

The Photon Driven Reduction of Zn(II) to Zinc Metal by Transition Metal Complexes

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Abstract

The photon driven reduction of Zn(II) to zinc metal is a novel field of study with many potential applications including the use of zinc metal as a solar fuel. Although it has not been widely considered for such a role in the past, zinc is an appealing means to store solar energy as a stable fuel without the safety risks of hydrogen gas. As a solar fuel, zinc metal would be used in efficient zinc air batteries and then regenerated by the photocatalytic reduction of Zn(II) and a concurrent oxidation reaction.

In this vein, this work reports the photocatalytic reduction of Zn(II) to zinc metal using visible light. Heteroleptic bis-cyclometallated iridium complexes and zinc quinolates that form in situ are found to be effective photocatalysts. Zinc generating photoreactions are conducted on a custom-designed home-built photoreactor, with triethylamine (TEA) employed as the sacrificial reductant. Photocatalyst structure–activity relationships, ideal reaction conditions, and reaction kinetics are described for the iridium catalyzed reaction. Cyclic voltammetry of zinc salts is used to supplement the investigation of the Zn(II) reduction mechanism. A maximum of 430 catalyst turnovers is reported.

Similar experiments are performed in order to characterize the zinc quinolate catalyzed reduction of Zn(II) and confirm aspects of the reaction mechanism. Additionally, fluorescence quenching and ^1H NMR titration experiments are employed to identify the zinc quinolate that forms in situ from 5,7-dichloro-8-hydroxyquinoline. Subsequently, ligands with extended conjugated pi systems relative to 8-hydroxyquinoline are synthesized and their photocatalytic activity is assessed. Second

generation iridium photocatalysts with bridging nitrile functionalities are also synthesized and evaluated in an attempt to improve catalytic activity.

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Chapter 1. Merits of and Approaches to Photocatalyzed Zn(II) Reduction

Importance and Means of Metal Ion Reduction

Almost all commonly used metals such as iron, aluminum, and zinc are currently acquired through the mining of metal ores or the recycling of metals whose ores were originally mined. This is done because these elements overwhelmingly exist in the earth's crust as cationic ores, typically oxides or sulfides. However the utility of metals is in their neutral atomic state, so the reduction of metal ores is an important, large-scale industrial process.

Industrially, metal cations are reduced by smelting, which employs either chemical or electrical energy to drive these endothermic reactions. Iron is produced by traditional chemical smelting. In this process metal oxide ores and coke, a coal derivative, are heated in a blast furnace under partially oxygenated conditions to yield reduced metal and CO₂. This partial combustion produces poisonous carbon monoxide as an intermediate reducing agent. Chemical smelting also has all of the deleterious environmental effects traditionally associated with burning coal. Aluminum is produced by direct electrolytic smelting. This process is not only energy intensive but also produces large quantities of fluoride waste due to degradation of the Na₃AlF₆ electrolyte employed.¹ Zinc ores are commonly sulfides, so similar electrical and chemical reduction processes are applied after the roasting of zinc ore to produce ZnO and sulfuric acid.

Perhaps due to these established electrolytic and chemical metal ion reduction methods, photocatalyzed metal ion reduction has been investigated only sparingly. While

there are many intricacies in the design of effective photocatalysts, the overall chemistry of photocatalytic metal ion reduction is quite simple. The generation of neutral metal would require only a photocatalyst, a metal cation source, and an electron source capable of reducing either the excited or oxidized photocatalyst. Such a schematic for metal ion photoreduction would have several applications, including in areas in which traditional smelting processes are not applicable. One value-added, smaller scale application of photocatalyzed metal ion reduction is as a coatings method, which could potentially stimulate its initial development. Another application is the use of photoreduced metals, particularly zinc, as solar fuels. Energy dense metals such as zinc also find uses as a reducing agent in the cross coupling of aryl and alkyl halides.²⁻⁴ These applications validate the pursuit of photocatalyzed metal ion reduction and merit further discussion, particularly solar fuels.

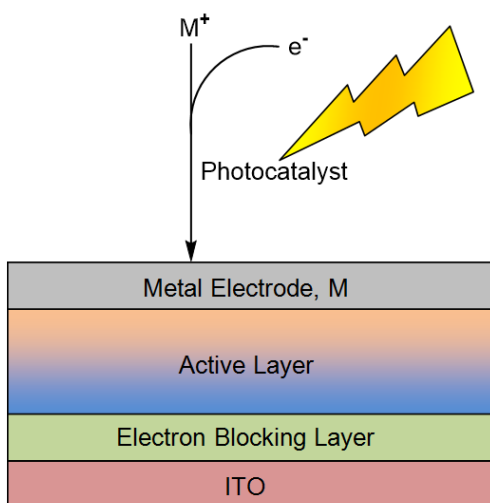


Figure 1-1 – Proposed fabrication of OPV electrodes by photocatalyzed metal ion reduction.

Whereas the large scale and low cost of traditional smelting prevent its immediate replacement, metal ion photoreduction could be successfully applied to coatings in the short term. The photo-reductive deposition of low work function metals could reasonably

be a viable alternative to current coatings methods, particularly in the fabrication of electrodes for photovoltaic (PV) cells. Strong incentives exist to pursue this technique for electrode fabrication because the electrode contact is pivotal to the overall performance of PV cells. An alternate method of electrode fabrication could potentially achieve superior electrode integrity, morphology, or contact quality and substantially improve device performance, which would be very lucrative. Relatively poor photocatalyst activities and yields could thus be tolerated, making electrode deposition a suitable method for the initial development of photocatalyzed metal ion reduction. A basic depiction of electrode fabrication by photocatalyzed metal ion reduction is shown in Figure 1-1.

Bulk heterojunction organic photovoltaic devices (OPVs) representatively illustrate the importance of electrodes to device function. In these devices a low work function metal such as Ca or Al is used as the cathodic material. The nature of the contact between the cathode and the photoactive layer is extremely important to achieving charge separation and avoiding recombination.⁵ Charge recombination is a chief cause of inefficiency and low quantum yields in OPVs and is largely responsible for preventing the commercial viability of these devices thus far. For an OPV to function ideally, the metal electrode should form an ohmic contact with electron transporting material and a rectifying contact with the hole transporting material.^{6,7} In achieving this, an interface dipole forms, thus pinning the work function of the metal electrode to the Fermi level of the n type semiconductor. This facilitates charge separation by electron transfer to the electrode, while the rectifying contact between the p type semiconductor and the metal electrode prevents recombination.

The current method of electrode fabrication by metal vapor deposition is not without its flaws. The vaporization of the metal requires high heat and low pressures, frequently below 10^{-6} mbar. This renders metal vapor deposition an energy intensive and expensive process. Additionally, the technique is limited to small scales. Excluding free and abundant light energy, electrode deposition via photocatalyzed metal ion reduction would be less energy intensive and could potentially allow for greater control over the electrode fabrication process. Morphology and other important characteristics of the deposited electrode could be manipulated through the use of nucleation sites and by varying a wealth of parameters such as catalyst concentration, metal ion concentration, etc. Photocatalyzed metal ion reduction could thus replace metal vapor deposition to produce lower cost, higher performance photovoltaic devices.

Metal Ion Photoreduction for Solar Fuel Synthesis

On a larger scale, the synthesis of solar fuels represents another appealing use of metal ion photoreduction. It is necessary to develop renewable energy technology because current human energy usage is unsustainable. As the global population and its standard of living rises, energy consumption is expected to increase from already high levels, as Figure 1-2 illustrates. In the United States, 71% of electricity generated and almost all the energy used in vehicular transport and heating is derived from fossil fuel combustion.⁸

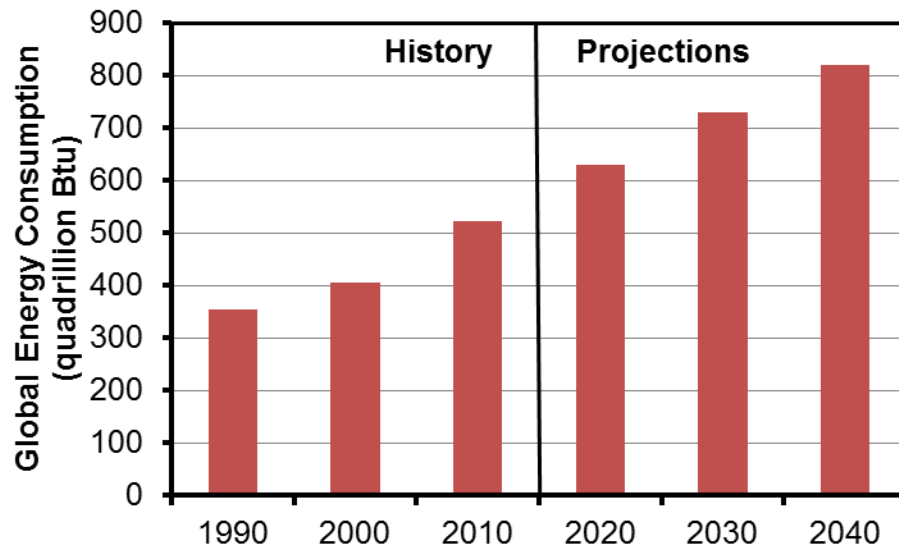


Figure 1-2 – Historical and projected global energy consumption⁸

This high use of fossil fuels is unsustainable in the face of rising energy consumption because of limited supply, geopolitics, and its many hazardous environmental effects. Chief among these effects is the strong correlation between the rise in global temperature and the output of CO₂ and other gases from the combustion of fossil fuels.⁹ This correlation is thought to be a result of the greenhouse effect, in which these gases insulate the atmosphere by trapping solar radiation that would otherwise escape back into space. It is anticipated that global warming will have negative consequences such as a rise in sea levels and decreased agricultural production. An alternative to fossil fuels is thus necessary.

Solar fuels are appealing in both aspects of their identity, as a solar energy source and as a fuel. The utilization of sunlight is advantageous primarily due to its abundance. Solar energy is the only alternative renewable energy source large enough to viably replace fossil fuels on the scale of its current use. Using 7 Wh/m²/day and 20% as realistic assumptions for solar radiation intensity and PV cell efficiency respectively,

~21,600 mi² of PV cells would be required to supply all the energy consumed in the US on a per year basis. As a frame of reference, the Mojave Desert is over 47,800 mi². While this is obviously a large area, similar achievements would be impossible using wind or hydroelectric energy, and current photovoltaic technology is improving.

However it would be prudent to convert at least some solar energy to fuel instead of directly to electricity. Electricity represents only 40.5% of current energy consumption in the US; fuels are often used directly for heating or transportation.⁸ The direct production of solar fuels would more readily facilitate the replacement of fossil fuels in these areas. Transportation stands out as a possible application of solar fuels due to the currently limited drive range and popularity of electric cars. Additionally, electricity markets such as Germany's that rely heavily on photovoltaic power are subject to undesirable seasonal and diurnal price fluctuations. Generation often fails to coincide with demand, which leads to spikes in price during periods of weak solar irradiation but high electricity consumption. Solar fuels would remedy this; they can be generated during the day and easily stored for night or off site use.

The use of metals as a solar fuel would require employing light energy to drive the endothermic splitting of metal oxides to the neutral metal and O₂. Metal oxide splitting is a reversal of the discharge cycle of metal air batteries, in which metals are oxidized as fuel. The photo-regenerated metal would then be used to manually recharge the battery in a closed loop system. In such a way, metals such as zinc could serve as a renewable solar fuel, a promising CO₂ neutral energy source. The light driven splitting of water to produce H₂ (and O₂) for use as a solar fuel is a similar scheme currently under much investigation. One can easily envision a renewable zinc economy similar to a H₂

economy. Zinc would be consumed in vehicles as fuel through oxidation in a zinc-air battery. These vehicles will refuel by exchanging cassettes from their car battery full of spent zinc oxide with fresh cassettes of powderized zinc metal. Current gasoline stations could be easily outfitted to sell, stock, and receive large shipments of zinc fuel. At a sunnier or otherwise more desirable separate location, zinc metal would then be regenerated by the photocatalytic splitting of ZnO. While other zinc salts such as ZnS are more abundant, ZnO splitting is most desirable because ZnO is produced as spent fuel in the battery. The initial production of zinc metal will require roasting ZnS to produce ZnO, or the direct reduction of ZnS. Figure 1-3 illustrates the basics of this zinc economy.

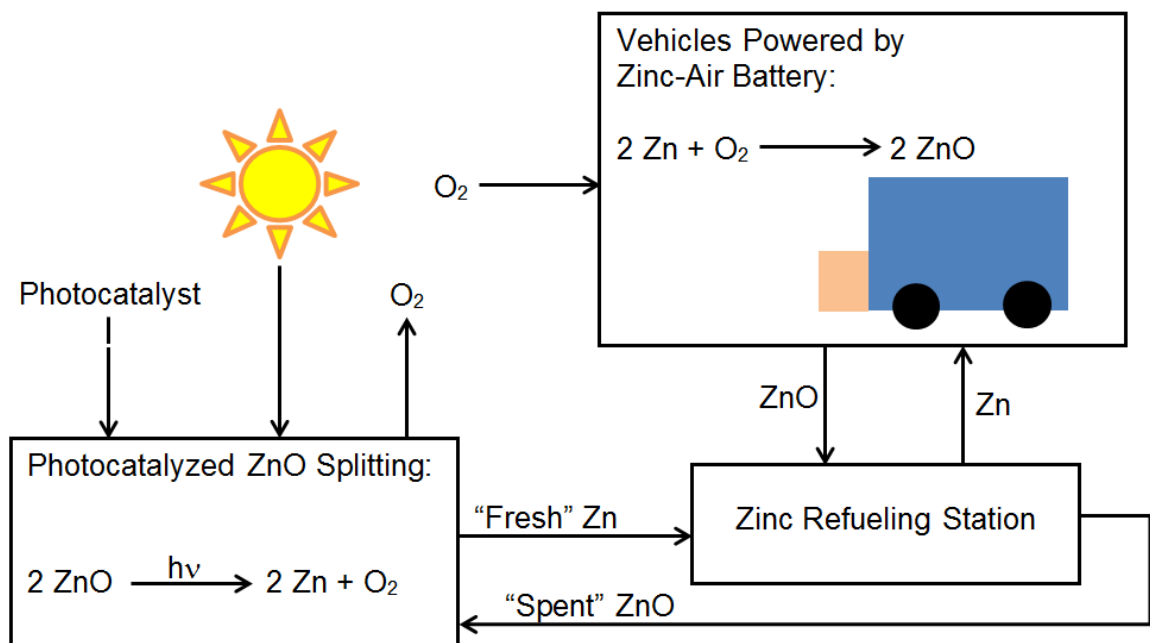
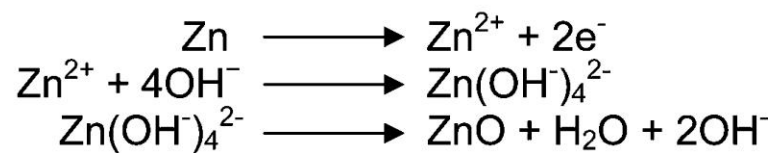


Figure 1-3 – Proposed zinc economy. ZnO is split photocatalytically to regenerate zinc metal used as fuel in vehicles.

The success of a zinc economy heavily rests on the virtues of the zinc air battery, particularly for vehicular use. The zinc air battery efficiently oxidizes zinc metal and reduces oxygen from the air concurrently at opposite electrodes, generating electrical

power and zinc oxide as a spent fuel product. Basic electrolytes such as KOH are primarily used. Unlike other conventional batteries the oxidant does not require storage; O₂ can be reduced directly from ambient air. Figure 1-4 shows the chemistry of the zinc air battery. Zinc air batteries show power densities as high as 265 mW/cm,¹⁰ which ensures that zinc powered vehicles will accelerate adequately. Zinc air batteries are also simple and lightweight. A charged zinc air battery has an energy density of 1.08 Wh/kg, which is 5 times higher than the energy densities of lithium ion batteries currently used in electric vehicles.^{11,12} This translates into longer driving ranges; which is important because short driving radii is a major barrier to the use of electric vehicles. Preliminary tests on vehicles powered by zinc air batteries have demonstrated driving ranges of 400-600 km between manual rechargings.¹³

Anode:



Cathode:



Overall reaction ($E^0 = 1.65 \text{ V}$):

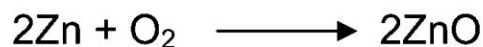


Figure 1-4 – Chemistry of the zinc air battery

Of course, batteries of this quality could also be used for centralized electricity generation, but zinc air batteries are most economically viable in small scale vehicular applications. Due to a smaller scale, the internal combustion engines of cars are less efficient than electricity generation for the grid through fossil fuel combustion. The efficiency of a zinc air battery does not suffer at lower scales, so photoreduced zinc metal

would be more competitive as a vehicular fuel than as a fuel for centralized electricity generation.

It is fitting that the proposed zinc economy requires manual battery recharging, because electrolytic recharging is a major pitfall of the zinc air battery. Problematic, inefficient electrolytic recharging has hindered the widespread commercial success of zinc air batteries to date. During electrolytic recharging, zinc dendrites can form at the anode, which can breach the electrolyte membrane and short circuit the battery.^{14,15} To limit dendrite formation, alternative non-aqueous electrolytes such as ionic liquids have been investigated.¹⁶ Furthermore, high overpotentials in the electrolytic recharging of zinc air batteries have limited the overall efficiency of the combined charge/discharge cycle to 65% or lower.¹⁰ This has prompted much research into the development of efficient bifunctional electrodes, particularly for the air cathode, where the highest overpotentials exist.¹⁷ The proposed manual recharging of zinc air batteries with photoreduced zinc metal is thus immensely advantageous because zinc dendrite formation and high overpotentials of electrolytic battery recharging could be circumvented.

While photon driven water splitting has been extensively researched and other metal air batteries exist, zinc has a few advantages over H₂ and other metals as a solar fuel. Solid state metals have simplified storage compared to the gas tanks required for H₂ storage. This renders metals more appropriate for use in vehicles. The omission of gas tanks by using a solid fuel eliminates concerning safety issues associated with placing a flammable pressurized gas on vehicles that are prone to crashes. The requisite gas tank also significantly affects the practical energy density of H₂. Consider lithium, aluminum,

and zinc; all three have highly efficient metal-air batteries and are therefore plausible solar fuels. When the mass of a typical 700 bar H₂ gas tank developed for vehicular use is considered,¹⁸ the energy densities of all three metals are comparable to H₂, as Table 1-1 illustrates. Among metals, zinc is the best solar fuel candidate. While lithium is remarkably energy dense, it is also unstable in air and water reactive. Aluminum also has superior energy density to zinc but the photocatalyzed reduction of Al(III) would be a complicated three electron process with multiple intermediates. Al(II) and Al(I) are uncommon oxidation states of aluminum and would likely be unstable intermediates. On the other hand, zinc metal is more stable than lithium and has only one intermediate, Zn(I), in its reduction from Zn(II). Additionally, zinc is abundant and inexpensive; reagent grade zinc is cheaper than both lithium and aluminum.

Fuel	Generation	$E_{\text{red}}, M^{n+}/M$, V vs SHE	Reduction Process, M^{n+}/M # e ⁻	Energy Density, kWh/kg
H ₂	$2 \text{ H}_2\text{O} \longrightarrow 2 \text{ H}_2 + \text{O}_2$	0	2	1.89
Zn	$2 \text{ ZnO} \longrightarrow 2 \text{ Zn} + \text{O}_2$	-0.76	2	1.35
Al	$2 \text{ Al}_2\text{O}_3 \longrightarrow 4 \text{ Al} + 3 \text{ O}_2$	-1.66	3	8.04
Li	$2 \text{ Li}_2\text{O} \longrightarrow 4 \text{ Li} + \text{O}_2$	-3.05	1	11.23

Table 1-1 – Properties of potential solar fuels. Energy density is defined as the theoretical energy derived from oxidation of the fuel (with O₂) by mass.

