 mm² platinum disk working electrode. All voltammograms were collected under an argon purge in acetonitrile solutions containing 1 mM analyte and 0.1 M (tBu)₄NPF₆ as supporting electrolyte.

Positive scan polarity was used with a scan rate of 0.10 V/s. Potentials were referenced to SCE using a ferrocene internal standard $(fc/fc^+= 0.40 \text{ V})$.⁴³

4.2.4 Photophysical Characterization

Photophysical measurements were carried out at room temperature on 10 μ M methanol solutions which were purged with argon for 10 min in septa-equipped capped quartz cuvettes. UV–vis absorption spectra were then obtained with a Shimadzu UV-1800 spectrophotometer. Photoluminescence was measured using a Fluorolog-3 spectrophotometer equipped with dual monochromators and a photomultiplier tube (PMT) at right angle geometry. Excited-state lifetimes were measured by employing the fourth harmonic (266 nm) of a Nd:YAG (Continuum Minilite) laser as an excitation source. The light train of the Flourolog-3 in combination with a digital oscilloscope (Tektronix TDS 3032B) was used to measure luminescence decay. Quantum yields were determined relative to a 33 μ M [Ru(bpy)₃](PF₆)₂ solution in methanol. Quenching experiments were carried out with **3a** (10 μ M in MeOH) by measuring the excited state lifetimes at 505 nm in air (~21% O₂) and subsequently by degassing the solution for at least 10 minutes with argon/oxygen standards.

4.2.5 Water Reduction Photosensitization Protocol

All water reduction photolysis experiments were carried out by Husain Kagalwala following previously reported procedures.⁴⁴ In general, 10 ml solutions containing specified concentrations of the photosensitizer, catalyst, water and triethylamine (TEA) were prepared in 40 ml clear EPA vials (Thermo Scientific). Addition of TEA was

always the last step and done in the dark. The vials were then placed in a home-built 16well photoreactor equipped with pressure transducers, an orbital shaker, and bottom illumination (460 nm, 500 \pm 50 mW). Post-degassing (7 periodic cycles of vacuum and back-filling with argon), the solutions were subject to illumination and corresponding pressure traces recorded. Quantification of H₂ produced was done by injecting small quantities of the vial headspace in a GOW-MAC gas chromatograph (thermal conductivity detector, Ar carrier gas), pre-calibrated using 10% H₂/Ar gas mixtures.

4.2.6 Zinc Photoreduction Studies

Zinc photoreduction studies were carried out according to previous literature.⁴⁵ Briefly, samples were prepared in 40 mL EPA vials with open top caps containing PTFE/silicone septa (ICHEM SB36-0040). Photoreaction mixtures contained 9 mL of solvent, 1 mL of TEA, 1.1 µmol of Ir(III) photocatalyst, and 420 mg ZnCl₂. The mixture was sealed and purges with 6 consecutive cycles of vacuum and argon. Following degassing, the samples were illuminated under argon with magnetic stirring in a custom designed photoreactor comprised of a 5 m long 24 W 460 nm LED strip with 300 diodes (Solid Apollo SA-LS-BL-3528-300-24 V) mounted inside an 8" galvanized steel tube in a uniform, spiral pattern. Following illumination, photoreduced zinc metal was measured by injecting an aliquot of concentrated hydrochloric acid and measuring the headspace for hydrogen content.

4.3 Results and Discussion

4.3.1 Density Functional Theory Results

DFT calculations were performed to investigate the electronic structure and relative energy gaps of the chromophores. The complexes' singlet orbital energies and their frontier orbitals are shown below in **Figure 4-5**. The HOMO of both complexes is the typical combination of Ir *d* and CNmppy π orbitals.^{29,46} The LUMO of both complexes is composed of the bpy π^* orbitals, with **3b** showing significant contribution from the nitrile groups in agreement with previous literature.³⁵ The nitrile moiety in both complexes is a significant contributor to frontier orbitals located on the cyclometalating ligands.



Figure 4-5. Singlet energy diagrams for **3a** (left) and **3b** (right). Highlighted transitions (numbered 1-6) correspond to major predicted transitions and experimental spectra as
discussed below. Figure reprinted with permission from ref 1. Copyright The Royal Society of Chemistry 2016.