Further thermodynamic considerations of zinc electrochemistry reinforce that zinc metal is the preferred metallic solar fuel. Zinc metal has the close to ideal balance between energy density and feasibility of wide scale, efficient synthesis. This is not the case for lithium and aluminum. While it is clear from Table 1-1 that lithium and aluminum are much more energy dense than zinc, the photosynthesis of each under sunlight would result in much lower solar conversion efficiencies. The energy density of

a fuel rises as the potential difference between the redox couples of the reductant or fuel (eg. Al/Al^{3+} or Zn/Zn^{2+}) and the oxidant (almost always O_2/O^{2-}) increases. This potential difference not only represents the theoretical open circuit discharge voltage of the respective battery, but also the endothermic energy required to regenerate the fuel and O_2 from its metal oxide. As such, the energy dense Al and Li require lower wavelength, higher energy light than Zn to be generated by photocatalytic reduction. The photocatalytic reduction of Zn(II) to zinc metal can thus utilize a larger fraction of the solar spectrum. The capacity to more solar energy in the reduction of Zn(II) gives zinc a higher theoretical maximum solar conversion efficiency than Al and Li while maintaining a reasonable energy density. This interplay between energy density and solar conversion efficiency assumes that one incident photon excites a chromophore to a vibrationally relaxed excited state, which then catalyzes the transfer of one electron from the reduced oxygen species to the metal cation. Some areas of research, such as triplet triplet upconversion, seek to bypass this requisite but the most efficient photocatalysts to date have not successfully applied such techniques.¹⁹

Photon Driven Metal Ion Reduction to Date

Photosynthesis of Metal Nanoparticles

Past research in metal ion photoreduction has not concerned zinc or other energy dense metals for solar fuels applications. The bulk production of metals is largely not the goal of these endeavors; instead the aim is often the synthesis of metal nanoparticles. Metal nanoparticles have many potential applications in catalysis and medicine due to their durability, nontoxicity, and photophysical properties.²⁰ Localized surface plasmon

resonance (LSPR) occurs on silver, gold, iridium, platinum, palladium, and other transition metal nanoparticles due to the oscillation of free electrons upon the incidence of electromagnetic radiation at a resonant frequency.²¹ As a result of this resonance, strong electric fields are generated on the metal surface. Furthermore, the optical cross section of metal nanoparticles at their LSPR frequency is extremely high, on the order of 10^5 times higher than the absorption cross section of organic dyes.²² In medicine, the surface modification of metal nanoparticles with antibodies or other relevant biomolecules causes the metal nanoparticle to bind to specific cell surface receptors. The heat released upon nonradiative decay of the resonant plasmon has been found to be ablative to cancer cells and is a promising non-invasive, highly targeted, photo-thermal cancer therapy.²³

Metal nanoparticles and particularly metal-semiconductor nanocomposites also demonstrate abilities as bifunctional catalysts in redox reactions.^{24–26} Inorganic semiconductors such as TiO_2 and perovskites are most commonly used. The electric fields generated from the LSPR on the metal domain of these nanocomposite photocatalysts facilitate charge separation and higher photocurrents than for free semiconductor systems.^{27,28} The Schottky contact between the metal and semiconductor facilitates electron transfer to the metal and limits recombination at semiconductor surface defect sites.²⁹ In addition, LSPR in such nanocomposites has been shown to promote an increase of localized charge carriers within the exciton diffusion length of the semiconductor-metal interface.³⁰ As a result of these phenomena, metal-semiconductor nanocomposites have proven effective catalysts for many reactions including dye degradation and solar fuels generation.^{30–33}

Given their remarkable properties and applications, several approaches to the synthesis of metal nanoparticles have been investigated, including photocatalyzed metal ion reduction. The photocatalyzed approach has many advantages compared to direct chemical reduction. The photoreductive approach is tolerant to a variety of mediums. This tolerance permits the use of templates for metal nanoparticle synthesis such as polymer matrices, colloids, glasses, and zeolites, and biological cells.³⁴ Photocatalyzed metal ion reduction is also conducive to the site selective deposition of metal ions to achieve otherwise unattainable architectures. For instance, Pt and Pd deposition onto CdS_{0.4}Se_{0.6} can selectively be achieved on sulfur or selenium rich portions of the semiconductor through the use of different excitation wavelengths.³⁵ Photocatalytic metals deposition method also allows for fine control over particle size by manipulation of illumination time.³⁶ Such control is critical because the resonant frequency of the surface plasmon varies with the size of the metal nanoparticle.

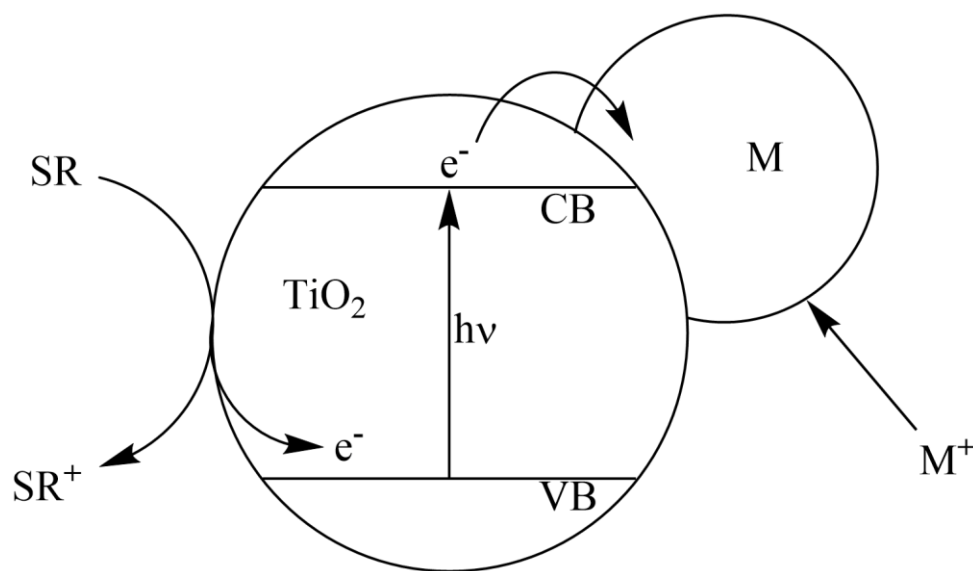


Figure 1-5 – Synthesis of metal- TiO_2 nanocomposites by the photocatalyzed reductive deposition of metal ions. SR = Sacrificial Reductant, VB = Valence Band, CB = Conduction Band, M = Metal.

The basic mechanism for the photocatalytic synthesis of semiconductor nanocomposites is straightforward. A large band gap semiconducting nanoparticle, an electron source, and the desired metal ion are the three requisite reagents. UV light is used because visible light is insufficient to excite the unmodified semiconductor nanoparticle. Most research in this area has employed TiO_2 and silver, although other second and third row noble transition metal ions and semiconductors have been used as well.^{27,34,37} In these reactions, electrons excited to the conduction band of TiO_2 ($E_0 = -0.5$ V vs SHE @ pH = 7, -0.63 V @ pH = 8)³⁷ reduce metal ions in solution, as shown in Figure 1-5. The reduced metal adheres to the TiO_2 surface and serves as a nucleation site for further metal ion reduction. The resulting holes in the TiO_2 valence band are filled by electrons generated from the oxidation of the sacrificial reductant. While many sacrificial reductants can be used in this role, solvents such as ethanol and octane are frequently employed.^{29,37,38} The strongly exergonic oxidation of these solvents and their high concentrations ensures that holes on the semiconductor are short lived and recombination is minimal. Isolated metal nanoparticles are synthesized in a very similar manner, but organic chromophores can be substituted for semiconducting nanoparticle.^{38,34}

Wastewater Treatment by Metal Ion Photoreduction

Similar to the synthesis of metal nanoparticles, the purification of metal-contaminated wastewater can be accomplished by photocatalyzed metal ion reduction. Metal ions often contaminate wastewater streams as the result of various industrial processes such as electroplating, photography, and the manufacturing and/or use of pesticides, batteries, and paints. Polluting metal ions that have been targeted for removal include Ag(I) , Pb(II) , Cd(II) , Hg(II) , Cu(II) , Ni(II) , Cr(IV) , and Zn(II) .^{39,40} Methods used

to remove metal ions from wastewater streams include photocatalytic reduction, adsorption, chemical precipitation and electrodeposition.⁴¹ The photocatalytic method of metal ion removal from wastewater occurs by a very similar mechanism as photocatalytic metal nanoparticle synthesis. Semiconductor photocatalysts such as TiO₂, ZnO, ZrO₂, CdS, MoS₂, Fe₂O₃, and WO₃, reduce metal ions, precipitating them out of solution.⁴² UV light is primarily used, although the use of sunlight concentrated by parabolic reflectors has also been successful.⁴⁰ Sacrificial reductants include formate, oxalate, EDTA, salicylic acid, methanol, nitrophenol and citric acid.^{42,39} However sacrificial reductants are undesirable for wastewater treatment as they essentially amount to another pollutant in the wastewater stream. As a result, photocatalyzed metal ion reduction has recently fallen out of favor in wastewater treatment research.

Photocatalyzed Zinc(II) Reduction in the Literature

While extremely limited, there are some reported cases of photocatalyzed zinc(II) reduction. All were in low yields and none successfully utilized visible light. For example, Stroyuk et. al. observed a hypsochromal shift in the absorption edge of ZnO nanoparticles from 365 to 354 nm and a color change of the mixture from white to grey-brown after illumination under UV light.⁴³ An inert atmosphere was required in addition to ethanol or isopropanol as the sacrificial electron source. They attributed the observed hypsochromal shift to the reduction of ZnO along the edge of the semiconductor, although the product was never definitively determined to be zinc metal. Additionally, this reaction proved reversible upon air exposure.

Kabra et. al. observed the photocatalyzed reduction of Zn(II) along with Cu(II), Ni(II), and Pb(II) to their metallic states.⁴⁰ The photocatalyst and sacrificial reductant used were TiO₂ and citric acid respectively. Out of these metals, yields of Zn were the lowest with only 22% conversion, compared to 36% for Ni, 41% for Pb, and 97% for Cu. These yields were consistent with basic thermodynamic predictions that the metal with the most negative reduction potential would be the most difficult to reduce and have the lowest conversion. However the authors noted that the reduction potential of Zn(II) is actually more negative than the conduction band of TiO₂ used (-0.76 eV vs -0.3 eV). Given this, an organic radical was instead assumed to be the reducing species.⁴⁴ A similar work by Chenthamarakshan et. al. investigated the reduction of Zn(II) and Cd(II) by TiO₂.⁴⁵ Again, UV light was used and ethanol was sacrificially oxidized. In this work the cathodic deposition of ZnO was observed in competition Zn(II) reduction, which would be detrimental to solar fuel synthesis. Also they observed that EDTA could be substituted as the sacrificial reductant for the reduction of Cd(II) but not Zn(II). This reaffirmed the role of an organic radical as the true reducing species in these experiments.

The Incompatibility of Previous Metal Ion Photoreduction with Solar Fuels

A few common themes can be found in recent literature concerning the photocatalyzed reduction of metal ions for wastewater treatment and metal nanoparticle synthesis:

1. UV Light source
2. Large band gap semiconductor catalysts, commonly TiO₂
3. Adherence of metals to the semiconductor surface

4. Reduction of more noble metal ions than Zn

These trends in the recent literature are incompatible with the photoreduction of Zn(II) for solar fuels because they prohibit the large scale production of zinc metal at high yields and high conversion efficiencies. The adherence of deposited metals to the catalyst surface prevents high yields of metal. In a solar fuel production scheme, yields of zinc would be limited because metal accumulating on the photocatalyst would block light absorption. The reverse oxidation of photoreduced metal has also been observed on the surface of colloidal semiconductor catalyst, which would limit yields in a solar fuel scheme.⁴⁶ Such reoxidation would surely occur in photocatalyzed Zn(II) reduction given the low work function of zinc relative to previous metals generated by photoreduction.

Another drawback is that the previous use of high band gap semiconductors and exclusively UV radiation would severely limit solar conversion efficiency in solar fuels generation. 42% of the energy in the solar spectrum originates from visible radiation while less than 3% originates from UV light. The failure to absorb visible light therefore limits any solar fuels scheme to less than 3% solar conversion efficiency. Failure to absorb and convert visible photons would drastically lower the overall solar conversion efficiencies of a solar fuels system. It would thus be economically prohibitive to employ high band gap semiconductors that do not absorb in the visible region as photocatalysts for solar fuel generation.

In response to such a deficiency, surface modification of TiO₂ is one commonly used approach to red-shift the onset of absorption in an effort to utilize visible light for the production of solar fuels. A variety of chromophores including azo dyes, phthalocyanines, and ruthenium complexes have been used to modify TiO₂ based

photocatalysts, in an approach is similar to that employed in dye sensitized solar cells (DSSCs).^{32,29,47–49} While such surface modification successfully increases the visible absorption of TiO₂, the lifetime of these catalysts is limited by higher rates of decay of the modifying organic dye or transition metal complex.⁵⁰ These shorter catalyst lifetimes undercut durability, which was a significant purported advantage of TiO₂ photocatalysts.

Alternatively, doping of TiO₂ with other materials such as Cu, Y, NH₃, and I⁻ has been successfully utilized to decrease the band gap of TiO₂.³² For example, ammonia doped TiO₂ (N-TiO₂) absorbs blue-green photons up to 500 nm, a substantial redshift of TiO₂.³⁰ However, these doping methods inherently incorporate defects into the semiconductor lattice, which lowers the internal quantum conversion efficiency of these systems. Photocorrosion, a process in which the dopant leaches out of the TiO₂ crystal lattice after repeated excitation, is also an issue.^{51,52} Metal-semiconductor nanocomposites with LSPR induced visible absorption, which were discussed earlier, represent the most promising avenue to visible light driven solar fuels synthesis by colloidal semiconductor photocatalysts.

Previous instances of photocatalyzed metal ion reduction are poor models for the generation of zinc as a solar fuel also because of the particular metal ions targeted. These metal ions, such as Ag(I), Au(I), Pt(II), Cd(II), Cu(II), and Pb(II), all have more positive reduction potentials than Zn(II) ($E_{\text{red}} = -0.76$ V vs SHE). Using the same light source and catalyst, it is substantially easier to photocatalytically reduce these metal ions than Zn(II) due to greater thermodynamic losses. Such heat losses could not be tolerated in the photocatalytic reduction of Zn(II) for use as a solar fuel because high conversion efficiencies are required. Since there is literature precedent only for metal ion

photoreduction with significant thermodynamic losses, it is uncertain whether the same photocatalysts would be capable of reducing Zn(II). It is often necessary to judiciously tailor the orbital energies of photocatalysts in order to achieve high catalytic activity photocatalysts and low heat losses. It would be more prudent to target photocatalysts that can meet these thermodynamic requirements instead of using those that are simply proven to reduce metal ions in much more strongly exothermic reactions.

Current Approaches to Solar Fuels Photosynthesis

Solar fuels represent a better model from which to approach the visible light driven photocatalyzed reduction of Zn(II). Approaches to solar fuels production have been optimized for maximum yields and high catalytic rates. Solar fuels catalysts operate with minimum heat losses in order to maximize solar conversion efficiency. These considerations are largely ignored in previous work on the photocatalyzed reduction of metal ions yet would be crucial for the large scale, visible-photon driven reduction of Zn(II). The approaches taken to generate solar fuels include: biological, electrolytic, semiconductors, and molecular catalysts.

The biological method for solar fuels generation utilizes the metabolism of microorganisms or plants to produce a variety of fuels popularly known as biofuels. The production of biofuels can be accomplished by a few different means. Microorganisms can be metabolically engineered to excrete high energy compounds. Microbes employed in this process must either be photosynthetic (e.g. algae) or fed plant matter if non-photosynthetic (e.g. yeast). Some of these high energy compounds such as EtOH and H₂ can be used directly as fuel, whereas fatty acids must be esterified to form biodiesel.^{53,54}

Alternatively, plants can be harvested and processed directly into fuels. Biofuels are promising because they employ the enzymes of natural photosynthesis to achieve higher charge separation quantum yields than are currently achieved by man-made systems. Still there are drawbacks to biofuels. Yields of excreted fuels or fuel precursors are often limited due to their toxicity towards the microorganism that produces them.⁵⁵⁻⁵⁷ Additionally it is irresponsible to use arable land for the explicit cultivation of biofuel stock considering the growing global food shortage.

One artificial approach to solar fuel generation is by photoelectrochemical cells (PECs). For water splitting PECs such as Nocera's 'artificial leaf,' this approach essentially amounts to powering an electrolyzer by a photovoltaic cell.⁵⁸ PECs differ from photovoltaic cells in that their electrodes do not connect a circuit to drive an external load but are instead modified with catalysts for water splitting. The photocurrent generated drives water reduction at the cathode and water oxidation at the anode. Often, external circuitry exists between the cathode and the photoactive materials so the anode is referred to as a photoanode or photoelectrode.^{59,60} Such photoanodes often consist of TiO_2 or GaN sensitized by a dye or WOC.^{61,62} A basic PEC is depicted in Figure 1-6. In order to generate methanol, carbon monoxide, formaldehyde, or methane, the appropriate CO_2 reduction catalyst is employed at the cathode instead of a WRC.

The electrolytic generation of solar fuels is advantageous because interested researchers can divert most of their attention to development of the electrodes and catalytic materials themselves. Charge separation and photocurrent generation, which are significant issues in solar energy research, is effectively outsourced to the larger photovoltaic research community. There are multiple approaches to PV energy currently

under research: DSSCs, bulk heterojunction PVs, thin film PVs utilizing doped semiconductors other than Si, notably CdTe, as well as traditional silicon PVs, which are still targeted for improvement.

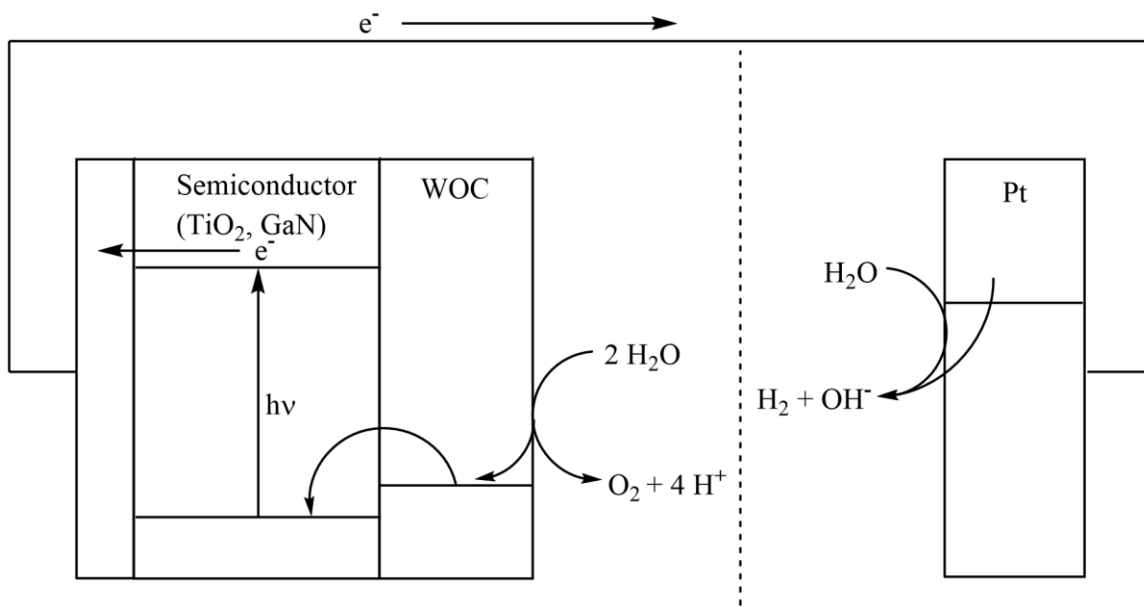


Figure 1-6 – Set-up of a typical PEC. Water reduction at the platinum cathode and water oxidation at the photoanode are separated by a nafion membrane.

Semiconductors such as TiO_2 , ZnO , SrTiO_3 , CeO_2 , WO_3 , Fe_2O_3 , GaN , Bi_2S_3 , CdS and ZnS have also been investigated as potential colloidal photocatalysts for solar fuel generation.⁶³ These completely inorganic materials are inexpensive and durable. Prominent examples of these successful photocatalysts include anatase TiO_2 and ABO_3 perovskites such as bismuthates and ferrites.^{33,64,65} High catalytic activities have been achieved through the fine control of particle size and polymorph.^{66–68} However in the absence of surface modifications or doping, the photophysical properties of such semiconductors can only be tuned over a limited range. The advantages and disadvantages of these materials were discussed earlier in the context of photocatalyzed metal ion reduction, so their merits will not be discussed at any further length here. To

recap, durability is a significant advantage of such a system while poor visible light absorption is a drawback.

In another approach, organic dyes and metal complexes can be used as molecular catalysts and photosensitizers (PSs) for solar fuels production.

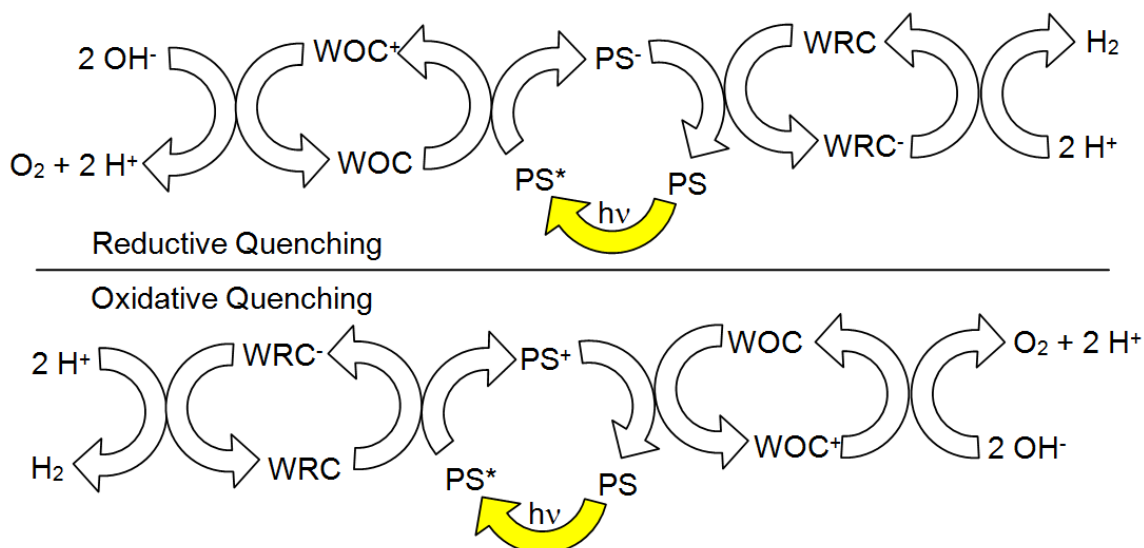


Figure 1-7 - Flow diagrams of photocatalyzed water splitting via both oxidative and reductive quenching mechanisms. WRC = Water Reduction Catalyst. WOC = Water Oxidation Catalyst. PS = Photosensitizer.

Molecular catalytic systems for solar fuels generation rely on successive electron transfers reactions between the PS and the oxidation and reduction catalysts (OC, RC). Initially the photosensitizer is both electronically and vibrationally excited by incident light but quickly relaxes into its lowest energy excited state. Subsequently the excited PS is either oxidatively quenched by the RC or reductively quenched by the OC. If PS^* was oxidatively quenched, PS^+ is then reduced by the OC to regenerate the initial ground state PS. In the case of reductive quenching, PS^- is oxidized by the RC to regenerate the ground state PS. Whether reductive or oxidative quenching occurs is dictated by the electron transfer rates and the relative stabilities of PS^* , PS^+ and PS^- .⁶⁹ Experimentally, electron transfer rates are measured by fluorescence quenching or transient absorption

spectroscopy. Photosensitizer stability in each oxidation state can be determined electrochemically, often by cyclic voltammetry. Multiple oxidative or reductive equivalents may build up on the RC and/or OC before the transfer of those equivalents to generate the fuel and O₂. This tendency manifests in bipyridyl rhodium(III) WRCs, which are reduced to Rh(I) prior to the formation of a metal hydride and its protonation to evolve H₂.⁷⁰

Using water splitting as a representative example, the electron transfer reactions of molecular solar fuels catalysis are shown in Figure 1-7. In addition to the components depicted in Figure 1-7, electron relays can also be used to act as electron shuttles between the PS and appropriate catalyst. Popular electron relays include methyl viologen and Co(bpy)₃³⁺ in addition to ubiquinone, which performs a similar role in natural photosynthesis.^{71,72} While Figure 1-7 only depicts one photosensitizer, it is important to note that two photosensitizers can also be utilized for solution based solar fuels catalysis in an approach popularly known as the Z scheme.⁵⁰ The Z scheme is advantageous because two lower energy photons can be used to drive a reaction that would require a higher energy photon with a single PS. However, the additional requisite electron transfer compounds the difficulty of limiting back reactions.

While there are many technical challenges to the development of commercially viable molecular solar fuels catalysts relative to other methods for solar fuels generation, they have significant upside. Especially appealing is the low materials cost that stems from a superior atom economy of molecular catalysts.⁷³ Each metal atom in a molecular system possesses an active catalytic site. In contrast, a large fraction of metal atoms in colloidal catalysts are completely surrounded by the bulk material. However molecular

catalysts are prone to photobleaching, ligand dissociation, and other decay pathways that often endow them with shorter catalytic lifetimes than colloidal semiconductor catalysts.^{73,74} High rates of recombination are also an issue.

Energy Requirements of Solar Fuel Synthesis

For the electron transfer reactions depicted in Figure 1-5 to proceed at a rapid rate and with high efficiency, certain requirements exist with regards to the energies of the participating orbitals. Due to these thermodynamics, there exists a tradeoff between solar conversion efficiency and catalytic rate for any particular solar fuel such as zinc. Since economic viability requires both high solar conversion efficiency and high catalytic rates, an optimal balance exists. This concept readily becomes apparent with a broad examination of the thermodynamics of solar fuels generation and particularly the sources of energy loss in such a system. While these thermodynamics can be more or less applied to any artificial scheme for solar fuel generation, they will largely be discussed through the lens of molecular catalysis.

There are multiple sources of energy losses during solar energy conversion for solar fuels generation. For simplification, a single photosensitizer system is assumed; similar losses occur in a Z scheme and can be extrapolated from the following explanation. The first source of energy losses result from the fixed HOMO-LUMO gap of the PS and the spectrum of irradiated solar photons. The absorption of blue and UV photons with energy exceeding the HOMO-LUMO gap initially results in the population of higher energy vibrational excited states. The excited electron then rapidly decays into the lowest energy excited state of the PS, releasing energy lost as heat. Red and infrared

photons with energy lower than the absorption edge of the PS will not be absorbed and are wasted as entirely unconverted light energy.

Poor quantum yields of charge separation also result in energy loss. Three routes exist for the excited electron of PS*: nonradiative decay back to the ground state, radiative decay (photoluminescence) back to the ground state, and successful charge separation. For molecular systems, charge separation exists as the oxidative or reductive quenching of the PS. The quantum yield of charge separation is equal to the percentage of excited PSs that are quenched (oxidatively or reductively). Only charge separation leads to successful generation of solar fuels; any decay of PS* directly to its ground state represents energy lost. In light of all these losses, Shockley and Quieser established an energy gap-dependent limit on the efficiency of silicon based photovoltaic devices.⁷⁵ A PS with a 1.1 eV energy gap has the maximum theoretical efficiency of 30%, with that efficiency decreasing as the energy gap increases or decreases from 1.1 eV. They estimated that no more than 90% of absorbed photons can result in charge separation and used blackbody radiation to estimate sunlight.

Further energy losses in solar fuels generation arise from the need for a successful electron transfer to be spontaneous. Generally, at least two electron transfers are required, one to the PS from the oxidation catalyst and another to the reduction catalyst from the PS. More electron transfer reactions will be required if electron relays are used. Fewer are required if the PS also acts as one of the catalysts, as in this work. To maximize solar conversion efficiency, the HOMO-LUMO gap should be minimized so to absorb photons of higher wavelengths. The minimization of the PS HOMO-LUMO gap also minimizes the energy lost in electron transfer to the catalysts.

However if the energy lost in electron transfer between the PS and catalysts is too low then catalysis will slow or may not proceed at all. Marcus theory dictates that the rate of outer sphere electron transfers such as those between molecular solar fuel catalysts and PSs will increase as ΔE between the donor and acceptor increases.⁷⁶ (The inverted region of Marcus theory pertains to much greater distances and ΔE values.) As an approximate rule, 300 eV is required for a given electron transfer reaction to proceed at an acceptable rate for solar fuel catalysis.⁷⁷ Therefore in an ideal photocatalytic system comprised of a PS, RC and OC but no electron relays, the PS HOMO-LUMO gap would be approximately 600 eV greater than the change in energy between the photoproducts (1.23 eV for H_2O splitting and 1.65 eV for ZnO splitting). Figure 1-8 illustrates this concept.

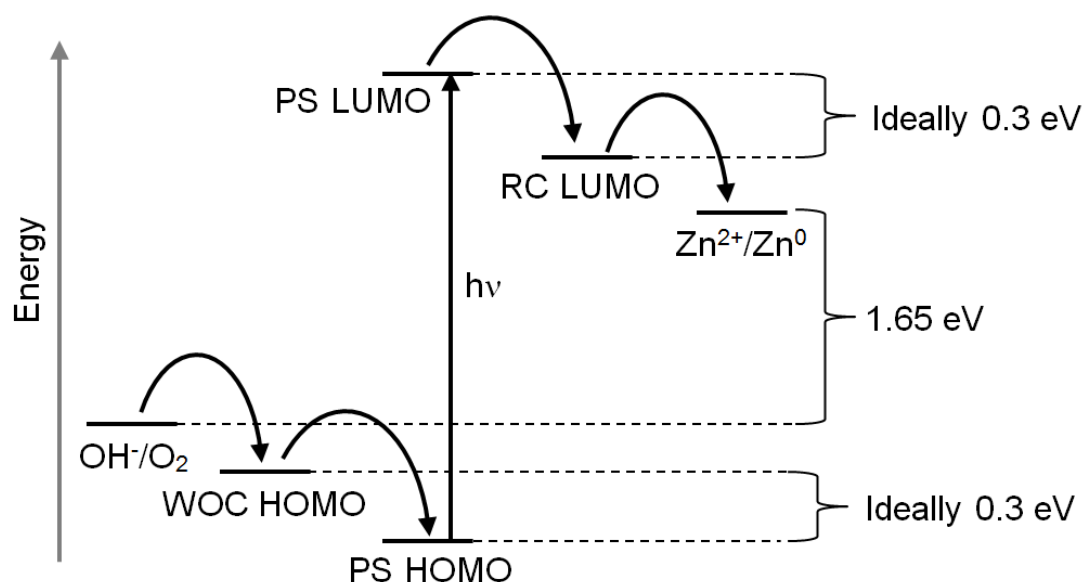


Figure 1-8– Jablonski diagram showing energy requirements for solar fuels catalysts

Transition Metal Complexes to Meet Energy Requirements of Solar Fuels

Generation

Due to these orbital energy requirements, there exist certain requisite photophysical properties for PSs and catalysts for solar fuels generation. These properties include:

1. Highly tunable orbital energies
2. Charge separated excited states
3. Long luminescence lifetimes and high quantum yields

Poor choice of photocatalytic materials would fail to maximize conversion efficiency and ultimately prevent the practical solar fuels generation. Materials with long lived, charge separated excited states have slower rates of nonradiative decay and will more readily undergo charge separation. Synthetic control over orbital energies is necessary to minimize thermodynamic losses and maximize catalytic rates. Luminescent transition metal complexes stand out relative to their completely inorganic counterparts as candidates that can meet these all these criteria, especially highly tunable orbital energies. As discussed earlier, this is one area that plagues heterogeneous semiconductor catalysts. Accordingly, the photophysical and electrochemical properties of transition metal complexes will be further examined, with an emphasis on the tuning of their orbital energies. Ir(III) and Zn(II) transition metal complexes will be used as representative examples, as they have been employed as photocatalysts in this work. Subsequently, transition metal complexes used as catalysts and PSs for solar fuels generation will be examined.

It is important to keep in mind the methodology used to assess the properties of transition metal complexes. Changes in orbital energies are often measured via cyclic voltammetry (CV) and indirectly by photophysical techniques such as absorption and fluorescence spectroscopy. They can also be estimated by theoretical techniques such as density functional theory (DFT). Fluorescence lifetimes and quantum yields can be measured directly by fluorescence spectroscopy. Often, the nature of the excited state and its extent of charge separation can be predicted fairly accurately by DFT. However the nature of the excited state of metal complexes should be confirmed using CV to measure the changes in oxidation and reduction potentials that occur upon systematic changes to the ligand structure.

Bis-cyclometalated Ir(III) complexes, which were originally investigated as emitters for OLEDs, are remarkable PSs for solar fuels generation. Bis-cyclometalated Ir(III) complexes meet all the criteria stated earlier: they have high emission quantum yields, long lived charge separated excited states, and their photophysical properties can be tuned over a wide range. Ir(III) complexes are commonly bis-cyclometalated by phenylpyridine (ppy) derivatives with an ancillary acetylacetonate (acac) or bipyridine (bpy) ligand. Strong spin orbit coupling in these complexes encourages intersystem crossing upon light absorption, which leads to long lived mixed triplet excited state and high quantum yields of phosphorescence.⁷⁸ Quantum yields of photoluminescence can approach unity and lifetimes as high as 1.50 μ s have been recorded.^{79–81} Heteroleptic biscyclometallated Ir(III) complexes tend to follow the energy gap law; as the HOMO-LUMO gap increases k_{nr} (nonradiative decay constant) also decreases. Longer lifetimes

and higher quantum yields result in complexes with blue shifted absorption, which is important to keep in mind when tuning the structure of these Ir(III) complexes.⁸²

Tuning the orbital energies of heteroleptic bis-cyclometalated Ir(III) complexes of the general structure $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+$ has been successful due to the nature of their excited states. $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+$ complexes tend to undergo mixed ligand centered (LC) and metal ligand charge transfer (MLCT) excited state transitions, the MLCT often favored.^{73,78} The distance of charge (electron and hole) separation in the excited state decreases the coulombic attraction between the electron and hole and facilitates charge separation in solar fuels generation. It also allows for the independent tuning of HOMO and LUMO energy levels through ligand modification. For most $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+$ complexes, the HOMO primarily resides on the Ir(III) center and partially on the cyclometalating ligand while the LUMO resides mostly on the coordinating ligand. Structural modifications to the $\text{N}^{\wedge}\text{N}$ and $\text{C}^{\wedge}\text{N}$ ligands can thus be used to independently tune the energies of the LUMO and HOMO respectively.

There are a few tactics that can be used to modify ligand architecture in order to alter the orbital energies of these cyclometalated Ir(III) complexes. For one, the conjugated pi system of ligands can be extended or shortened. This can be achieved in a straightforward manner simply adding or removing conjugated functional groups. Alternatively, bulky groups such as t-butyl or other branched alkanes can be used to apply steric strain on otherwise conjugated ligand architectures, twisting them out of conjugation. The other popular method for altering orbital energies is through the addition of electron withdrawing or donating groups. The addition of an electron withdrawing group will stabilize an orbital centered upon that ligand, lowering its energy.

The reverse is true for electron donating groups. Using these tactics, Ir(III) complexes with similar basic architectures have been tuned to achieve drastically HOMO-LUMO gaps.⁷⁸ Accordingly, Figure 1-9 depicts red, yellow, green, and blue emitting Ir(III) complexes.

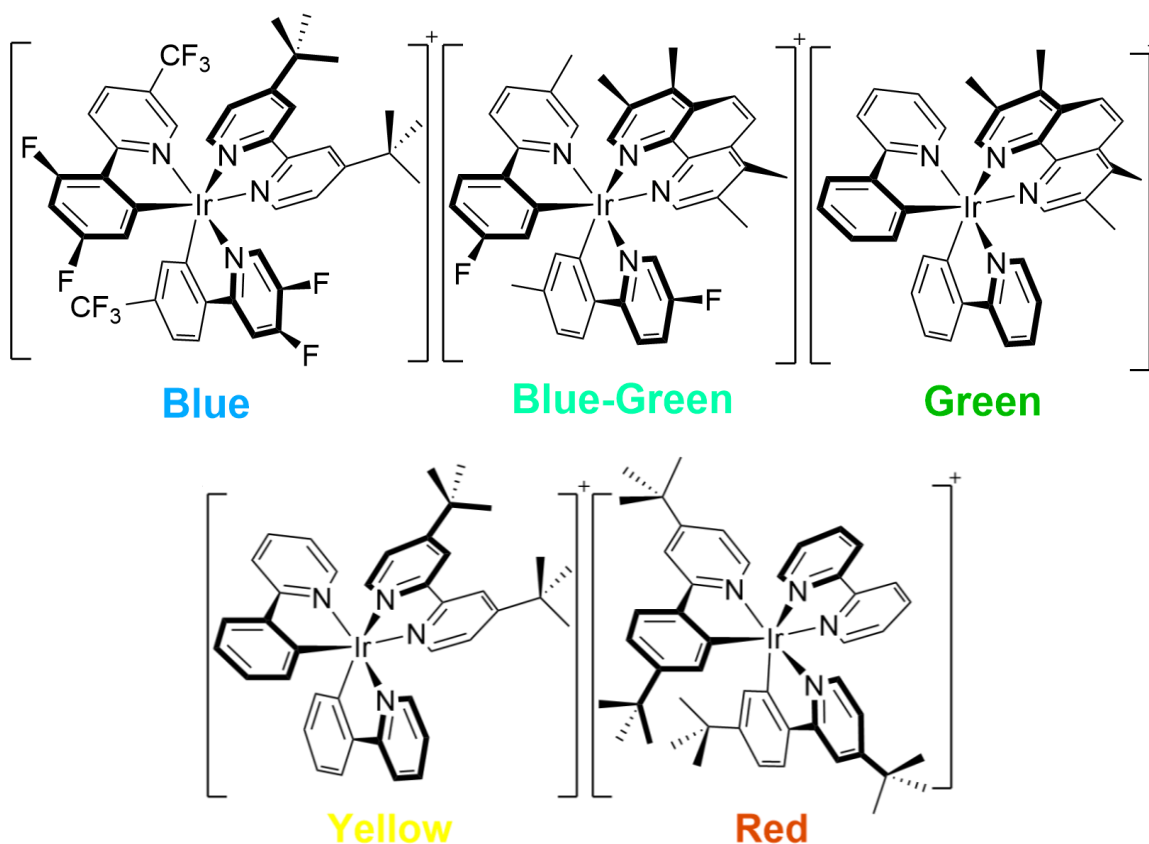


Figure 1-9- Structures and the colors of photoluminescence of iridium complexes synthesized by the Bernhard group⁷⁸

The emission of $\text{Ir}(\text{F-mppy})_2(\text{dtbbpy})^+$ is blue shifted relative to $\text{Ir}(\text{ppy})_2(\text{dtbbpy})^+$ because the electron withdrawing fluorine substituent on the ppy. Due to the mixed ligand and metal centered HOMO, the fluorine both inductively lowers the HOMO energy level through the Ir-C sigma bond and stabilizes it directly. Recently, blue emission of biscyclometallated Ir(III) complexes was achieved instead through the incorporation of a highly electron withdrawing nitrogen into the phenyl ring para to the

iridium bound carbon. Methoxy groups were incorporated meta to the iridium bound carbon to mitigate the blue shift. These fluorine free complexes synthesized in the Baranoff group represents another approach to tuning Ir(III) complexes and are shown in Figure 1-10.⁸³

Similar to iridium complexes, many zinc complexes were initially used as emitters and electron transport layers in OLEDs. Unsubstituted zinc quinolates are also yellow emitters but they have lower lifetimes than Ir(III) complexes, often in the 1-10 ns range.^{84,85} While their performance as electron transport layers in OLEDs indicates reversible solid state electrochemistry, not all zinc quinolates have reversible electrochemistry in solution. To the author's knowledge, reversible oxidation of Zn(II) quinolates has not been achieved. Reversible reduction electrochemistry is more expected because zinc quinolates are electron transporting semiconductors, but this is only sometimes the case. Cyclic voltammetry of zinc quinolates substituted at the 2 position has shown reversible two electron reductions, corresponding to one per ligand.⁸⁶ By contrast, the CV of the unsubstituted zinc quinolate (Znq_2) shows two irreversible reduction waves.⁸⁷

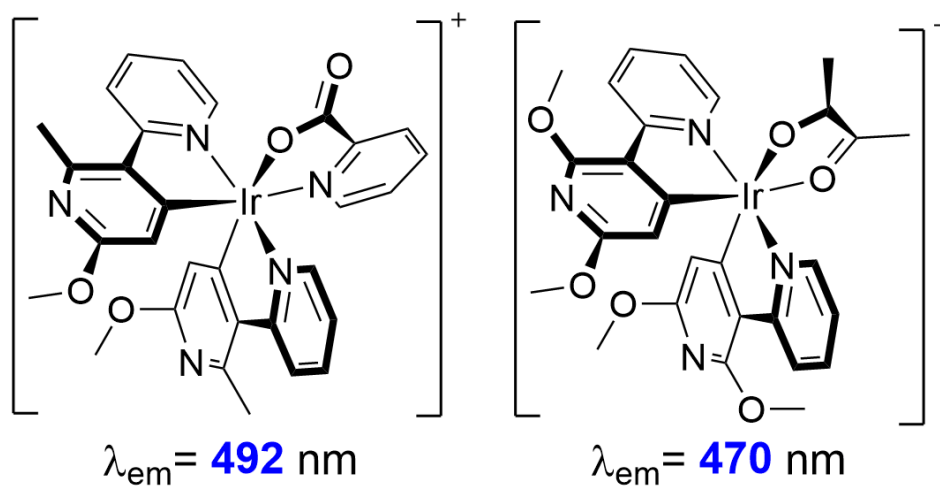


Figure 1-10– Fluorine-free, blue emitting iridium complexes⁸³

The vast majority of zinc quinolates are homoleptic, so the tuning of ligand architecture in order to separately alter the orbital energies is much more difficult. It has been found that the HOMO of zinc quinolates resides primarily on the phenoxide half of the ligand, while the LUMO resides on the pyridine moiety.^{87,88} The π to π^* excited state charge separation distance thus spans the quinoline ligand, allowing zinc quinolates to be tuned to some extent. The addition of electron withdrawing or donating groups (EWGs, EDGs) to the phenol half of the quinoline ligand will raise or lower the HOMO respectively. The same is true for EWGs and EDGs on the pyridine ring and the LUMO. However, these modifications can also have minor effects on the energy of the orbital centered on the opposite side of the ligand.