Static-DFT was also performed for the triplet states of the chromophores to elucidate the frontier orbitals and transitions responsible for emission (**Figure 4-6**). The character of **3b**'s HSOMO exactly matched the LUMO of the singlet; this was also true for the LSOMO and HOMO. Complex **3a**'s triplet states were much more remarkable in that while the LUMO and HSOMO had similar character, the LSOMO and HOMO did not; rather the LSOMO is structurally analogous to the HSOMO and also located on the dtbbpy. This suggests that the triplet emission of **3a** arises from an intra-ligand π - π * transition, whereas **3b**'s triplet emission arises from the inter-ligand (bpy-ppy) transitions seen in [Ir(ppy)₂(bpy)]⁺ chromophores with strong MLCT character.



Figure 4-6. Triplet energy diagram for **3a** (left), **3b** (right). Figure reprinted with permission from ref 1. Copyright The Royal Society of Chemistry 2016.

4.3.2 Electrochemical Properties

Cyclic voltammetry was performed on both complexes (**Table 4-1**). Both complexes featured a quasi-reversible oxidation at 1.5-1.7 V vs SCE. This feature can be ascribed to oxidation of the metal center which is coupled to the CNmppy moieties. As expected, the more cyanated **3b** has a higher oxidation onset than **3a** owing to its comparative electron deficiency and the greater stabilization of its energy levels. These potentials are also anodically shifted approximately +0.17 V from analogous $[Ir(Fmppy)_2(bpy)]PF_6$ (Fmppy = 2-(4-fluorophenyl)-5-methylpyridine) complexes (**Table 4-1**) due to the greater inductive stabilizing effect of the nitrile group vs the fluoro group on the HOMO of the ppy; it is also possible that greater resonance delocalization

due to the extended π system plays a role. Complex **3a** featured only one reversible reduction at -1.42 V vs SCE, consistent with comparable complexes.⁴⁶ This is assigned to reduction of the ppy moiety, which typically occurs beyond -1.00 V vs SCE.⁴⁷ Complex **3b** featured two reversible reductions at -0.72 and -1.32 V vs SCE. The first reduction is assigned to the nitrile of the dCNbpy as it occurs before -1.00 V, while the second reduction is likely from the nitrile moiety on the ppy.³⁵ The strong anodic shift of the first reduction potential relative to other bipyridine-based bis-cyclometalated complexes highlights the strong participation of the nitrile moieties in the frontier orbitals.

Table 4-1. Electrochemical properties of **3a** and **3b** with analogous Fmppy complexes for comparison. Potentials were determined from solutions containing 1 mM analyte and 0.1 M (tBu)₄NPF₆ as supporting electrolyte.

	<u>E</u> ox		$\underline{\mathbf{E}}_{\mathbf{red}}$	
<u>Compound</u>	(V vs SCE)	<u>ΔΕ (mV)</u>	(V vs SCE)	<u>ΔΕ (mV)</u>
[Ir(CNmppy) ₂ (dtbbpy)]PF ₆ , 3a	1.50	70	-1.42	60
[Ir(CNmppy) ₂ (dCNbpy)]PF ₆ , 3b	1.67	80	-0.72, -1.32	50, 60
[Ir(Fmppy) ₂ (dtbbpy)]PF ₆ ⁴⁶	1.33	85	-1.50	70
[Ir(Fmppy) ₂ (dCNbpy)]PF ₆ ³⁵	1.50	100	-0.79, -1.42	68, 71

The reversibility of the reductions of complexes **3a** and **3b**, coupled with their quasi-reversible oxidation, indicates they should be robust to redox processes during photocatalysis. The stabilization of both the CNmppy and dCNbpy ligands, along with a first reduction from the nitrile moieties at low potentials accounts for the small HOMO-LUMO gap seen in **3b**; the dtbbpy moiety in **3a** comparatively destabilizes the LUMO and features only one reduction at greater potential, accounting for the large HOMO-LUMO gap observed.