Zuppori et. al. successfully stabilized the LUMO of zinc quinolates through addition of substituents at the 2 position of the ligand in an attempt to red-shift the emission.⁸⁶ Ethyl ester, ethyl amide, and cyano groups were employed due to their electron withdrawing tendency. However, aggregation of these complexes in thin films quenched electroluminescence and no photoluminescence data was reported. Blue shifts in the emission of zinc quinolates has been achieved through the addition of sulfonamides or sulfonic acid at the 5 position.^{91,92} However, the bis-substituted zinc complex of 5,7-dichloro-8-hydroxyquinoline does not have a substantially shifted emission relative to the unsubstituted Znq_2 .⁸⁹ This is noteworthy because chapter three of this work details the superior catalytic activity of 5,7-dichloro-8-hydroxyquinoline (dCl-Hq) relative to 8-hydroxyquinoline (Hq). The structures and emission wavelengths of Znq_2 , Zn(dCl-q)_2 and the other aforementioned zinc quinolates can be seen in Figure 1-11.

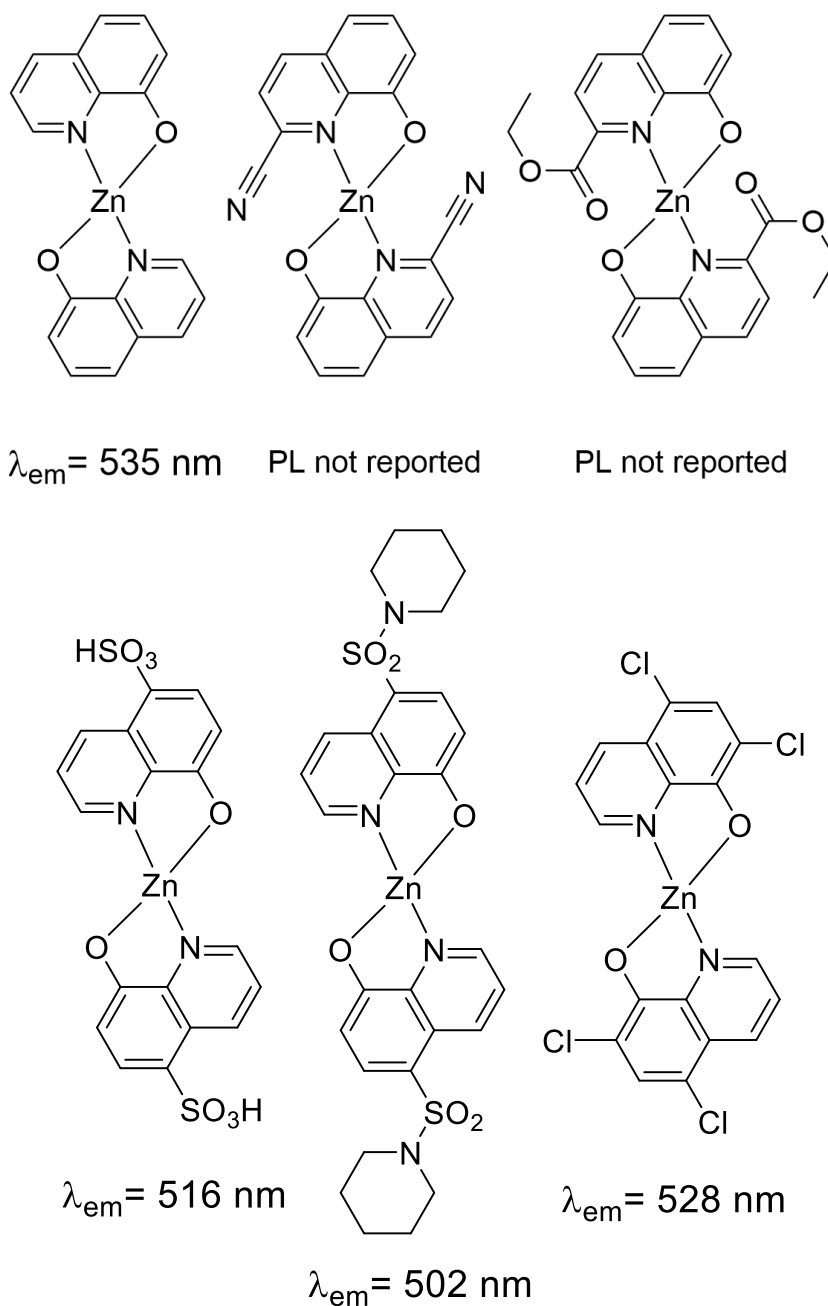
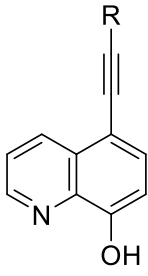


Figure 1-11 – Structures and photoluminescence wavelengths of zinc quinolates.^{86,89–92}

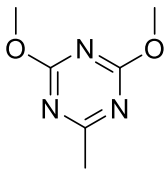
The larger body of work on aluminum quinolates can also be examined when attempting to identify desirable structural modifications for zinc quinolates. Both Zn and Al quinolates have LC π to π^* excited state transitions, and neither metal center participates directly in charge transport.⁸⁷ As a result, structural changes to aluminum quinolates will likely have a similar effect on zinc quinolates. In a representative

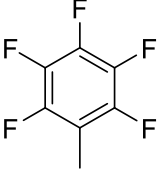
example, Anzenbacher et. al. synthesized a series of aluminum quinolates modified with ethynyl bridged aryl groups at the 5 position.⁹³ The aryl groups utilized were modified with a collection of both electron withdrawing and electron donating groups. As a result, both red shifted and blue shifted emissions were achieved over a range of 90 nm, as can be seen in Figure 1-12.

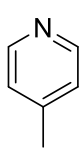
	Al(q1) ₃	Al(q2) ₃	Al(q3) ₃	Al(q4) ₃	Al(q5) ₃	Al(q6) ₃	Al(q7) ₃	Al(q8) ₃	Alq ₃
λ _{PL} , nm	520	538	541	545	561	569	573	600	526

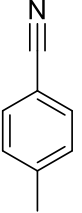


R =

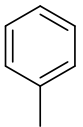

Hq1

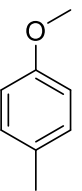

Hq2

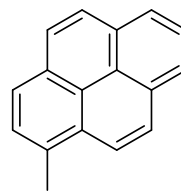

Hq3


Hq4

R =


Hq5


Hq6


Hq7

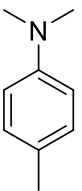

Hq8

Figure 1-12 – Structures and photoluminescence wavelengths of aluminum quinolates synthesized by Anzenbacher et al.⁹³

The photophysical properties of the free, protonated hydroxyquinoline ligand (Hq) are less reliable in predicting the corresponding properties of the zinc quinolate. Free 8-hydroxyquinoline and 10-hydroxybenzoquinoline (Hbq) ligands undergo excited state intramolecular proton transfer reactions.^{94,95} In the ground state, the hydroxyl group hydrogen bonds to the nearby nitrogen of the pyridine ring. Upon excitation, the proton of the hydroxyl group is transferred to the nitrogen of the pyridine ring. This causes a large stokes shift for the protonated hydroxyquinolines relative to metal quinolates.

Hydrogen Generation Catalysts and Photosensitizers

In pursuit of the photocatalytic reduction of Zn(II), it would be wise to consider transition metal complexes that are established solar fuels catalysts and chromophores. Among solar fuels, hydrogen generated via photocatalyzed water reduction is perhaps most similar to zinc metal produced by photocatalyzed Zn(II) reduction. Both processes are two electron transfers with minimal potential side products. In contrast, there are several potential side products in the photocatalytic reduction of CO₂ beyond the desired fuel (eg. carbon monoxide, methanol, formaldehyde). Photocatalysts for CO₂ reduction must also facilitate CO₂ activation and the dissociation of at least one C=O bond, which is a significant technical obstacle to their development. Such a parallel process does not exist for photocatalyzed proton and Zn(II) reduction, where dissociation of the parent compound occurs spontaneously. Given the similarities between the photocatalytic generation of H₂ and Zn⁰ and the lack of prior Zn(II) reduction catalysts, molecular H₂ evolving catalysts and photosensitizers used in such systems will be reviewed.

Photosensitizers for Water Reduction

Fortunately, water reduction catalysts and photosensitizers have been investigated extensively.^{71,69} The most robust molecular photosensitizers used in H₂ evolution to date are second and third row transition metal complexes from groups 5-8. Much research has concerned Ir(III), Ru(II), Pt(II), and Re(I) complexes. The complexes of each metal certainly have their merits but direct comparison between PSs is often difficult because

the light sources, sacrificial agents, concentrations, and co-catalysts employed vary in each study.

Ru(II) photosensitizers are perhaps the most common due to $\text{Ru}(\text{bpy})_3^{2+}$, which has been widely used as a model photosensitizer for over 30 yrs.^{96,97} Photocatalytic hydrogen evolution via a PS, WRC, and sacrificial reductant was pioneered using $\text{Ru}(\text{bpy})_3^{2+}$ and it is often used as a reference compound against which novel photosensitizers are assessed.⁷¹ Aryl diimine ruthenium complexes, which are also extensively investigated as dyes for DSSCs, are typically oxidatively quenched and cycle between Ru(II), Ru(II)*, and Ru(III).^{98,99} Similar to Ir(III) complexes, polypyridine ruthenium complexes also undergo a ³MLCT upon excitation. However, these complexes cannot be tuned over a similarly wide range due to their homoleptic bond structure and the thermal population of metal centered orbitals in the LC excited state.⁷⁸ Arylacetylide Pt(II) complexes compose another class of PSs. These complexes also undergo ³MLCT excited state transitions and are largely reductively quenched, although oxidative quenching has been demonstrated as well.^{100–103} Tricarbonyl rhenium aryl diimine complexes are less cost efficient than Ir, Ru, or Pt catalysts due to the rarity and price of rhenium, but have proven to be robust PSs, achieving over 6000 TONs when paired with a cobalt dioxime WRC.^{104,105} These Re(I) complexes are also reductively quenched from their ³MLCT excited state.¹⁰⁶ Representative Pt, Ru, and Re complexes are shown in figure 1-13.

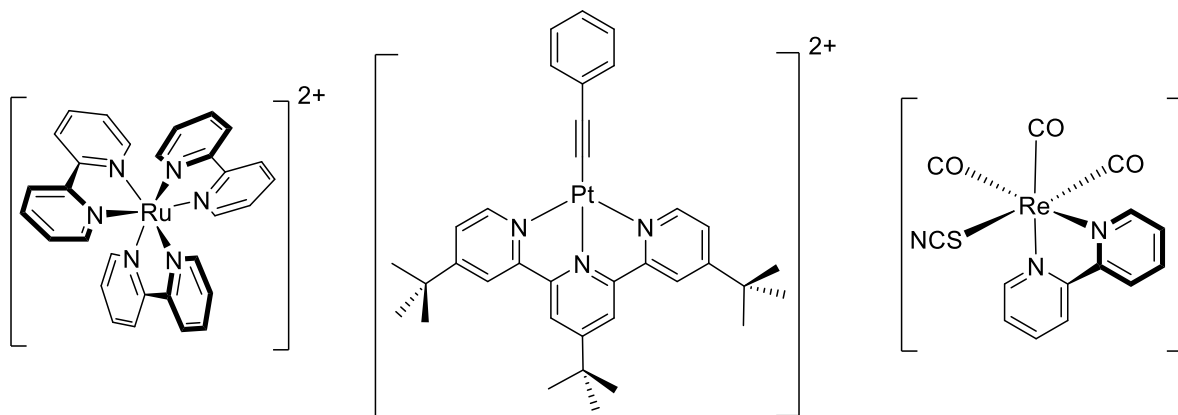


Figure 1-13 - Representative Pt, Ru, and Re photosensitizers for hydrogen evolution^{100,106}

Iridium complexes, which have already been discussed earlier, are appealing photosensitizers for water reduction because of their robust nature and high capacity for tuning. Cyclometalated Ir(III) complexes have been extensively investigated in this role, especially by the Bernhard group. Structure-activity relationships of Ir(III) complexes have been established by the systematic tuning of ligand architecture to produce systems for water reduction with high TONs (0.5 mol H₂ / mol Ir).⁷⁹

There is a growing recognition of the need for cheaper materials in order for molecular photocatalytic water splitting to be cost effective. As a result, completely organic dyes and complexes with more abundant metal centers have been identified to fit these needs. P-block and first row transition metals are commonly targeted. Biomimetic metalloporphyrins, which are present in chlorophyll, have been under investigation for over 30 years. Zinc and magnesium are common porphyrin metal centers, but Sn(IV), Cd(II), Al(III), metal free, and even Co(II) porphyrins have also been investigated.^{71,107,108} The electron structure and properties of metalloporphyrins vary depending on the metal center; for instance Zn-porphyrin is an electron donor whereas Sn-porphyrin is an electron acceptor.¹⁰⁹ Among organic dyes, fluorescein dyes such as

Rose Bengal are commonly used in solar fuels applications.^{110,111} Rhodamine dyes have improved upon fluorescein dyes by replacing the oxygen in the ether bridge with heavier chalcogen atoms such as sulfur and selenium.¹⁰⁵ Organic dyes are advantageous because they are inexpensive and emitters of every color can be obtained. However, the low cost of organic dyes, which is their chief upside, is neutered by poor durability. Additionally the most effective rhodamine dyes such as Eosin Y are halogenated. Rose Bengal, Eosin Y, and a phenyl-modified zinc-porphyrin are shown in Figure 1-14.

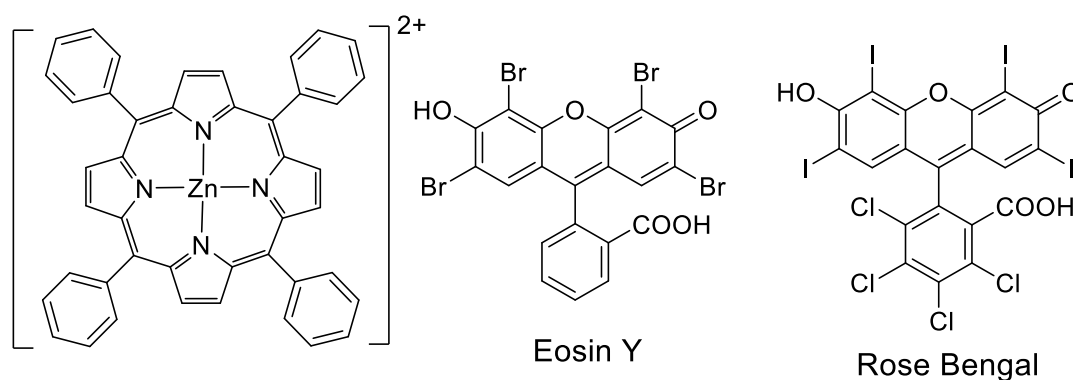


Figure 1-14- Organic and zinc photosensitizers for photocatalytic water reduction^{112,71}

Molecular Water Reduction Catalysts

Similar to photosensitizers, some of the most effective molecular water reduction catalysts are noble transition metal complexes, commonly platinum and rhodium. Among the catalysts reviewed in this work, Rh(III) WRCs are perhaps the least diverse in structure. Mononuclear rhodium catalysts tend to adhere to a bis-aryldiimine architecture such as $\text{Rh}(\text{bpy})_3^{+3}$ or $\text{Rh}(\text{bpy})_2\text{Cl}_2^+$.^{70,113} Ligands of these Rh(III) WRCs are prone to dissociation because an open coordination site is required to successfully catalyze water reduction. Hydrides form at this open site via the two electron reduction of a proton by a Rh(I) species with an open coordination site. Hydride formation regenerates

Rh(III) and results in H₂ evolution after protonation.¹¹⁴ In addition to rhodium, many Pt(II) complexes such as terpyridines and diamines are effective WRCs. However, most of these complexes have proven to be precursors to heterogeneous platinum colloids formed in situ.^{115,116} Given the facile reduction of Pt(II) to platinum metal ($\text{Pt}^{2+}/\text{Pt}^0$ $E_{\text{red}} = 1.2$ V vs SHE), high energy electrons donated from a PS are often more than sufficient to reductively generate such colloids. A combination of catalyst poisoning, kinetics, and spectroscopic techniques such as dynamic light scattering have proven effective in the identification of colloidal platinum reduction catalysts.¹¹⁵

As with photosensitizers, much recent research has concerned the development of earth abundant water reduction catalysts.¹¹⁷ While the catalytic properties of 2nd and 3rd row transition metals are mostly unmatched by more abundant counterparts, widespread commercialization is not feasible for these metals given their short supply. As such, the complexes of several first row transition metals have been employed as molecular water reduction catalysts: Fe, Ni, and Co. Similar to rhodium complexes, Co(III) and Co(II) oximes catalyze proton reduction and H₂ evolution via the formation and protonation of hydrides.^{104,106,118} Additional stability is imparted onto these catalysts due to a pseudomacrocyclic structure that arises from hydrogen bonding between two bidentate oxime ligands.⁷¹ Other Co(III) catalysts include bipyridines and thioles.^{82,119}

Nickel and iron WRCs differ from cobalt in that they are frequently explicit mimics of the Ni-Fe and Fe-Fe centers of hydrogenase enzymes. The metal centers of di-iron WRCs are almost always bridged by two sulfur atoms so to retain the basic Fe₂S₂ cluster of hydrogenases. Multiple carbon monoxide ligands have been found to be crucial to the performance of Fe₂S₂ WRCs due to the stability of iron carbonyl hydrides.^{120,121}

Similar sulfur-bridged dinuclear Fe-Ni WRCs have higher must lower activities, but macrocyclic mononuclear Ni(II) complexes have demonstrated considerable success as WRCs.^{122,110} Representative examples of rhodium, cobalt, iron, and nickel WRCs are shown in Figure 1-15.

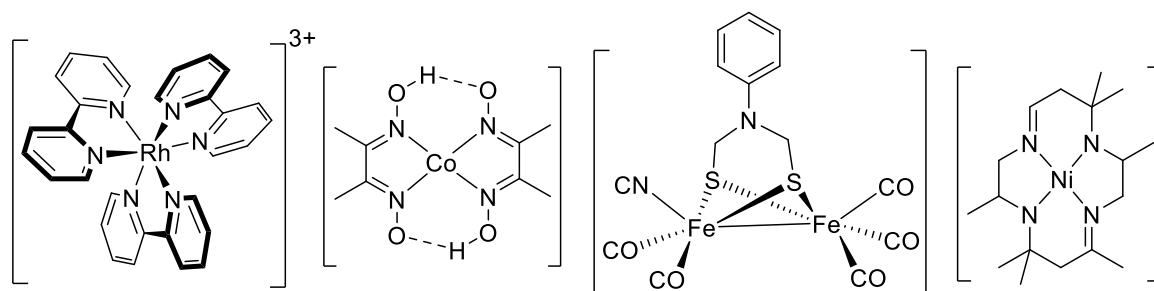


Figure 1-15 - Representative rhodium, nickel, cobalt, and iron centered water reduction catalysts^{117,70}

Sacrificial Reagents and Back Reactions

Sacrificial agents were employed in the initial development of all the molecular catalysts and photosensitizers discussed in this chapter. Sacrificial agents are either reductants or oxidants that are used as a source or sink of electrons in place of one solar fuel catalyst in order to isolate and study the other.⁷³ To clarify, a sacrificial reductant is an electron source permits the isolated study of RCs in the absence of any water oxidation catalysis. Similarly, sacrificial oxidants are acceptors of electrons that allow for the isolated study of WOCs in the absence of RCs. In water splitting, WRCs are almost always studied in tandem with a PS and a sacrificial reductant. However the photosensitizer is often omitted in studies involving WOCs and a sacrificial oxidant. When studying WOCs using sacrificial oxidants but no PS, the reduction potential of the oxidant must be sufficiently positive to oxidize the WOC. However, when a PS is

employed the sacrificial agent must be reactive with the excited but not the ground state PS. In addition to water reduction catalysts, CO₂ reduction catalysts are also investigated in this manner. Common sacrificial reductants include EDTA, cysteine, triethylamine (TEA) and triethanolamine (TEOA). Common sacrificial oxidants used in the study of WOCs include Ce(IV), persulfate, and Co(III).^{69,77} It should be noted that oxygen gas has no competitor and other OCs are not generally studied; O₂ is universally acknowledged as the ideal oxidant. Oxygen gas is ubiquitous in earth's atmosphere so out of all potential candidates, only O₂ does not need to be stored. This is a tremendous advantage. Moreover, alternative candidates such as Cl₂ are often poisonous. Figure 1-16 diagrams the use of sacrificial reagents.

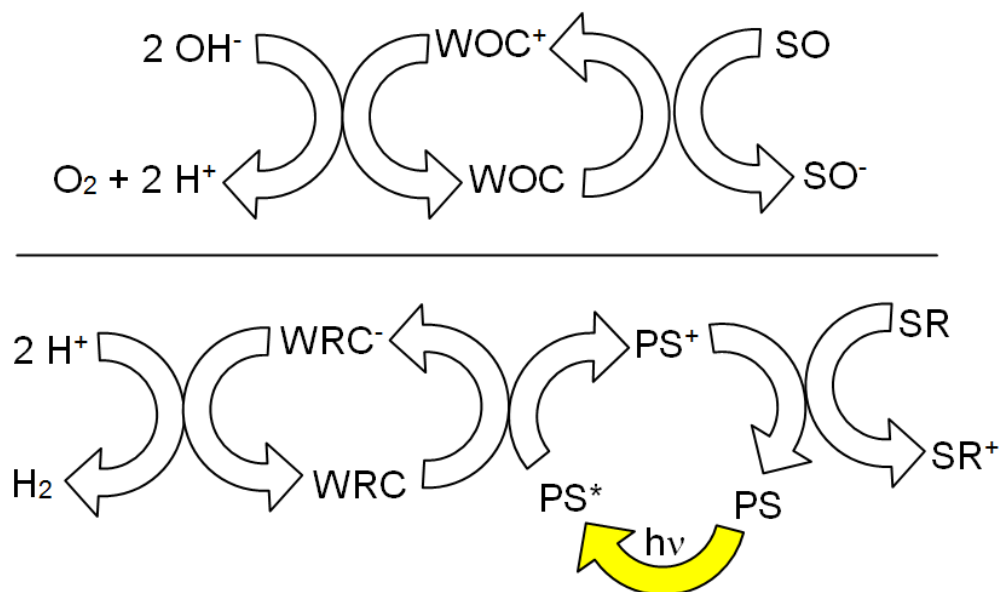


Figure 1-16 – Photocatalytic water reduction and oxidation using sacrificial reagents. SO = Sacrificial Oxidant, SR = Sacrificial Reductant.

Sacrificial agents allow for major challenges in solar fuels research to be addressed independently. Two currently significant barriers to the commercialization of solar fuel generation are the needs for higher performing catalysts and lower rates of

charge recombination. Charge recombination includes the decay of PS* back to the ground state. Recombination also encompasses several undesirable back reactions such as the transfer of an electron from the RC to either the OC, electron relay, or photosensitizer. Other recombination reactions include the reduction of the OC by the PS or electron relay. Figure 1-17 illustrates recombination through a simplified Jablonski diagram. Strong thermodynamic driving forces for recombination exist because the active OC and RC are highly reduced and highly oxidized species respectively. As a result, recombination rates are often very high in molecular nonsacrificial water splitting systems. When a sacrificial agent is employed to study a solar fuels catalyst a major source of recombination is eliminated due to the absence of the complimentary catalyst. The re-oxidation of the fuel by O₂ is also prevented. This permits the isolated optimization of solar fuels catalysts for maximal rate and durability.

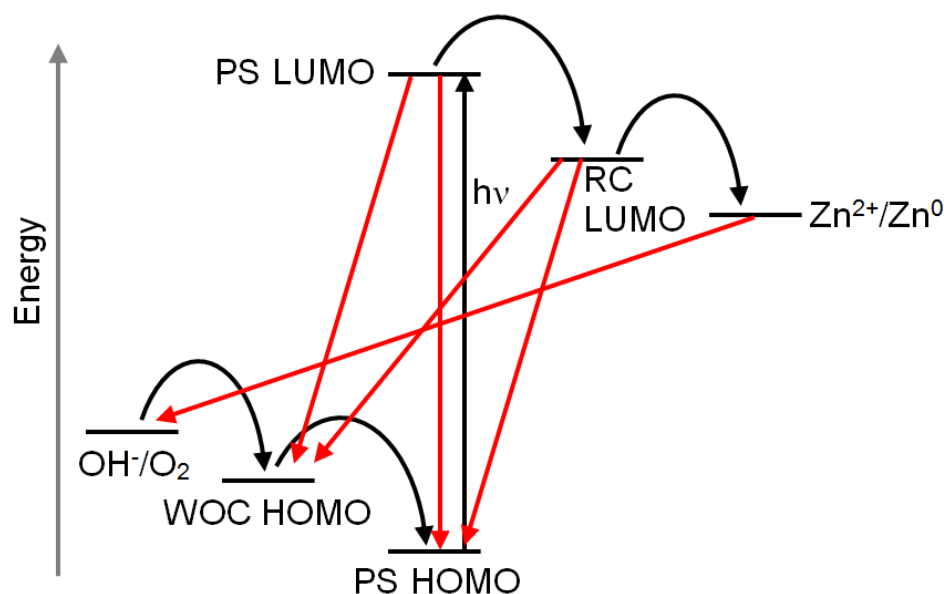


Figure 1-17– Possible recombination pathways in photocatalyzed water splitting. Forward electron transfer reactions are in black and back reactions are in red.

As high performance solar fuel catalysts are developed for water splitting, ZnO splitting, or CO₂ reduction, research interest shifts towards the development of molecular

architectures to overcome high recombination rates. In water splitting, such research has focused linking components of the catalytic system via multinuclear supramolecular complexes and molecular bridges.^{123–125} Higher rates of forward electron transfer have been achieved without significant alteration of the electronic structure of either component. However to the knowledge of the author, complete water splitting in which O_2 and H_2 are generated has not been achieved by an entirely molecular system to date. This remains a significant obstacle in the field of photon driven water splitting by molecular catalysts.

Once sacrificial agents are replaced, WOCs that were developed separately via sacrificial agents can then be paired with a PS and RC to generate solar fuels concurrently with O_2 . It is important to note that many different fuels can be produced this way. Water oxidation can be utilized to maintain charge balance in the nonsacrificial generation of not only H_2 but also zinc, MeOH or other solar fuels. This point cannot be understated given the focus of this work on developing photocatalysts for $Zn(II)$ reduction.

Chapter 2. Photon Driven Reduction of Zn(II) by Bis-cyclometallated Ir(III) Complexes

Introduction

The use of sacrificial agents promotes survival of only the fittest reduction catalysts and solar fuels. Using sacrificial agents, reduction catalysts for the production of different solar fuels can easily be initially developed in parallel. If a given fuel, such as zinc, shows particular promise over other solar fuels, then corresponding zinc reduction catalysts can be paired with water oxidation for nonsacrificial ZnO splitting. The same can be said for reduction catalysts that produce the same solar fuel; only the highest performers should be paired with water oxidation. The use of only the highest performing catalysts for the most desirable solar fuels ensures the greatest viability of a nonsacrificial system for solar fuels generation.

For this reason and the merits of zinc as a solar fuel mentioned earlier, initial Zn(II) reduction catalysts documented in this work have been developed using a sacrificial reductant. The presence of an oxygen evolving reaction might hinder, inhibit, or otherwise obscure important aspects of photocatalyzed Zn(II) reduction, which would hinder the development of an effective catalyst. As mentioned in chapter 1, recombination is possible between the active catalysts, or between an active catalyst and any intermediate. Additionally, the back reaction between zinc metal and O₂ is possible which could limit the forward reaction yield. Complete splitting of zinc oxide is not yet of a concern because the field of Zn(II) reduction is in its infancy. In no previous study was Zn(II) successfully photoreduced using visible light nor in an attempt to utilize zinc

metal as a solar fuel. It was therefore necessary to first establish in this work that the photocatalyzed Zn(II) reduction by visible light is feasible.

The use of TEA as a sacrificial agent in this work thus permitted the study of photocatalyzed Zn(II) reduction in isolation. In this chapter, biscyclometallated iridium(III) complexes are used as photocatalysts for Zn(II) reduction under visible light. A general schematic is given in Figure 2-1. The successful iridium photocatalysts have a $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+$ architecture, where $\text{C}^{\wedge}\text{N}$ = 2-phenylpyridine or a similar derivative and $\text{N}^{\wedge}\text{N}$ = 2,2'-bipyridine or a derivative.

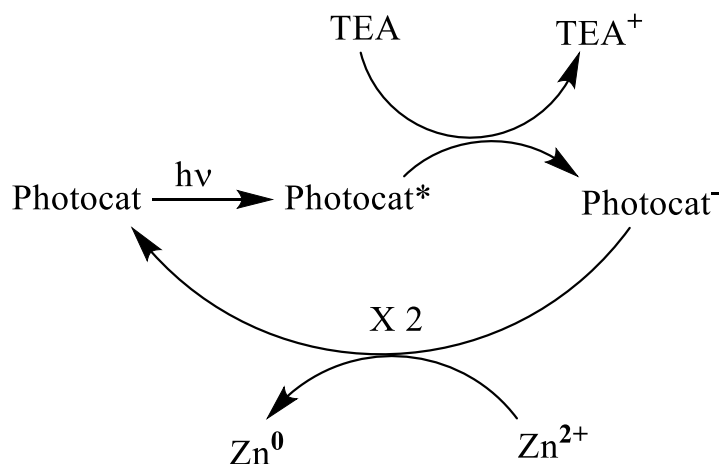


Figure 2-1– An outline of the photocatalytic reduction of Zn(II) using TEA detailed in this chapter.

$\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+$ complexes are ideal photocatalysts for this proof of concept for photocatalyzed Zn(II) reduction because they embody the previously outlined desirable characteristics of a molecular PS for solar fuels generation. They have long lived, charge separated excited states with high quantum yields of luminescence. Their orbital energies are both highly and independently tunable. And most importantly, electrons in the lowest excited state of $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+$ complexes are sufficiently energetic to reduce Zn(II) to zinc metal. The ligand centered reductions of $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+$ complexes (as measured

by cyclic voltammetry) typically occur at around -1.16 V vs SHE, compared to -0.76 V vs SHE for $\text{Zn}^{+2}/\text{Zn}^0$.⁸² This leaves ~400 eV excess for each electron transfer in the reduction of Zn(II) to be utilized as the thermodynamic driving force and lost as heat. Triethylamine is employed as the sacrificial reductant in this study largely because it is proven to reductively quench $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+$ complexes. The use of TEA insures that active $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^0$ complex with sufficient reducing capacity to generate zinc metal from Zn(II) will form. The oxidation of TEA is well documented and occurs at +0.934 V vs SHE.¹²⁶

Most of the results in this chapter have been previously published.¹²⁷ In this chapter optimal reaction conditions were determined with respect to solvent, zinc salt, and photocatalyst structure. Initial rate and catalyst decay kinetics were also investigated. The optimized photocatalytic system produced 430 catalyst turnovers (moles Zn/moles catalyst). As a whole, these studies allowed helped elucidate the reaction mechanism. The investigation of the reaction mechanism was augmented by the cyclic voltammetry of zinc salts.

Experimental Methods

Materials – All materials were used as received. ZnCl_2 and other zinc salts were purchased from Sigma. Triethylamine was purchased from Acros Organics, and Acetonitrile (MeCN) was purchased from Fisher Scientific. All ligands, including 4-4'-di-tert-butyl-2-2'-bipyridine and 2-phenylpyridine were purchased from Aldrich while $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Pressure Chemical.

Synthesis of iridium complexes – All bis-cyclometalated $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})](\text{PF}_6)$ complexes were synthesized similarly, according to established procedures.^{79,80,82,128} The synthesis of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ is described as a representative example. First, 100 mg (0.29 mmol) of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ was combined with 83 mg (0.59 mmol) 2-phenylpyridine in 8 ml of 3:1 2-ethoxyethanol/water. The solution was heated and stirred overnight at 120 °C. The yellow precipitate was filtered and washed with 20 ml water and 20 ml methanol to yield tetrakis-2-phenylpyridine-bis-(μ -chloro)-diiridium, $[\text{Ir}(\text{ppy})_2\text{Cl}_2]_2$. 100 mg (84 μmol) of the $[\text{Ir}(\text{ppy})_2\text{Cl}_2]_2$, was added to a solution of 46 mg (188 μmol) 4-4'-di-tert-butyl-2-2'-bipyridine in 4 ml of ethylene glycol. The solution was heated overnight at 150 °C. After cooling, 60 ml of water was added to the solution and it was washed three times with diethyl ether. To the aqueous layer 10 ml of 0.125 M ammonium hexafluorophosphate was added. The precipitate was filtered, dried, and recrystallized by acetonitrile/diethyl ether vapor diffusion recrystallization to obtain the product, $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$. Alternatively some $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})](\text{PF}_6)$ complexes were purified by acetone/pentane vapor diffusion recrystallization. ¹H NMR (300 MHz, acetone- d_6): δ 8.91 (d, 1H), 8.27 (dd, 1H), 8.01 (d, 2H), 7.98 (dt, 2H), 7.92 (dd, 2H), 7.82 (d, 2H), 7.74 (dd, 2H), 7.16 (dt, 2H), 7.06 (dt, 2H), 6.94 (dt, 2H), 6.37 (dd, 2H), 1.44 (18H, s).

Custom-Built Photoreactor- Ir(III) complexes were evaluated as photocatalysts for Zn(II) reduction in a custom-made, home-built photoreactor: A 5 m long 24 W 460 nm LED strip with 300 diodes (Solid Apollo SA-LS-BL-3528-300-24 V) was mounted inside an 8 in. (203 mm) galvanized steel tube in a uniform, spiral pattern. This inward illumination zone covered 60 mm vertically, to ensure the even illumination of the entire sample area. This inwardly illuminating steel tube was mounted onto a stir plate so that

the samples could be magnetically stirred during the photoreaction. Samples were held in place by a circular sample holder centered on the magnetic stir plate inside the steel tube. Transparent 1-1/4" (31.8 mm) polycarbonate tubes with a 1-1/8" inner diameter were cut into twelve 42 mm long pieces that served as sheaths in which the samples were mounted. Twelve of these sheaths were mounted along the outside of a clear 3-1/2" acrylic tube at a height of 40 mm, above the solvent line of the photoreaction vials. Septum covered EPA vials were used as illumination vessels. The distance between all sample vials and the LEDs along the inside of the steel tube was uniformly maintained at 28 mm. Figure 2-2 depicts the photoreactor.



Figure 2-2– The custom built photoreactor employed in photocatalytic Zn(II) reduction studies

General Procedure for Set-Up of Photoreactions – The zinc-generating photoreaction experiments detailed in this chapter were all set up in a uniform manner to ensure directly comparable results. Photoreaction samples were prepared in 40 mL EPA vials sealed by open top caps each containing a fluoropolymer resin/silicone septa (ICHEM SB36-0040).

Zinc chloride or an equimolar quantity of the appropriate zinc salt was massed directly into the vial. All photoreaction vials contained a small stir bar. Stock solutions of the iridium PS were prepared in the appropriate solvent, commonly acetonitrile. Aliquots of these stock solutions were added to each vial in order to evenly and accurately distribute PS in the desired concentration. Standard photoreaction conditions were 110 μ M iridium PS, 420 mg ZnCl_2 , 9 total ml of MeCN, and 1 ml TEA. Before illumination, sample vials were degassed by cycling 6 times between vacuum and Ar atmosphere. The final cycle of argon atmosphere was adjusted to atmospheric pressure by the purging of the overpressure through a bubbler.

General Procedure for Work-Up of Photoreactions – The quantification of zinc metal produced in photoreactions was performed indirectly by a hydrogen evolution reaction. After illumination, the samples were purged with argon for 10 min to vacate any potential H_2 from the headspace. Quantitative conversion of reduced Zn^0 to H_2 was achieved by injecting photoreaction mixtures with 2 mL of concentrated hydrochloric acid, similar to the technique described by Vogel.¹²⁹ After hydrogen evolution, a precisely measured volume of headspace gas was injected into Stanford Research Systems QMS200 Gas Analyzer. The instrument was calibrated with commercially available and pre-calibrated Ar- H_2 mixtures.

X-Ray Diffraction Measurement- X-ray diffraction was measured using a PANalytical X'Pert PRO diffraction system. A Θ - 2Θ scan was performed at 30 kV, 10 mA, from 20° to 60° . To prepare the zinc product from the photoreaction vials samples for X-ray diffraction, the solid phase of the photoreaction mixture was first allowed to settle. The solution phase was then extracted through the septum of the capped photoreduction vial

to preserve the argon atmosphere in the headspace. Approximately 10 ml of acetonitrile was then twice added and extracted similarly and the samples were purged with argon until dry. The zinc product was then briefly exposed to air during transfer and diffraction measurement.

Cyclic Voltammetry– The cyclic voltammograms shown in Figures 2-7 and 2-9 were performed under very similar conditions on a CH instruments 600C electrochemical analyzer potentiostat. A glassy carbon working, platinum counter, and silver wire pseudoreference electrode were employed. Against this setup, a ferrocene internal standard was referenced at 0.380 V vs SCE.¹³⁰ All scans in Figure 2-7 used acetonitrile as a solvent, while scans in Figure 2-9 employed either acetonitrile or tetrahydrofuran as specified. In all cases, the scan rate was 0.1 V/s and the concentration of the tetrabutylammonium hexafluorophosphate electrolyte was held steady at 0.1 M. Samples were purged with argon that was first bubbled through the appropriate solvent for ten minutes prior measurement.

Multiple Ir(III) PSs study – Aliquots from stock solutions of the hexafluorophosphate salt of each Ir(III) complex tested in Figure 2-5 were added to the appropriate photoreaction vial for a final concentration of 110 μ M in each. Each vial also contained 9 ml MeCN, 1 ml TEA, 420 mg ZnCl₂. The samples were set up and worked up after 48 hr according to the general procedure outlined earlier.

Zinc Salt study- Each photoreaction vial contained 9 ml MeCN, 1 ml TEA, 110 μ M [Ir(ppy)₂(dtbbpy)](PF₆), and 2.01 mmol of each zinc salt. The Ir PS was added to each vial from a stock solution, while the zinc salt was massed directly. The samples were set up and worked up after 24 hr according to the general procedures outlined earlier.

Solvent study - Each photoreaction vial contained 9 ml MeCN, 1 ml TEA, 110 μ M $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$, and 420 mg of ZnCl_2 . Stock solutions of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ were made in each solvent used for this study. Anhydrous solvents were used where applicable. The samples were set up and worked up after 24 and 72 hr according to the general procedures outlined earlier.

H₂O Concentration study – Water was added to each photoreaction vials via an initial serial dilution with acetonitrile. Each photoreaction vial contained 1 ml TEA, 110 μ M $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$, 420 mg of ZnCl_2 , and 9-x ml MeCN, where x = ml H₂O added. The samples were set up and worked up after 24 hr according to the general procedures outlined earlier.

Initial Rate Kinetics – Zinc Chloride study – All ZnCl_2 was massed directly into the photoreaction vials. Each vial contained 9 ml MeCN, 1 ml TEA, 110 μ M $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ and ZnCl_2 . Samples were set up and worked up after either 1, 2, 4, or 8 hr according to the general procedures outlined earlier. At each sampling hour, one vial of each mass concentration of ZnCl_2 was removed.

Initial Rate Kinetics – $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ study- Aliquots were taken from a stock solution was made of $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ in acetonitrile to ensure accurate concentrations in each photoreaction vial. Each vial also contained 9 ml MeCN, 1 ml TEA, and 420 mg ZnCl_2 . The samples were set up and worked up after 1, 2, 4, and 8 hr according to the general procedures outlined earlier.