4.3.3 TD-DFT and Photophysical Characterization

Complex **3a** showed strong absorption in the UV-region around 270 nm with additional visible absorption around 400 nm accounting for its yellow color. The absorption around 270 nm arises from π - π * transitions, while the absorptions around 375-425 nm arise from mixed MLCT-ILCT transitions. Complex **3b** showed similar features in the UV region with a strong absorptions from 270-300 nm being again assigned as π - π * transitions; additional absorptions in the 350-400 nm range are assigned as mixed MLCT-ILCT transitions. **3b** also showed an unusual absorption at 500 nm which likely arises from the forbidden ³MLCT transition.^{35,48} This absorption at 500 nm, coupled with the absorption from 350-400 nm, account for the complex's red-orange color.



Figure 4-7. Experimental spectra (blue), calculated spectra (red), and predicted oscillators (black) for **3a** (**A**) and **3b** (**B**). The numbered transitions correspond to transitions highlighted in Figure 4-5. Experimental spectra were obtained from 10 μ M solutions in Ar-degassed methanol. Calculated spectra and oscillator strengths were obtained from Gaussian TD-DFT calculations with methanol specified as the solvent. Figure reprinted with permission from ref 1. Copyright The Royal Society of Chemistry 2016.

Time-dependent DFT (TD-DFT) (**Figure 4-7**) was used to elucidate electronic transitions responsible for the observed spectra. Predicted spectra for both **3a** and **3b** matched closely with experimental spectra. Predicted high-intensity peaks for **3a** are clustered from 250-300 nm (1, **Figure 4-7**) and arise mostly from HOMO-6 \rightarrow LUMO+1 and HOMO-4 \rightarrow LUMO+3 transitions. A moderate intensity peak from 350-400 nm (2, **Figure 4-7**) arose from the predicted HOMO-1 \rightarrow LUMO transition, while the peak at 425 nm (3, **Figure 4-7**) is from the HOMO \rightarrow LUMO transition. These predicted transitions align well with the experimentally-obtained spectrum and literature assignments⁴⁹.

Complex **3b** featured similar peaks to **3a** with the HOMO-4 \rightarrow LUMO+3 transition again being predicted to contribute strongly to the absorptions around 270 and 300 nm (4, **Figure 4-7**). The peak around 400 nm (5, **Figure 4-7**) largely arises due to the HOMO \rightarrow LUMO+1 transition, and the absorption around 450 nm (6, **Figure 4-7**) again occurs due largely to the HOMO \rightarrow LUMO transition. Only the absorption around 475 nm, due to the forbidden ³MLCT transition, was not predicted by the transitions for **3a**.

Emission spectra, excited state lifetimes, and quantum yields were determined from 10 μ M solutions of the photosensitizers in methanol, which was the media most effective at photogenerating H₂. Quantum yields were determined relative to a 33 μ M Ru(bpy)₃(PF₆)₂ methanolic solution as a standard. All solutions were degassed with argon to prevent luminescence quenching of the chromophores by oxygen.

Emission spectra (**Figure 4-8**) were markedly different for each chromophore, showing great tunability for the emission maxima. **3a** luminesced strongly yellow-green as indicated by the strong emission maxima at 500 nm and 540 nm; **3b** luminesced a weak orange-red from 600-650 nm. The photophysical properties of **3a** and **3b** are summarized in **Table 4-2** below. **3b** was found to perform similarly to previously published³⁵ bis-cyclometalated complexes of iridium with the dCNbpy moiety, with slightly increased quantum yield and lifetime being ascribed to greater stabilization of the HOMO by the ppy nitrile moiety. **3a** was found to have an extremely long-lived lifetime for a luminophore of almost eight microseconds. The vibronic structure of the emission spectrum of **3a** is also characteristic of a π - π * transition, which is consistent with the long excited-state lifetime and can be readily seen in the triplet electronic structures in **Figure 4-6. 3a** was also found to be a highly efficient emitter with a quantum yield of approximately 63 percent. These extreme differences in lifetime and quantum yield of **3a** and **3b** can be ascribed to the combination of the wider HOMO-LUMO gap in the singlet state which mirrors the wider gap in the triplet excited state, as well as the π - π * transition occurring from **3a**'s triplet excited state.