Kinetics – Catalyst Decay study – $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ was aliquotted from a stock solution to each vial for a concentration of 110 μ M. Each photoreaction vial also contained 9 ml MeCN, 1 ml TEA, and 420 mg ZnCl_2 . The samples were set up and

worked up after either 1, 2, 4, or 8 hr according to the general procedures outlined earlier. At each sampling hour, one vial of each concentration of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ was removed.

Results and Discussion

Initial Observation of Photoreduced Zinc Metal

Zinc metal was observed after mixtures of zinc salts in acetonitrile were exposed to visible light under an argon atmosphere and in the presence of an iridium(III) complex and triethylamine. Control experiments were run and it was found that the removal of either the iridium complex, TEA, light, or argon all prevented the generation of zinc metal. The reaction required only catalytic quantities of the iridium complex but TEA was needed in stoichiometric excess. TEA is known to reductively quench excited cyclometallated $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^{+*}$ complexes by the basic mechanism outlined earlier. In this way, an $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^0$ species is generated, with the additional electron residing on the aromatic diimine $\text{N}^{\wedge}\text{N}$ ligand.⁷⁰ In previous work on photocatalytic water reduction, $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^0$ iridium complexes have been shown to transfer this reducing equivalents document to a WRC. H_2O or H^+ is subsequently reduced to evolve H_2 . In the currently reported reactions, H_2 evolution was not observed due to the absence of water. Instead, Zn^{2+} is photocatalytically reduced to zinc metal by the iridium complex, with TEA similarly serving as a sacrificial source of low energy electrons.

Previous water reduction experiments have shown that triethylamine is oxidized by excited iridium complexes to yield one equivalent each of diethylamine and acetaldehyde, and two protons.⁷⁰ Water is a required as a reagent to supply the oxygen

necessary to form acetaldehyde. The occurrence of this mechanism, shown in Figure 2-3 is supported by the inability of anhydrous zinc salts to yield any zinc metal under otherwise identical reaction conditions. It can be concluded that the water trapped in the crystal lattice of the zinc salt is required to supply the oxygen atom for the formation of acetaldehyde. Without that water, the reaction solution of MeCN and TEA lacks any oxygen source, so TEA oxidation by the established mechanism is prevented.

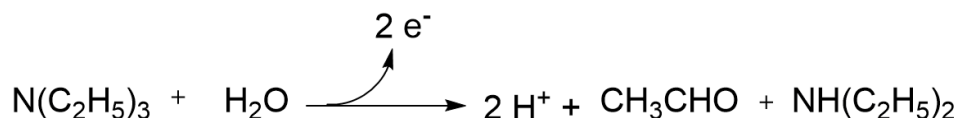


Figure 2-3– Overall oxidation of triethylamine observed in these photoreactions.

The confirmation of this oxidation mechanism raises the question of whether zinc metal generated will be stable as protons are released. The oxidation of zinc metal is known to be acid catalyzed, an effect that is actually exploited in this work in order to quantify zinc metal photoproduct by its acidification to yield H_2 .¹²⁹ The release of protons from TEA oxidation, especially in the presence of chloride ions from ZnCl_2 , could therefore potentially result in the re-oxidation of any zinc product. This reaction is avoided however due to the excess of triethylamine in the reaction mixture, which exceeds the concentrations of chloride ions by 7:2. This excess TEA is protonated as protons are released, effectively buffering the reaction mixture and preventing any oxidation of the zinc metal photoproduct. The reduction of Zn(II) in basic conditions will actually be advantageous in future work concerning complete ZnO splitting because the potential of the water oxidation half reaction drops as pH rises according to Nernst equation. This will result in faster rates of O_2 evolution.

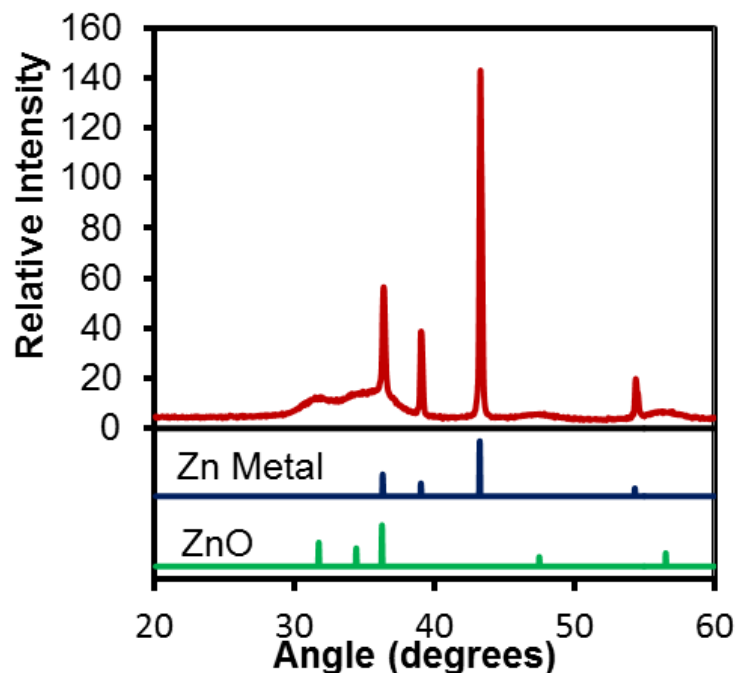


Figure 2-4 – The X-ray diffraction pattern of zinc photoproduct (red) with accepted literature patterns for Zn^0 (blue) and ZnO (green) shown underneath.¹³¹

While the grey product generated in these photoreactions had similar appearance and reactivity to zinc metal, it was necessary to verify that this product truly was zinc metal. X-ray diffraction (XRD) was used for this end. A Θ - 2Θ XRD scan performed on the product confirms the photoproduct to be zinc metal. The XRD pattern obtained is shown in Figure 2-4 as well as literature scans for zinc metal and ZnO .¹³¹ Zinc chloride, which was used as the Zn(II) source, was removed by several rinses with acetonitrile and was not detected in the XRD pattern. However, zinc oxide was observed as a minority product. The surface of zinc metal is known to spontaneously oxidize upon exposure to the oxygen in air, forming a thin layer of zinc oxide on the surface that surrounds the metal interior, protecting it from further oxidation. This phenomenon, known as passivation, explains the presence of ZnO in the XRD pattern. The broad ZnO peaks

likely indicate slightly different ZnO morphologies, which could arise from the non-uniformity of the zinc metal particles.

Optimization of Conditions and Mechanistic Investigations

Several cyclometallated Ir(III) complexes were evaluated in their effectiveness as photocatalysts for the reduction of Zn(II) to zinc metal. A priori, it is expected that the variation of the ligand architecture in these iridium complexes would influence their photophysical properties and thus their capabilities as catalysts. Changes to orbital energy levels caused through this ligand tuning could substantially alter both the molar absorptivity of the complex at 460 nm and the rate of electron transfer between the reduced photocatalyst and Zn(II). Each of these effects should in theory alter the yield of zinc metal over a given time period. Such outcomes have been observed in water reduction experiments employing an Ir(III) PS and were discussed earlier. However, strong structure-activity relationships were not found for the iridium(III) complexes evaluated in this work for their effectiveness in Zn(II) photoreduction. The yields of zinc metal afforded by these iridium(III) complexes are shown in Figure 2-5.

All iridium complexes in Figure 2-5 proved to be to some degree effective in the photocatalytic reduction of Zn(II) with one exception: $[\text{Ir}(\text{ppy})_2(\text{dppe})](\text{PF}_6)$. The substitution of diphenylphosphinoethane for the aromatic diimine ligands as the ancillary ligand of these bis-cyclometallated iridium complexes fundamental alters the excited state of the molecule. The $^3\text{MLCT}$ excited state described earlier for $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+$ complexes is replaced by an entirely ligand centered π to π^* transition in $\text{Ir}(\text{ppy})_2(\text{dppe})^+$.¹²⁷ The lack of a charge separated $^3\text{MLCT}$ excited state prevents

$\text{Ir(ppy)}_2(\text{dppe})^+$ from effectively photocatalyzing Zn(II) reduction.

$[\text{Ir(ppy)}_2(\text{dtbbpy})](\text{PF}_6)$ was the best performer of all the iridium complexes tested and was employed as the catalyst in subsequent Zn(II) reducing photoreactions.

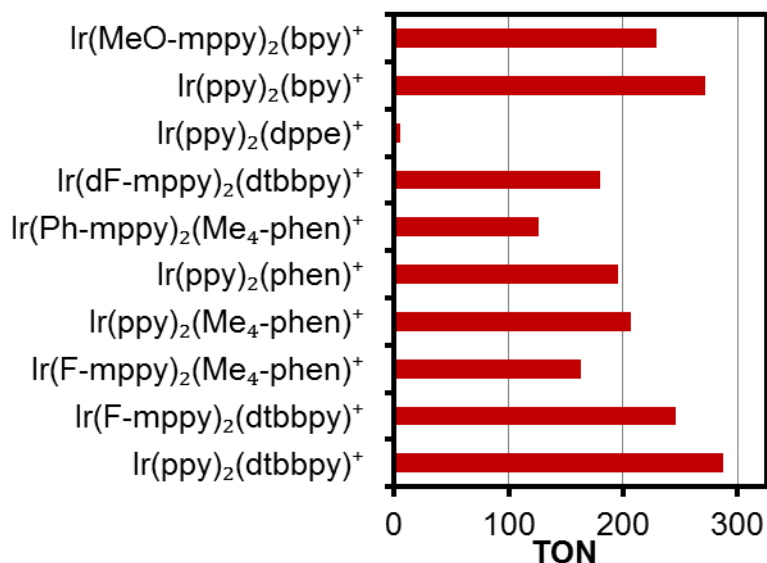


Figure 2-5 - Catalytic TONs afforded by various heteroleptic bis-cyclometalated iridium(III) complexes at $110\ \mu\text{M}$ after 48 hr of illumination under otherwise standard conditions.

In addition to iridium tuning experiments, the photocatalytic system of Zn(II) reduction was systematically optimized. Several experimental parameters were varied such as zinc salt, solvent, and water content, in order to maximize catalytic yields and investigate the reaction mechanism. It was found that the use of different zinc salts as the starting material and source of Zn^{2+} had a profound effect on the yield of zinc metal. ZnSO_4 , $\text{Zn(BF}_4)_2$, ZnNO_3 , ZnCl_2 , ZnBr_2 and ZnI_2 were all used in otherwise identical zinc generating photoreactions. The results of this experiment are seen in Figure 2-6.

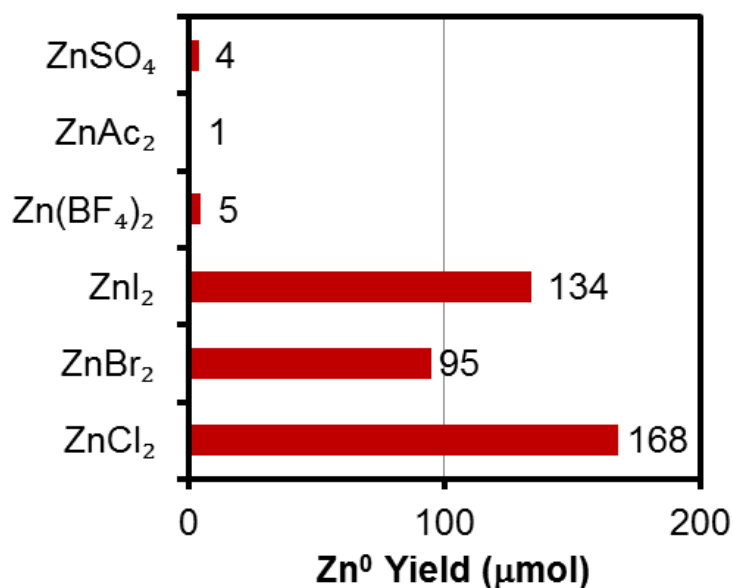


Figure 2-6 – Dependence of the yield of zinc metal on the zinc salt used as a starting material. Samples contained 2.01 mmol zinc salt and were illuminated for 24 hr under otherwise standard conditions.

Of all the zinc salts tested in Figure 2-6, zinc chloride afforded the most reduced zinc metal product. The most remarkable trend however, is the superior performance of zinc halides relative to the other salts tested. There was no correlation between salt solubility and the yields of zinc metal generated. Among the salts tested, only zinc tetrafluoroborate completely dissolved in the reaction solution, but this salt afforded almost no zinc metal. Zinc acetate had the second highest solubility in the reaction solution, but again afforded almost no zinc metal photoproduct. Additionally, there was no correlation between the electronegativity of the counterion and yield of zinc metal afforded by the use of that salt. Nor was any correlation observed between hydration of the zinc salt and yields of zinc metal.

Cyclic voltammetry was performed on zinc salts to investigate the results shown in Figure 2-6. It was initially hypothesized that the reduction of zinc halides occurred at higher potentials than their counterparts, and as such zinc halides were more easily be

reduced by $\text{Ir}(\text{ppy})_2(\text{dtbbpy})^+$ due to an increased thermodynamic driving force. This would explain the higher yield of zinc metal from zinc halides. This turned out not to be the case however, cyclic voltammetry of $\text{Zn}(\text{BF}_4)_2$ and zinc halides ZnCl_2 , ZnI_2 and ZnBr_2 revealed that the onset potential of $\text{Zn}(\text{II})$ reduction is not a predictor for the yield of zinc metal produced by photocatalytic reduction. Among the zinc halides, ZnCl_2 afforded the most zinc metal photoproduct, but its $\text{Zn}(\text{II})$ reduction peak occurred at the most negative potential. The cyclic voltammograms of the zinc halides are shown in Figure 2-7.

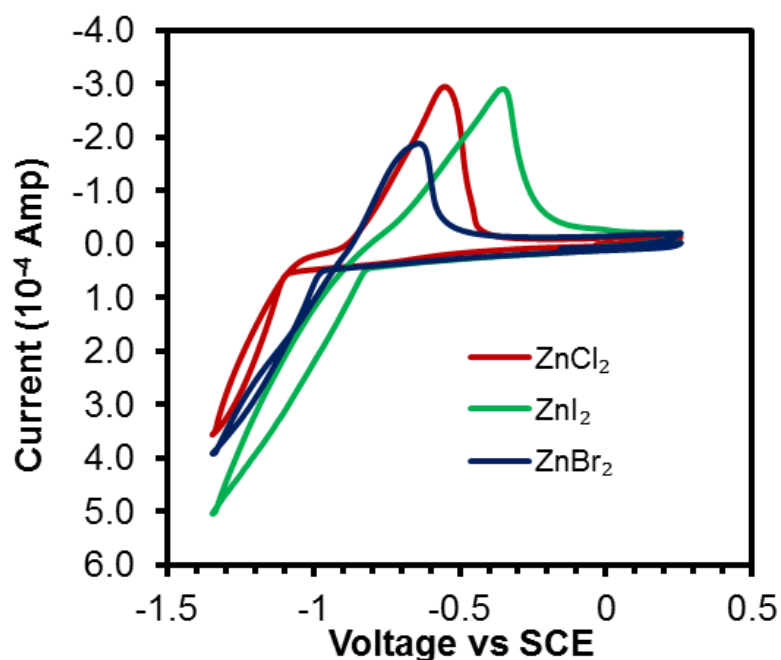


Figure 2-7 - Cyclic voltammograms of ZnCl_2 , ZnBr_2 , and ZnI_2 in acetonitrile

The onset potential of $\text{Zn}(\text{II})$ reduction is referenced instead of the more commonly used redox potential because of the unique nature of zinc salt electrochemistry. In traditional cyclic voltammetry for compounds with reversible electrochemistry, the voltages of the local current maxima in these two waves are only slightly offset due to small overpotentials. The reduction or redox potential of the redox

couple is taken as the average of these voltages. Cyclic voltammograms featuring the $\text{Zn}^{2+}/\text{Zn}^0$ redox couple differ from traditional CV scans due to the phase change that occurs. Once sufficiently negative voltages are reached, Zn(II) is reduced and the solid zinc metal is deposited onto the working electrode. As the voltage sweeps back towards the positive, the re-oxidation of zinc metal is referred to as a stripping peak due to the need for the deposited metal to resolubilize. The peak current for zinc oxidation occurs at much more positive voltages due to the solvent reorganization energy required in the phase change. The redox potential cannot be calculated conventionally and as a result, it is best to refer to the onset potential of Zn^{2+} reduction for the $\text{Zn}^{2+}/\text{Zn}^0$ redox couple. The onset potential of reduction is also most pertinent to this work, which focuses on the reduction of Zn(II) .

The inability of cyclic voltammetry to explain the success of zinc halide salts lies in the different mechanisms of Zn(II) reduction by cyclic voltammetry and an Ir(III) photocatalyst. The cyclic voltammograms in Figure 2-7 show no sign of Zn^+ , a highly unstable species. Instead, the reduction of Zn(II) at the working electrode surface is essentially a simultaneous two electron transfer in which zinc metal is produced directly. To contrast, the reduction of Zn(II) by biscyclometallated heteroleptic iridium(III) complexes either involves two sequential one electron transfers or the disproportionation between two singly reduced Zn(I) species. An Ir(I) species is not a possible candidate for the activated photocatalyst because formation of such a species is outside of the potential window of this study. In previous electrochemistry experiments it has been demonstrated that the $\text{N}^{\wedge}\text{N}$ and then the $\text{C}^{\wedge}\text{N}$ ligands of $\text{Ir(C}^{\wedge}\text{N)}_2(\text{N}^{\wedge}\text{N})^+$ complexes are reduced first.⁷⁹ Regardless, these complexes are known only to be singly reduced by TEA to produce an

$\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^0$ complex characterized by the populated π^* orbital of the $\text{N}^{\wedge}\text{N}$ ligand.^{79,132}

Either possible mechanism for the photocatalytic reduction of $\text{Zn}(\text{II})$ to zinc metal thus requires the existence of a $\text{Zn}(\text{I})$ intermediate. This species is highly unstable, is not observed in the $\text{Zn}^{2+}/\text{Zn}^0$ CV, and would likely have a short lifetime in the photoreaction environment. Relatively stable $\text{Zn}(\text{I})$ compounds are known to exist as diamagnetic Zn_2^{2+} species which bind an array of bridging ligands to form dinuclear complexes.^{133–135} It seems likely then that the success of zinc halides in the photocatalytic generation of Zn^0 is due to their capacity as bridging ligands to stabilize a $\text{Zn}(\text{I})$ intermediate. In fact, the use of ZnCl_2 over other zinc salts is necessary in some published literature for the successful synthesis of aryldiime and Cp^* stabilized $\text{Zn}(\text{I})$ - $\text{Zn}(\text{I})$ complexes.¹³³ The extension of the lifetime of a $\text{Zn}(\text{I})$ intermediate by Cl^- , I^- , and Br^- would explain the greatly increased yields of Zn^0 metals afforded by these salts and the lack of CV evidence to support their success.

The optimal solvent environment for the photocatalytic reduction of $\text{Zn}(\text{II})$ was also investigated. A variety of organic solvents were tested under otherwise identical standard conditions, with TEA remaining 10% v/v. Yields of zinc metal in THF were poor, despite the success of previous photocatalytic water reduction experiments employing the $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+/\text{TEA}$ tandem in THF.^{70,79} The highest yields of zinc metal among all solvents tested were instead obtained in acetonitrile. However, no relationship could be established between solvent polarity and the yield of zinc metal photoproduct afforded by the solvent. The solubility of ZnCl_2 was neither the highest nor the lowest in acetonitrile.

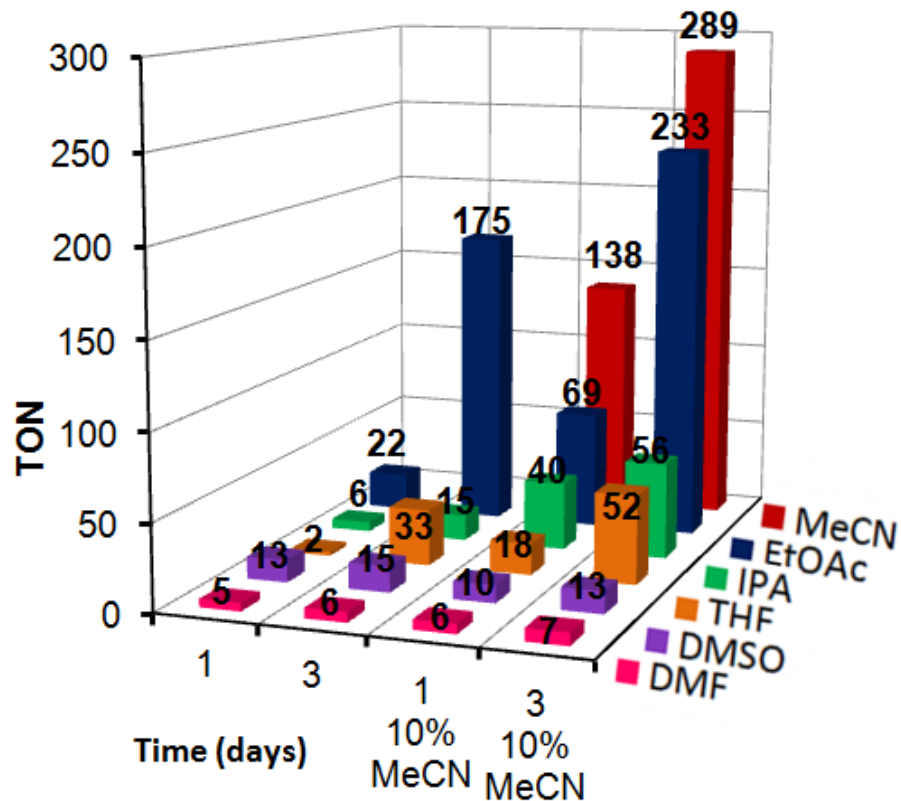


Figure 2-8 – Catalyst TONs after 24 and 72 hr in a variety of solvents. Solvents were evaluated both with and without 10% v/v acetonitrile.

To further probe the role of acetonitrile in the photocatalytic reduction of Zn(II), acetonitrile was added in 10% v/v to all other solvents tested. The complete results of the solvent study are shown in Figure 2-8. It was found that this addition of acetonitrile substantially improved the yields of zinc metal in almost all the solvents evaluated. This is particularly interesting given that at its 10% concentration, acetonitrile plays a relatively minor role in the greater solvent body and the solubility of zinc salts. It is likely that acetonitrile, a known ligand, interacts directly with the coordination sphere of Zn(II) to produce these effects. It is noteworthy that DMSO, which is also a ligand with an affinity for Zn(II), was the only solvent to produce over 10 TONs whose yield of zinc metal was not increased by the addition of acetonitrile. The effect of acetonitrile in these

small quantities is encouraging; it leaves open the possibility of replacing most of acetonitrile with a more benign solvent, ideally water.

Cyclic voltammetry of ZnCl_2 was performed in similar solvent conditions to that of Figure 2-8 in order to evaluate the effect of acetonitrile. Figure 2-9 shows cyclic voltammograms of ZnCl_2 in pure THF, and in 90% THF with 10% acetonitrile. These experiments were performed at low concentrations, below solubility limit of ZnCl_2 in THF (and MeCN). It was found that the addition of acetonitrile produces a drastically different CV. The CV of ZnCl_2 in 9:1 THF:MeCN bears a much stronger resemblance to the CV of ZnCl_2 in pure acetonitrile in Figure 2-6 than that of ZnCl_2 in pure THF. When 10% acetonitrile is added, higher currents for the reduction of Zn(II) are observed and there is a positive shift in the onset voltage of Zn(II) reduction. This shift in voltage results in an increase in the potential difference between the onset of Zn(II) reduction and reduction potential of $[\text{Ir(ppy)}_2(\text{dtbbpy})](\text{PF}_6)$ ($E_{\text{red}} = -1.18\text{V}$ vs SHE).¹²⁸ This difference in energy is ultimately responsible for the driving force of the reaction, so its increase accounts for the faster rate of photocatalysis in acetonitrile. The addition of water to these samples resulted in a dominating water reduction peak at less negative voltages than Zn(II) reduction. The Zn(II) reduction peak was obscured and nothing could be ascertained as to the effect of H_2O on the $\text{Zn}^{2+}/\text{Zn}^0$ redox couple.

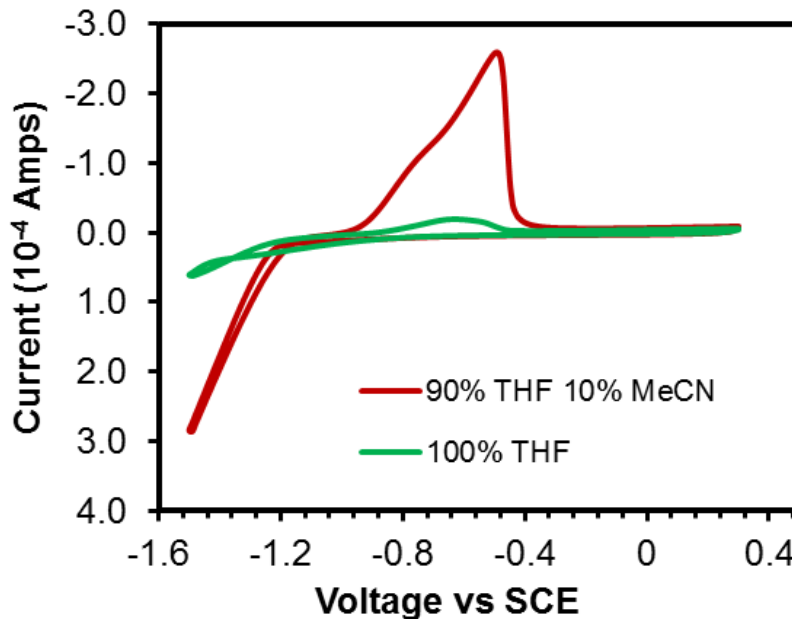


Figure 2-9 – Cyclic voltammograms of ZnCl_2 in THF and in 90% THF, 10% MeCN.

The results shown in Figure 2-9 reinforce the hypothesis that the coordination of Zn(II) by acetonitrile causes the higher yields of zinc metal photoproduct in that solvent. While the solvent study alone could permit speculation as to other mechanisms of increased zinc generation, Figure 2-9 confirms that this effect is rooted in Zn(II) electrochemistry. The stark difference voltammograms of ZnCl_2 in THF with and without 10% MeCN provides compelling evidence that this effect is caused by the coordination of acetonitrile to Zn(II) . Solvent effects insufficiently explain such a drastic change in Zn(II) electrochemistry, a change in the Zn(II) coordination environment must be occurring. This also explains the ineffectiveness of acetonitrile in increasing the yield of zinc metal when added in 10% to DMSO. MeCN has a lower ligand field splitting parameter than DMSO and would be unable to displace DMSO from coordination to Zn(II) . The shift in the onset potential of Zn(II) reduction upon bonding to MeCN can be explained by pi backbonding. The sp hybridized MeCN ligand has low lying π^* orbitals

which could accept electron density from an electron rich metal center such as the d10 Zn(II) cation. A loss of electron density would make Zn(II) more prone to reduction, thus explaining the increased photogeneration of zinc metal in acetonitrile. Figure 2-10 illustrates this scheme.

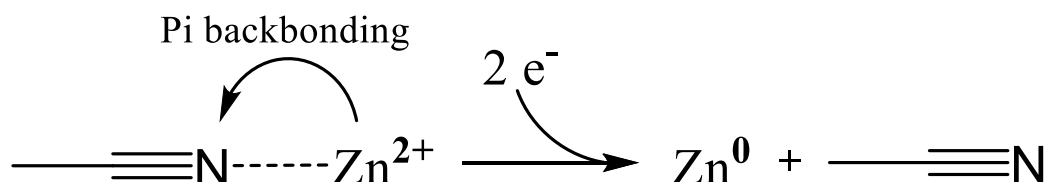


Figure 2-10 – Proposed coordination between Zn(II) and acetonitrile

In addition to organic solvents, the effect of water on the photocatalytic reduction of Zn(II) to zinc metal was examined. It was found that addition of small quantities of water, down to 50 μl /10 ml completely inhibited the ability of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ to photocatalytically reduce Zn(II). The production of H_2 coincided with the addition of water, as can be seen in Figure 2-11. The inhibition mechanism can be characterized as noncompetitive due to the steep drop in zinc generation and gradual rise in H_2 evolution. Water likely plays an active role in inhibiting the Zn(II) reduction process and does not simply compete with Zn(II) for electrons from $\text{Ir}(\text{ppy})_2(\text{dtbbpy})^0$. Given the strong affinity of ZnCl_2 for H_2O , the addition of H_2O could readily displace MeCN bound to Zn(II). This would eliminate the positive potential shift in the onset of Zn(II) reduction, likely shifting the potential more negative than even when both MeCN and H_2O are absent. As stated earlier, the effect of H_2O on the $\text{Zn}^{2+}/\text{Zn}^0$ redox couple could not be discerned due to the overwhelming H_2O reduction peak seen on the CV which obscured the Zn(II) reduction peak.

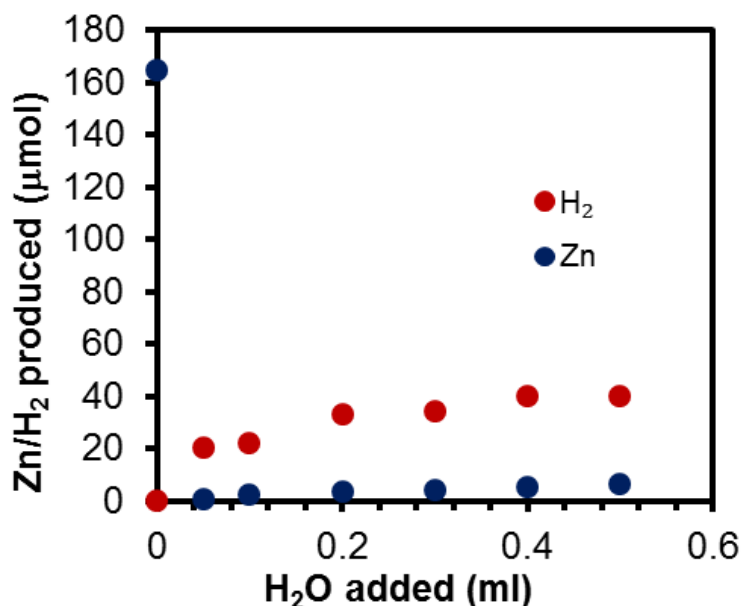


Figure 2-11 – The effect of added H₂O on the yields of zinc metal and hydrogen gas via photocatalytic reduction by [Ir(ppy)₂(dtbbpy)](PF₆) under otherwise standard conditions.

The dominance of MeCN on the coordination environment is further supported by the lack of TEA coordination to Zn(II). ¹H NMR spectra of TEA in a solution d₃-MeCN remained unchanged upon the addition of ZnCl₂. If TEA were to coordinate ZnCl₂, shifted peaks corresponding to bound TEA would be expected. Alternatively, if TEA coordinated ZnCl₂ but underwent rapid exchange, broader TEA peaks in the ¹H NMR spectra would be observed. Still, these results are surprising because relative to MeCN, TEA is expected to have stronger affinity for Zn(II) due to its additional electron density. Additional investigation into the coordination sphere of the active Zn(II) reactant would be required for a clearer understanding of the mechanism.

Kinetics Studies

To further investigate the mechanism of photocatalyzed Zn(II) reduction, several kinetics experiments were performed. One such experiment was the investigation of the

catalyst lifetime of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$, which is an important parameter in assessing the viability of any solar fuels photocatalyst. At $110\ \mu\text{M}$ $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$, 430 catalyst TONs were observed after 10 days. Photocatalytic activity had largely decreased before that, after approximately 100 hr. The rate of photocatalytic Zn(II) reduction was largely constant over the first 24 hr of the reaction. Figure 2-12 shows these results. The data shows a strong first order decay fit, which is also shown in Figure 2-12.

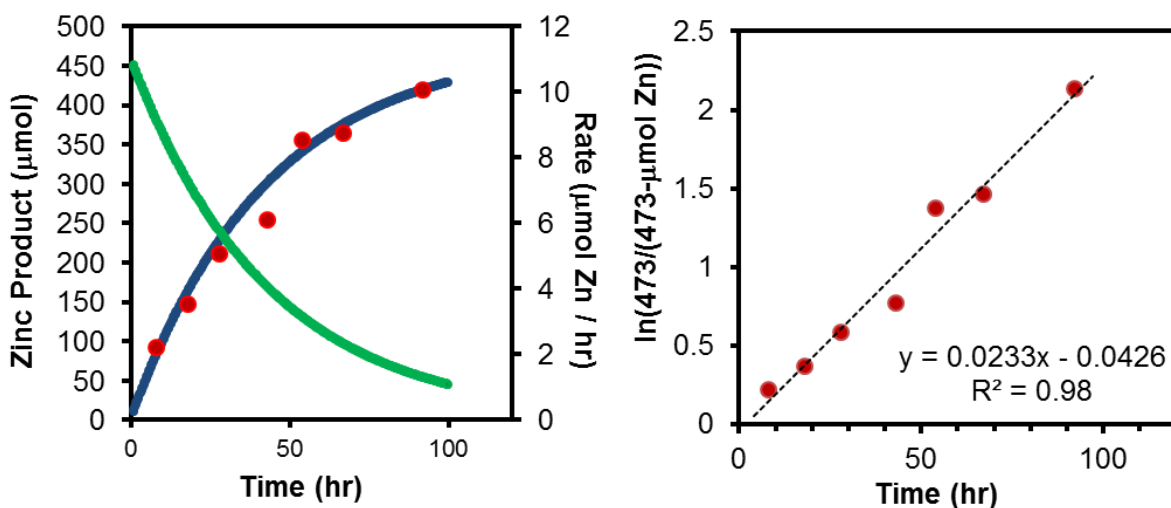


Figure 2-12 – Left – Yield of zinc metal generated over illumination time (red). The initial rate equation (green) and optimal kinetic fit are also given (blue). Right – The linearized kinetic fit for the first order decay of zinc metal generation.

This decrease in zinc photogeneration over time could possibly be attributed to the consumption of ZnCl_2 , TEA, or the degradation of the photocatalyst. The consumption of TEA is not a likely culprit. The reductive quenching of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ by TEA is very strong and the rate of quenching will not change over the range of TEA concentrations seen in these experiments.⁷⁰ The consumption of ZnCl_2 is also likely not the case. ZnCl_2 is saturated in the reaction solutions, so the initial rate would be expected to be constant over a longer period of time before the onset of decay if decay were due to a decrease of ZnCl_2 . Unfortunately due to the insoluble nature

of ZnCl_2 in MeCN, it was not possible to add more ZnCl_2 to the photoreaction vial after commencement of illumination. However it is most likely that first order decay occurs due to the decay of the iridium photocatalyst. $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+$ complexes are known to decay in similar water reduction experiments by the dissociation of $\text{N}^{\wedge}\text{N}$ diimine ligand.⁷³ Such a mechanism is consistent with the first order decay observed in Figure 2-12.

Initial rate kinetics of photocatalyzed $\text{Zn}(\text{II})$ reduction by $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ were also studied. The effect of photocatalyst concentration on the initial rate was first investigated. For any given concentration of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$, samples were taken after 1, 2, 4, and 8 hr of illumination and the Zn^0 produced was measured. The initial rate was determined for each of these concentration values from the plot of zinc produced over time. This basic experiment was carried out over a range of photocatalyst concentrations, from 25 to 200 μM , under otherwise standard conditions. The results are given in Figure 2-13. A best fit equation for the plot of rate vs concentration of $\text{Ir}(\text{ppy})_2(\text{dtbbpy})^+$ could then also be generated, also shown in Figure 2-13. The linear fit of this plot indicates that the dependence of initial rate upon concentration of iridium photocatalyst is first order in nature.

This first order dependence is consistent with consecutive electron transfers from a single photocatalyst both to a single $\text{Zn}(\text{II})$ ion to produce Zn^0 and also the single reduction of two individual $\text{Zn}(\text{II})$ ions which then disproportionate to produce Zn^0 . However it is noteworthy that this is also consistent with the radical species generated from initial TEA oxidation directly reducing $\text{Zn}(\text{II})$. In this latter scenario, on average one electron used to generate zinc metal from $\text{Zn}(\text{II})$ would be transferred from the reduced

iridium photocatalyst and one electron would be transferred directly from this organic radical.

Either way, a disproportionation mechanism is likely. The reduction of Zn(II) to Zn(I) is likely the rate limiting step, it is much more energy intensive than the reduction of Zn(I) to zinc metal. Due to the significant energy required to generate Zn(I), disproportionation between two Zn(I) species to yield Zn(II) and Zn⁰ is common. Such disproportionation has been an obstacle to the synthesis of Zn(I)-Zn(I) complexes, which were first synthesized relatively recently, in 2004.¹³³ Low temperatures (< 0 °C) and the absence of air were required for successful synthesis of these Zn(I)-Zn(I) complexes.¹³⁶ Compounds such as methanol and isocyanide with few discernable common properties are known to induce disproportionation, which underscores the instability of Zn(I)-Zn(I) complexes. Given that photoreactions in this work are employed at room temperature, disproportionation of a Zn(I)-Zn(I) species is the likely route to zinc metal generation.

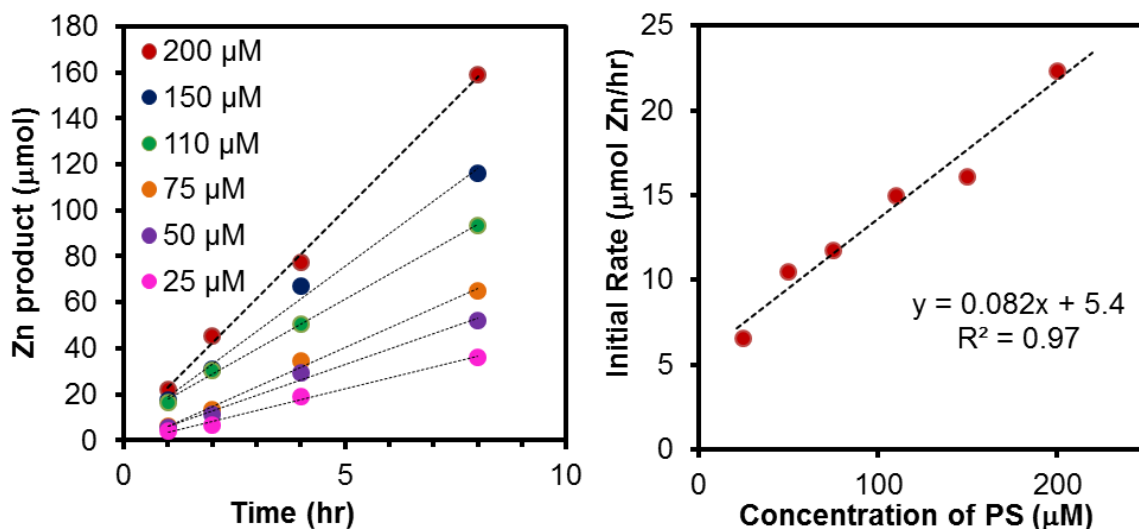


Figure 2-13 - Initial zinc production at various concentrations of [Ir(ppy)₂(dtbbpy)](PF₆) under otherwise standard conditions (left). First order kinetic dependence of the initial reaction rate on concentration of the [Ir(ppy)₂(dtbbpy)](PF₆) (right).

Similar initial rate studies were also performed by instead the varying the mass concentration of ZnCl_2 added as a reagent. At different mass concentrations of ZnCl_2 that ranged from 125 to 420 mg / 10 ml, the initial steady state production of zinc was measured under otherwise standard conditions. For each mass concentration of ZnCl_2 tested, samples were taken after 1, 2, 4, and 8 hr of illumination and the Zn^0 produced was measured. Initial reaction rates were calculated from the best fit lines of zinc production over the initial 8 hr time period. Initial rate was then plotted against the mass concentration of ZnCl_2 to determine the dependence of the initial reaction rate on the mass concentration of ZnCl_2 . Mass concentration of ZnCl_2 is employed instead of traditional concentration because ZnCl_2 was saturated in the photoreaction mixture. These results are shown in Figure 2-14. A first order dependence of the initial rate on the mass concentration of ZnCl_2 was observed.