Figure 4-8. Emission spectra of 10 μ M solutions of **3a** (blue) and **3b** (red, 5X amplified) in MeOH. Solutions were degassed using Ar to prevent luminescence quenching by O₂. Figure reprinted with permission from ref 1. Copyright The Royal Society of Chemistry 2016.

Table 4-2. Photophysical properties of **3a** and **3b** obtained from argon-degassed 10 μ M solutions of the analyte in methanol. [Ru(bpy)₃](PF₆)₂ was used as a reference for quantum yield determination.

Sample	<u> </u>	<u>τ (ns)</u>	λ_{\max} (nm)	<u>K_{svP} (mbar⁻¹)</u>	$\underline{k_{q}} (M^{-1} s^{-1})$
$[\operatorname{Ru}(\operatorname{bpy})_3](\operatorname{PF}_6)_2$	6.20^{50}	950		0.024 ⁵¹	2.9 x 10 ⁹
[Ir(CNmppy) ₂ (dtbbpy)](PF ₆), 3a	62.7	7940	502, 541	0.054	6.8 x 10 ⁸
[Ir(CNmppy) ₂ (dCNbpy)](PF ₆), 3b	0.689	120	628		
$[Ir(ppy)_2(bpy)](PF_6)$	6.22^{50}	330 ⁵⁰		0.026 ⁵¹	8.8 x 10 ⁹

The photophysical behavior of the synthesized complexes highlights the drastic effects that proper placement of electron-deficient cyclometalating ligands and electron-rich diimine ligands can have on photophysical performance. A recent study⁴⁸ which probed similar complexes showed a clear trend where "push-pull" architectures as those described above possessed high quantum yields and remarkably long excited state lifetimes. In keeping with this, it follows naturally that **3a** with the extremely electron-deficient cyclometalating ligand and very electron-rich diimine would photophysically outperform **3b** which does not benefit from this push-pull effect.

Due to the extremely long-lived excited state of **3a**, a Stern-Volmer oxygen quenching study was performed to determine the suitability of the complex for sensor applications. Luminescence quenching of **3a** by oxygen was measured in methanol at various partial pressures of oxygen (**Figure 4-9**). While the rate of luminescence quenching was low for **3a** (k_q =6.8 x 10⁸ M⁻¹s⁻¹) the complex is approximately twice as efficiently quenched by oxygen (K_{svP} = 0.054 mbar⁻¹) than previous [Ir(ppy)₂(bpy)]⁺ and

 $[Ru(bpy)_3]^{2+}$ analogues (K_{svP}= 0.026 and 0.024 mbar⁻¹ respectively)⁴⁹. K_q values were calculated from the K_{svP} values using the expressions K_{svP}=K_{sv}K_H and K_{sv}=K_qτ₀ where K_{sv} is the concentration-based Stern-Volmer constant, K_H is the Henry's law constant for oxygen solubility in methanol (K_H= 10.2 M mbar⁻¹), and τ₀ is the excited state lifetime of each complex in argon.⁵²



Figure 4-9. Stern-Volmer plot showing quenching of **3a** by O_2 . Excited state lifetimes at 505 nm were measured using a 10 μ M solution of **3a** in MeOH following degassing with Ar/O₂ standards for 10 min. Figure reprinted with permission from ref 1. Copyright The Royal Society of Chemistry 2016.

4.3.4 Photosensitization Studies

The new complexes were explored as light harvesters for photo-driven water reduction using K₂PtCl₄ as the water reduction catalyst (WRC) and triethylamine as sacrificial reductant in a typical water photoreduction scheme (**Figure 4-10**). Both photosensitizers were found to generate H₂ in MeCN as solvent, with **3a** generating more than twice the turnovers (~1700) of **3b** (~680). The ability of **3a** to perform well in a coordinating solvent highlights its overall robustness. In comparison, **3b** with its electronpoor ancillary ligands would be more susceptible to ligand dissociation and hence achieves fewer turnovers. To confirm this, solvents with varying ligating abilities were employed. As depicted in **Figure 4-11**, **3b** increasingly performs well in weakly coordinating solvents, the only exception being THF in which it evolved negligible H₂. The performance of **3a**, however, does not seem to be affected by solvent ligation. Rather, the solvent polarity seems to play a major role in determining its photosensitizing capability, generating more turnovers with increasing polarity.



Figure 4-10. Typical reductive quenching mechanism for $[Ir(ppy)_2(bpy)]^+(PS)$ observed in photo-driven water reduction with K₂PtCl₄ (WRC) and TEA



Figure 4-11. Effect of solvent on photosensitizing capability for water reduction. Solvent polarity plays a key role in determining the performance of **3a** while **3b** is affected by solvent coordination ability. Photoreactions were carried out using 0.1 mM photosensitizer, $30 \ \mu M \ K_2 PtCl_4$ and 0.7 M TEA. Photoreactions with no photosensitizer, no TEA, or no K_2 PtCl_4 produced negligible hydrogen. Figure reprinted with permission from ref 1. Copyright The Royal Society of Chemistry 2016.

Given their similar performance in a benign solvent like MeOH, the photosensitizers were further tested in four different alcohols. As seen in **Figure 4-12A**, both **3a** (solid lines) and **3b** (dotted lines) evolved negligible H_2 in presence of tertiary butyl alcohol (*t*-BuOH). Additionally, each generated relatively similar turnovers in isopropyl alcohol (IPA, 400-550 TONs) and 2-methoxyethanol (2-MeOEtOH, 800-970 TONs), with **3b** outperforming **3a** in these solvents. A vastly different response was seen using EtOH; **3b** achieved ~1400 turnovers while **3a** achieved only ~600 turnovers.

Attempts to generate hydrogen using water as the solvent were not fruitful, possibly due to poor PS solubility.



Figure 4-12. **A**) H_2 evolution traces and corresponding Ir turnovers for **3a** (solid lines) and **3b** (dotted lines), using alcohols as solvents (0.1 mM photosensitizer, 30 μ M K₂PtCl₄ and 0.7 M TEA). **B**) Photosensitizer concentration study using EtOH and MeOH as solvents, using 30 μ M K₂PtCl₄ and 0.7 M TEA. Figure reprinted with permission from ref 1. Copyright The Royal Society of Chemistry 2016.

Using MeOH and EtOH as solvents, photosensitizer concentration studies were carried out to maximize the performance. The output is depicted by **Figure 4-12B** (above). An improvement in turnovers was observed for **3a** on employing lower concentrations in both alcohols. As noted previously, **3a** works better in MeOH, generating up to 2000 turnovers at low concentrations compared to 600 in EtOH. **3b**, on the other hand, does not show any major changes in performance on varying the concentration or solvent (lowest concentration in MeOH being the exception).

Due to the remarkable solvent stability demonstrated by both photosensitizers, and the trend that increasing solvent polarity increased maximum turnovers, additional water reduction photolysis studies were carried out in a variety of common household liquors (**Figure 4-13**). **3b** showed greater solvent tolerance to these ethanolic solutions, similar to previous tests in lab-grade ethanol solutions. While these studies did not show an increase in observed turnovers, they do serve to highlight the remarkable solvent tolerance and stability of these complexes to impurities expected in flavored beverages.



Figure 4-13. Ir photosensitizer turnovers obtained under standard conditions from kirsch (cherry brandy), moonshine (unaged brandy), single malt scotch (aged whiskey), and amaretto. All alcohols were 40% alcohol by volume. Data for figure obtained by Husain Kagalwala of the Bernhard Group.

4.3.5 Zinc Photoreduction Results

Due to the complexs' remarkable photostability and their high performance under a variety of conditions, the complexes were assessed as zinc reduction photocatalysts. Both **3a** and **3b** proved effective at zinc photoreduction catalysis, but failed to surpass $[Ir(ppy)_2(dtbbpy)]^+$, which remains the most successful photocatalyst for this reaction. The catalysts did perform better than previous nitrile-decorated complexes (**Table 4-3**), though no clear trend in maximum turnovers can be discerned from structural features.

Photocatalyst	<u>µmol Zn⁰</u>	<u>Ir TON</u> 352.2	
[Ir(ppy) ₂ (dtbbpy)] ^{+b}	387.5		
$[Ir(CNmppy)_2(dtbbpy)]^+$ 260.8		237.1	
[Ir(CNmppy) ₂ (dCNbpy)] ⁺	237.0	215.5	
[Ir(ppy) ₂ (dCNbpy)] ^{+b}	$(ppy)_2(dCNbpy)]^{+b}$ 253.8		
[Ir(Fmppy) ₂ (dCNbpy)] ^{+b}	169.4	154.0	

Table 4-3. Photoreduction catalysis turnovers for ZnCl₂ under standard conditions^a

^{*a*} Standard system comprised of 420 mg ZnCl₂, 1.1 umol Ir catalyst, and 1 mL TEA in 9 mL MeCN with 72 hrs illumination. ^{*b*} From ref 35.

4.4 Conclusions and Future Directions

In summary, herein is reported the use of a new cyclometalating ligand, CNmppy, for complexation with iridium. The inclusion of nitrile- instead of fluoro- moieties afforded diverse and impressive electrochemical and photophysical properties in the chromophores without the need for expensive or environmentally deleterious fluorinated materials. Using two different ancillary ligands resulted in the complexes displaying very different photophysical properties. 3a, with dtbbpy as the ancillary ligand, exhibits an unusually long lifetime ($\sim 8 \ \mu s$) and an impressive 63% luminescence quantum yield. **3b**, on the other hand, possesses a shorter-lived excited state; it exhibits however, a much longer lifetime than dCNbpy-bearing Ir(III) predecessors (120 ns vs 30-70 ns). The inclusion of the nitrile groups on the ppy greatly stabilizes the HOMO of both complexes and leads to rich electrochemistry as well as impressive photosensitization performance. Complex 3a in particular showed remarkable photosensitizing ability for water reduction with Pt colloids across a variety of solvents, achieving approximately 2000 turnovers under optimized conditions. Additionally, both complexes performed very well in alcohols, which can be used *in lieu* of acetonitrile or tetrahydrofuran as environmentally benign, inexpensive alternatives. Both complexes were competent zinc reduction photocatalysts, but could not surpass the current best-performing catalyst. Due to its particularly long lived excited state, **3a** was also much more sensitive than other $[Ir(ppy)_2(bpy)]^+$ complexes to oxygen luminescence quenching, and may be a suitable candidate for oxygen sensing applications.

Future work with these complexes would focus on enhancement of the excited state lifetimes *via* modification of the chelating ligand to enhance performance in oxygen

103

sensing and light emitting applications. Modification of the chelating ligand would also serve to build a library of complexes to gain better insight into structure-activity correlations in both photocatalytic and sensory applications. Additionally, future work would include enhancement of solvent tolerance during water reduction toward the goal of robust hydrogen evolution from water without a co-solvent.

References

- (1) Mills, I. N.; Kagalwala, H. N.; Bernhard, S. Dalt. Trans. 2016, 45, 10411–10419.
- Blakemore, J. D.; Schley, N. D.; Balcells, D.; Hull, J. F.; Olack, G. W.; Incarvito,
 C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H.; Gerhardt, I. C. J. Am. *Chem. Soc.* 2010, 132, 16017–16029.
- (3) Hetterscheid, D. G. H.; Reek, J. N. H. Chem. Commun. 2011, 47, 2712–2714.
- Hull, J. F.; Balcells, D.; Blakemore, J. D.; Incarvito, C. D.; Eisenstein, O.;
 Brudvig, G. W.; Crabtree, R. H. J. Am. Chem. Soc. 2009, 131, 8730–8731.
- (5) Mcdaniel, N. D.; Coughlin, F. J.; Tinker, L. L.; Bernhard, S. J. Am. Chem. Soc.
 2008, 130, 210–217.
- Petronilho, A.; Rahman, M.; Woods, J. a; Al-Sayyed, H.; Müller-Bunz, H.; Don MacElroy, J. M.; Bernhard, S.; Albrecht, M. *Dalt. Trans.* 2012, *41*, 13074–13080.
- Woods, J. a.; Lalrempuia, R.; Petronilho, A.; McDaniel, N. D.; Müller-Bunz, H.;
 Albrecht, M.; Bernhard, S. *Energy Environ. Sci.* 2014, *7*, 2316–2328.
- (8) Kaeffer, N.; Chavarot-Kerlidou, M.; Artero, V. Acc. Chem. Res. 2015, 48, 1286–
 1295.
- (9) Das, A.; Han, Z.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. ACS Catal.
 2015, 5, 1397–1406.
- (10) Khnayzer, R. S.; Thoi, V. S.; Nippe, M.; King, a. E.; Jurss, J. W.; El Roz, K. a.;
 Long, J. R.; Chang, C. J.; Castellano, F. N. *Energy Environ. Sci.* 2014, *7*, 1477–1488.

- Gärtner, F.; Boddien, A.; Barsch, E.; Fumino, K.; Losse, S.; Junge, H.; Hollmann,
 D.; Brückner, A.; Ludwig, R.; Beller, M. *Chem. Eur. J.* 2011, *17*, 6425–6436.
- (12) Wang, C.; Kathryn, E.; Lin, W. J. Am. Chem. Soc. 2012, 134, 7211–7214.
- (13) Kagalwala, H. N.; Gottlieb, E.; Li, G.; Li, T.; Jin, R.; Bernhard, S. *Inorg. Chem.* **2013**, *52*, 9094–9101.
- (14) Han, Z.; Qiu, F.; Eisenberg, R.; Holland, P. L.; Krauss, T. Science (80-.). 2012, 338, 1321–1325.
- (15) Whang, D. R.; Sakai, K.; Park, S. Y. Angew. Chemie 2013, 52, 11612–11615.
- (16) Esswein, A. J.; Veige, A. S.; Nocera, D. G. J. Am. Chem. Soc. 2005, 14, 16641–
 16651.
- (17) Heyduk, a F.; Nocera, D. G. Science (80-.). 2001, 293, 1639–1641.
- (18) Teets, T. S.; Nocera, D. G. Chem. Commun. 2011, 47, 9268–9274.
- (19) Yang, H.; Gabbaï, F. P. Nat. Chem. 2015, 7, 12–13.
- (20) Friedrich, A.; Schneider, S. ChemCatChem 2009, 1, 72–73.
- (21) Fujita, K.; Tanino, N.; Yamaguchi; Ryohei, Y. R. Org. Lett. 2007, 9, 109–111.
- (22) Kagalwala, H. N., Maurer, A. B., Mills, I. N., Bernhard, S. *ChemCatChem* 2014, 6, 3018–3026.
- (23) Kawahara, R.; Fujita, K.; Yamaguchi, R. J. Am. Chem. Soc. 2012, 134, 3643– 3646.
- (24) Kawahara, R.; Fujita, K.; Yamaguchi, R. Angew. Chemie 2012, 51, 12790–12794.

- (25) Zeng, G.; Sakaki, S.; Fujita, K.; Sano, H.; Yamaguchi, R. ACS Catal. 2014, 4, 1010–1020.
- (26) Musa, S.; Shaposhnikov, I.; Cohen, S.; Gelman, D. Angew. Chemie 2011, 50, 3533–3537.
- (27) Lowry, M. S.; Bernhard, S. Chem. Eur. J. 2006, 12, 7970–7977.
- (28) Ladouceur, S.; Swanick, K. N.; Gallagher-Duval, S.; Ding, Z.; Zysman-Colman, E. Eur. J. Inorg. Chem. 2013, 5329–5343.
- (29) DeAngelis, F.; Fantacci, S.; Evans, N.; Klein, C.; Zakeeruddin, S. M.; Moser, J.;
 Kalyanasundaram, K.; Bolink, H. J.; Gratzel, M.; Nazeeruddin, M. K. *Inorg. Chem.* 2007, 46, 5989–6001.
- (30) Nguyen, J. D.; Tucker, J. W.; Konieczynska, M. D.; Stephenson, C. R. J. J. Am.
 Chem. Soc. 2011, 133, 4160–4163.
- (31) Shih, H.; Wal, M. N. Vander; Grange, R. L.; Macmillan, D. W. C. J. Am. Chem. Soc. 2010, 132, 13600–13603.
- (32) Wallentin, C.; Nguyen, J. D.; Finkbeiner, P.; Stephenson, C. R. J. J. Am. Chem.
 Soc. 2012, 134, 8875–8884.
- (33) Kozhevnikov, V. N.; Zheng, Y.; Clough, M.; Al-attar, H. A.; Gri, G. C.; Abdullah,
 K.; Raisys, S.; Jankus, V.; Bryce, M. R.; Monkman, A. P. *Chem. Mater.* 2013, 25, 2352–2358.
- (34) Kang, Y.; Chang, Y.-L.; Lu, J.-S.; Ko, S.-B.; Rao, Y.; Varlan, M.; Lu, Z.-H.;
 Wang, S. J. Mater. Chem. C 2013, 1, 441–450.

- (35) Mills, I. N.; Kagalwala, H. N.; Chirdon, D. N.; Brooks, A. C.; Bernhard, S.
 Polyhedron 2014, 82, 104–108.
- (36) Mills, I. N.; Kagalwala, H. N.; Chirdon, D. N.; Brooks, A. C.; Bernhard, S. Polyhedron 2014, 82, 104–108.
- (37) Tinker, L. L.; McDaniel, N. D.; Curtin, P. N.; Smith, C. K.; Ireland, M. J.;
 Bernhard, S. *Chem. Eur. J.* 2007, *13*, 8726–8732.
- (38) Losse, S.; Görls, H.; Groarke, R.; Vos, J. G.; Rau, S. Eur. J. Inorg. Chem. 2008, 2008, 4448–4452.
- (39) Xie, H. Z.; Liu, M. W.; Wang, O. Y.; Zhang, X. H.; Lee, C. S.; Hung, L. S.; Lee, S. T.; Teng, P. F.; Kwong, H. L.; Zheng, H.; Che, C. M. *Adv. Mater.* 2001, *13*, 1245–1248.
- (40) Panne, P.; Fox, J. M. J. Am. Chem. Soc. 2007, 129, 22–23.
- (41) M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J. R. C.; G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. C.; X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M.; Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y.; Honda, O. Kitao, H. Nakai, T. Vreven, J.A.J. Montgomery, J.E. Peralta, F. O.; M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J.; Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M.; Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. A.; J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C.; Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G. A. V.;

P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J. B. F.; J.V.Ortiz, J. Cioslowski, D. J. F. GAUSSIAN 09, revision A.01, Gaussian Inc.,Wallingford, CT, 2009.

- (42) AMPAC 10 GUI, Semichem Inc., Shawnee Mission, KS, 2011.
- (43) Connelly, N. G.; Geiger, W. E. Chem. Rev. 1996, 96, 877–910.
- (44) Cline, E. D.; Adamson, S. E.; Bernhard, S. Inorg. Chem. 2008, 47, 10378–10388.
- (45) Brooks, A. C.; Basore, K.; Bernhard, S. Inorg. Chem. 2013, 52, 5794–5800.
- (46) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A.; Malliaras, G.
 G.; Bernhard, S.; V, C. U.; York, N.; June, R. V; Re, V.; Recei, M.; August, V. *Chem. Mater.* 2005, *17*, 5712–5719.
- (47) Goldsmith, J. I.; Hudson, W. R.; Lowry, M. S.; Anderson, T. H.; Bernhard, S. J.
 Am. Chem. Soc. 2005, *127*, 7502–7510.
- (48) Fantacci, S.; Angelis, F. De; Wang, J.; Bernhard, S.; Selloni, A.; Chimica, D.; Uni,
 V.; Elce, V. J. Am. Chem. Soc. 2004, 126, 9715–9723.
- (49) Chirdon, D. N.; Mccusker, C. E.; Castellano, F. N.; Bernhard, S. *Inorg. Chem.* **2013**, *52*, 8795–8804.
- (50) Caspar, J. V; Meyer, T. J. J. Am. Chem. Soc. 1983, 105, 5583–5590.
- (51) Jenkins, D. M.; Bernhard, S. Inorg. Chem. 2010, 49, 11297–11308.
- (52) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*;3rd edition; CRC Publishing, 2006.