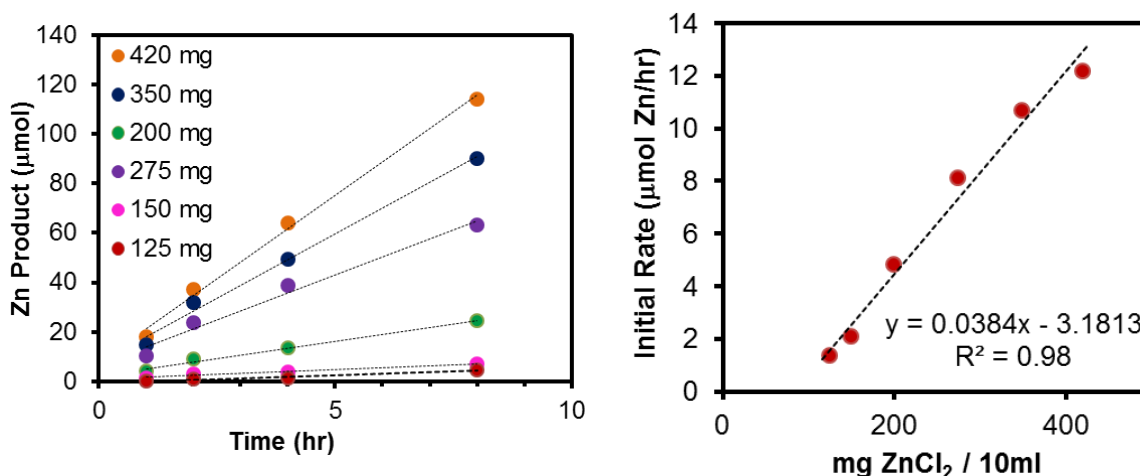


Figure 2-14 - Initial zinc production at various mass concentrations of ZnCl_2 under otherwise standard conditions (left). First order kinetic dependence of the initial reaction rate on ZnCl_2 mass concentration (right).

The Case for a Heterogeneous Reaction

The results shown in Figure 2-14 are not consistent with the expectations of a homogeneous reaction pathway. It would be expected in a homogeneous reaction where solubilized Zn(II) is reduced that reaction rates would decrease after saturation of the reaction solution by ZnCl₂. With no increase in any reagent concentration, the addition of insoluble ZnCl₂ would increasingly block light solution, decreasing the concentration of activated catalyst and in turn the reaction rate as well. Instead, the reaction rate increases as mass concentration of ZnCl₂ increases beyond the saturation of the reaction mixture. This is consistent with a heterogeneous mechanism, where insoluble ZnCl₂ is reduced by the iridium photocatalyst. Additionally, the kinetic fit shown on the right in Figure 2-14 has a positive x intercept, which indicates that there is a minimum concentration of ZnCl₂ required for photocatalytic Zn(II) reduction to proceed. This x intercept lies approximately at the solubility limit of ZnCl₂ in the 9 MeCN : 1 TEA reaction solvent. When low mass concentrations of ZnCl₂ are used (< ~100 mg ZnCl₂ / 10 ml), all ZnCl₂ is dissolved and the reaction does not proceed. It should be pointed out that the first order rate dependence shown in Figure 2-14 is atypical of heterogeneous reactions, which typically adhere to more complicated kinetics. However, an R² of 0.98 was observed for this reaction, so it is possible that a larger data set would elucidate more nuanced kinetic trends.

The case for a heterogeneous reaction mechanism was further substantiated through attempts to improve the performance of non-halide zinc salts. Sodium chloride was added to a photoreaction containing Zn(BF₄)₂ under otherwise standard conditions in an attempt to improve the yields of zinc generated by the use of Zn(BF₄)₂ alone, which

Figure 2-6 shows to be quite low. Sodium chloride was used as a source of Cl^- in hopes of duplicating the success of ZnCl_2 as a Zn(II) source, also shown in Figure 2-6. In a homogeneous reaction, the source of Cl^- should be irrelevant because the salt(s) would dissolve the Zn^{2+} and Cl^- would be free to interact. The chloride ion could stabilize a Zn(I) as postulated, or otherwise coordinate a zinc species to aide in the photocatalytic generation of zinc metal. Therefore it is anticipated that in a homogeneous reaction, the use of NaCl and $\text{Zn}(\text{BF}_4)_2$ a photoreaction would afford similar yields of zinc metal as to the use of ZnCl_2 . However this was not the case. The addition of NaCl to a photoreaction containing $\text{Zn}(\text{BF}_4)_2$ failed to increase the yields of zinc metal compared to photoreactions in which exclusively $\text{Zn}(\text{BF}_4)_2$ was employed. This strongly indicates a heterogeneous reaction in which undissolved ZnCl_2 is reduced to zinc metal.

Conclusion

Heteroleptic biscyclometallated iridium(III) catalysts of the general formula $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})](\text{PF}_6)$ were proven to be effective catalysts in the photon driven reduction of Zn(II) to zinc metal. In these experiments, triethylamine was used as a sacrificial reductant to reductively quench the excited iridium photocatalyst, similar to previous water reduction experiments. Light, TEA, an Ir(III) photocatalyst, and an argon atmosphere all proved necessary for zinc reduction, the removal of any of which failed to afford zinc metal. X-Ray diffraction confirmed the product to be zinc metal.

Experimental parameters were varied in order to investigate the reaction mechanism and optimize photocatalytic yield. Several Ir(III) complexes were evaluated for their ability to photocatalyze the reduction of Zn(II), with $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$

achieving the highest yields. It was found that a metal to ligand charge transfer triplet ($^3\text{MLCT}$) excited state was required for successful catalysis. Acetonitrile was found to be the most effective solvent. The addition of 10% acetonitrile proved to substantially increase the yields of zinc metal in other solvents. Cyclic voltammetry revealed that acetonitrile increased the rate and positively shifted the onset potential of Zn(II) reduction. This potential shift resulted in an increased thermodynamic driving force of the reaction, thus explaining the higher yields of zinc metal in MeCN. Direct coordination of acetonitrile to zinc is the most plausible explanation for this potential shift. Water was found to inhibit the photocatalytic reduction of Zn(II) by $[\text{Ir(ppy)}_2(\text{dtbbpy})](\text{PF}_6)$.

Among the zinc salts evaluated, zinc halides were found to afford the highest yields of zinc metal. Cyclic voltammetry of ZnCl_2 , ZnBr_2 , and ZnI_2 revealed no relationship between the electrochemistry of the zinc salt and the zinc metal photoproduct yielded by the use of that salt. The halide counterion then must stabilize or otherwise interact with a reaction intermediate that was not generated in the CV, likely an unstable Zn(I) species.

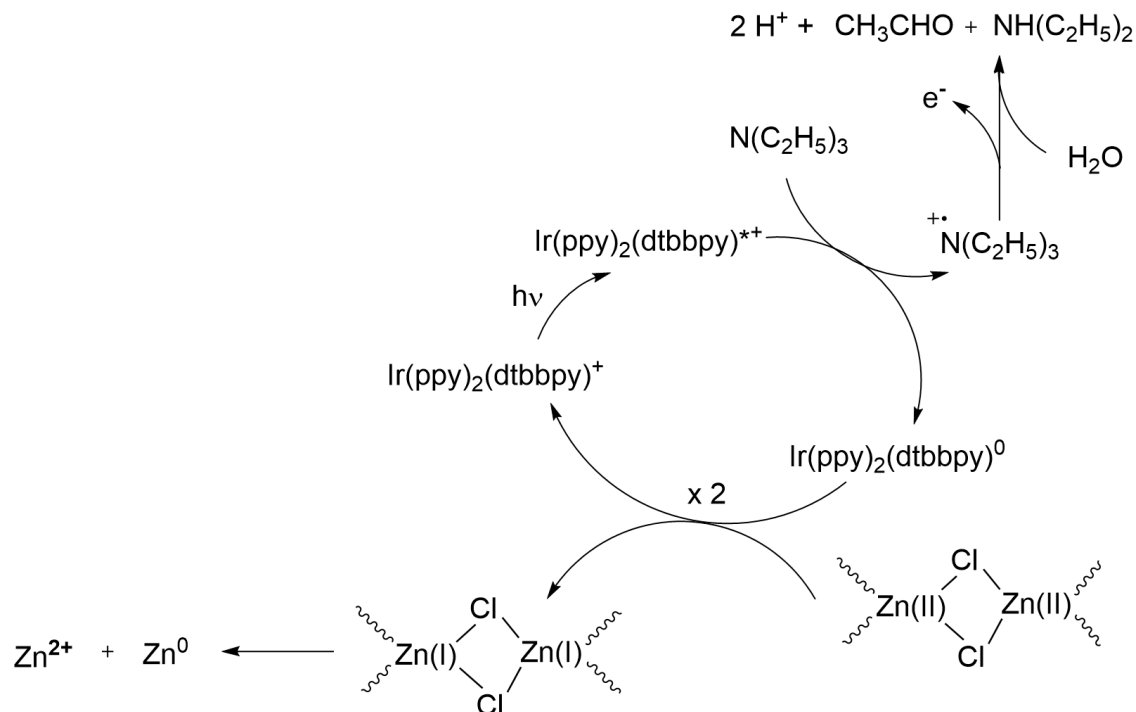


Figure 2-15 Postulated mechanism of photocatalyzed reduction of Zn(II) to zinc metal by $\text{Ir}(\text{ppy})_2(\text{dtbbpy})^{+*}$ with triethylamine as a sacrificial electron source.

Reaction kinetics were also investigated. Decay in zinc production over illumination time was found to be first order. A total of 430 catalyst TONs were achieved after 10 days. Initial rate kinetics were also investigated. The initial rate of photocatalyzed zinc reduction was determined to have a first order dependence on the concentration of iridium photocatalyst. A first order relationship was also found for the dependence of the initial rate on the mass concentration of ZnCl_2 . The existence of a minimum mass concentration of ZnCl_2 required for the generation of zinc metal and the increase of initial rate with the increase in mass concentration of ZnCl_2 beyond saturation engendered the possibility of a heterogeneous reaction mechanism. This possibility was substantiated by the failure of the addition of NaCl to photoreactions containing $\text{Zn}(\text{BF}_4)_2$ to increase yields of zinc metal, despite the success of ZnCl_2 as a Zn(II) source. Figure 2-15 depicts a basic reaction scheme for the photocatalytic reduction of Zn(II) to zinc metal

by an iridium photocatalyst, including the reductive quenching of $\text{Ir(ppy)}_2(\text{dtbbpy})^{+*}$ and the reduction of insoluble ZnCl_2 .

Chapter 3. Photocatalyzed Reduction of Zn(II) by Zinc Quinolate Catalysts formed In-Situ

Introduction

One issue with the photocatalytic system for Zn(II) reduction described in chapter 2 is the use of an iridium photocatalyst. Despite the remarkable photophysical properties of bis-cyclometallated iridium(III) complexes, iridium is not the ideal metal for use in such systems. Iridium is rare and expensive, it is among the rarest of all elements found in the earth's crust. The use of iridium deters both the commercial viability and potential for widespread use of such a photocatalytic system. It would be prudent to replace iridium with a less expensive, more abundant metal. In accord with this rationale, this chapter describes the photocatalytic reduction of Zn(II) by zinc quinolates that form in situ. Zinc is ideal among potential first row transition metals, which mostly meet the low cost and high abundance criteria. The use of zinc as a catalyst eliminates the requirement of adding an additional metal (such as iridium) to photoreaction mixtures that are already rich in zinc. This system combines the price benefits of organocatalysis with the established, desirable properties of transition metal complexes. In commercialization, processing costs would also be greatly reduced and the potential for contamination of zinc metal or zinc chloride with other metals would be eliminated.

A further advantage of the work documented in this chapter is that the zinc quinolates are synthesized in situ through chelation, which has additional advantages. In situ catalyst formation eliminates the need for catalyst synthesis, which cuts costs further. When 8-hydroxyquinoline ligands are added to the photoreaction mixture they

spontaneous coordinate Zn(II) in situ to form a mono-substituted zinc quinolate photocatalyst. This zinc quinolate then acts similarly to $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ in the previous chapter by catalyzing the photon driven reduction of Zn(II) by a similar means as in chapter 1. The general scheme for this approach is shown in Figure 3-1.

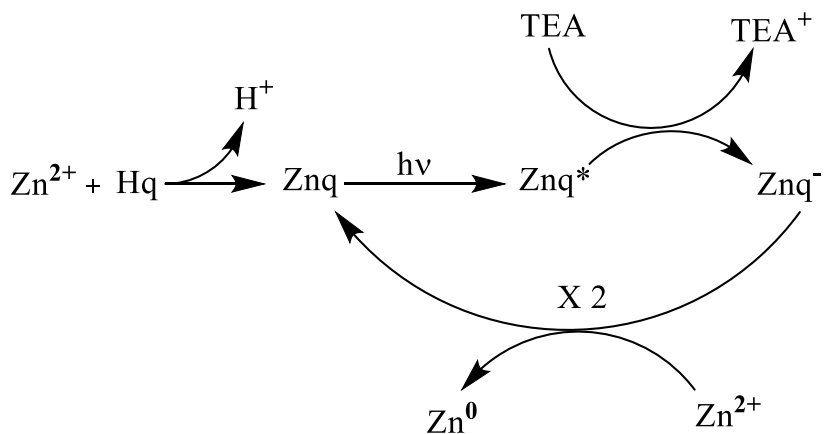


Figure 3-1 - A basic scheme of the photocatalytic reduction of Zn(II) by a zinc quinolate formed in situ described in this chapter.

To date, solar fuels catalysts that form in situ have relied upon the reducing or oxidizing environments to which they are subjected. Platinum salts such as K_2PtCl_4 have been found as effective precursors to platinum colloids, which are reduced in situ by the PS prior to photocatalytic water reduction.^{79,137} Platinum colloids formed in this manner are highly effective water reduction catalysts. Cobalt salts have been used in a parallel way as water oxidation catalysts. Effective electrocatalysts for water oxidation have been synthesized by the exposure of cobalt(II) salts to anodic currents. The films are generally amorphous and have a low overpotential for water oxidation but their compositions vary. Both cobalt tungstenates and cobalt phosphates have been deposited by this method and exhibit promise as water oxidation catalysts.^{138,139} The cobalt phosphate films have also been touted as self-healing. When these cobalt electrodes are deposited onto photoelectrochemical devices they will leach cobalt(II) back into solution over the course

of water oxidation catalysis under open circuit conditions. However it has been demonstrated that an applied voltage of 1.3 V vs NHE will re-deposit the cobalt onto the electrode and extend the lifetime of this WOC.¹⁴⁰ Self-healing is thus another appealing aspect of catalysts generated in situ.

Self-healing of in situ formed zinc quinolate photocatalysts in this chapter could potentially occur by ligand dissociation and re-ligation. Ligand dissociation is thus eliminated as a potential decay mechanism, so any catalyst decay would then require the degradation of the fused-ring quinolone architecture. The in situ mechanism of catalyst formation depicted in this work is further advantageous because unlike previous in situ catalysts, the zinc quinolate catalysts form spontaneously without reductive or oxidative force. 8-hydroxyquinoline ligands have been utilized in this role in part because they have a documented ability to chelate Zn(II).¹⁴¹ Zinc quinolates were also targeted as second generation catalysts because they exhibit similar properties as the Ir(III) complexes utilized in chapter 1 that meet the requisites of solar fuels catalysts. Quinolates were discussed in detail earlier in chapter 1, so they will not be discussed further here.

The description of the photocatalytic reduction of Zn(II) by zinc quinolates formed in situ given in this chapter is primarily drawn from results published by the author in Chemical Communications in 2014.¹⁴² Reaction conditions and kinetic studies were performed similar to those documented in chapter 2 for Ir(III) complexes. These studies helped confirm the reaction mechanism postulated earlier. ¹H NMR titration studies and fluorescence quenching experiments were also employed to investigate the identity of the active catalyst.

Experimental Methods

Materials – All materials were used as received. ZnCl_2 and other zinc salts were purchased from Sigma. Triethylamine was purchased from Acros Organics, and Acetonitrile (MeCN) was purchased from Fisher Scientific. All ligands, including 5,7-dichloro-8-hydroxyquinoline, were purchased from VWR International.

Synthesis of bis(5,7-dichloro-8-hydroxyquinolinato) zinc complexes – Zn(dCl-q)_2 was synthesized as a reference compound according to previously established procedures.⁸⁹ The product was purified by recrystallization in acetone.

Custom-Built Photoreactor- 8-hydroxyquinoline ligands were evaluated as catalyst precursors in the same home-built photoreactor described earlier in chapter 2.

General Procedure for Set-Up of Photoreactions – The zinc-generating photoreactions detailed in this chapter were all set up in a uniform manner to ensure directly comparable results. Similar to chapter 2, photoreaction samples were prepared in 40 mL EPA vials sealed by open top caps containing a fluoropolymer resin/silicone septa (ICHEM SB36-0040). Zinc chloride or the appropriate zinc salt was massed directly into the vial. All photoreaction vials contained a small stir bar. Stock solutions of the 8-hydroxyquinoline photocatalyst precursor were prepared in the appropriate solvent, commonly acetonitrile. Aliquots of these stock solutions were added to each vial in order to evenly and accurately distribute the ligand in the desired concentration. Standard photoreaction conditions consisted of 300 μM dCl-Hq, 420 mg ZnCl_2 , 9 total ml of MeCN, and 1 ml TEA. Before illumination, sample vials were degassed by cycling 6 times between vacuum and Ar atmosphere. The final cycle of argon atmosphere was adjusted to atmospheric pressure by the purging of the overpressure through a bubbler.

General Procedure for Work-Up of Photoreactions – Zinc generating photoreactions in this chapter were worked up by the same procedure as described in chapter 2. Vials were purged with argon, and acidified with 2 ml of concentrated HCl to evolve H₂. Zinc metal was quantified in a calibrated Stanford Research Systems QMS200 Gas Analyzer. The stoichiometric evolution of H₂ upon the acidification of zinc metal was verified using pre-massed zinc as a control.

Multiple 8-Hydroxyquinoline ligands study – Aliquots of stock solutions of each 8-Hq ligands in Figure 3-2 were added to the appropriate photoreaction vial for a final concentration of 300 μ M in each. Each vial also contained 9 ml MeCN, 1 ml TEA, 420 mg ZnCl₂. The samples were set up and worked up after 68 hr according to the general procedure outlined earlier.

Zinc Salt study- Each photoreaction vial contained 9 ml MeCN, 1 ml TEA, 300 μ M dCl-Hq, and 2.01 mmol of each zinc salt. Each zinc salt was massed directly. The samples were set up and worked up after 72 hr according to the general procedures outlined earlier.

Solvent study - Each photoreaction vial contained 9 ml MeCN, 1 ml TEA, 300 μ M dCl-Hq, and 420 mg of ZnCl₂. Stock solutions of dCl-Hq were made in each solvent used for this study. Anhydrous solvents were used where applicable. The samples were set up and worked up after 68 hr according to the general procedures outlined earlier.

H₂O Concentration study – ZnCl₂ was dried in a vacuum oven under heat and low pressure for 3 days. The dried ZnCl₂ was massed, and stored under argon. To determine degree of hydration, the dried ZnCl₂ was dissolved in H₂O, and titrated with an aqueous solution of EDTA to determine the molecular weight and thus degree of hydration of the

dried ZnCl_2 . Xylenol orange was used as an indicator. The EDTA was standardized against high purity calcium carbonate. Into each photoreaction vial, 420 mg of the dried ZnCl_2 was massed. H_2O was quickly added to each photoreaction vials after an initial serial dilution with acetonitrile. Each photoreaction vial also contained 1 ml TEA, 300 μM dCl-Hq, and 9-x ml MeCN, where x = ml H_2O added. The samples were immediately set up and then worked up after 24 hr according to the general procedures outlined earlier.

^1H NMR Titration study – Stock solutions of 9 mM ZnCl_2 and 9 mM dCl-Hq were prepared in d_3 -MeCN. Into each NMR tube, 185 μl of the ZnCl_2 stock solution and 79 μl of TEA were added. An aliquot of the dCl-Hq stock solution was added to each tube to obtain the desired ratio of dCl-Hq to ZnCl_2 . Deuterated acetonitrile was used to bring all samples to a constant volume of 0.75 ml. For the three highest ratios of ligand to ZnCl_2 (2.52:1, 2.94:1, and 4.40:1) it was necessary to add less ZnCl_2 stock solution in order to maintain constant volume. TEA was used as an internal standard in the calculation of the concentrations of each species observed in the ^1H NMR spectra. A Bruker 500 MHz NMR Spectrometer was employed in these studies.

Fluorescence Quenching study – Separate 5 mM stock solutions of ZnCl_2 and dCl-Hq in acetonitrile were prepared. Three quinolate stock solutions were then prepared: dCl-q, $\text{Zn}(\text{dCl-q})_1$, $\text{Zn}(\text{dCl-q})_2$. The dCl-q stock solution contained only one part dCl-Hq stock solution and two parts acetonitrile. The $\text{Zn}(\text{dCl-q})_1$ stock solution contained one part ZnCl_2 stock solution, one part dCl-Hq stock solution, and one part acetonitrile. The $\text{Zn}(\text{dCl-q})_2$ stock solution contained one part ZnCl_2 stock solution, one part dCl-Hq stock solution, and one part acetonitrile. All three stock solutions also contained TEA in 5

times molar excess relative to the quinolate species. For the quenching study, TEA was aliquotted (via serial dilution in MeCN) into each quinolate stock solution (dCl-q, Zn(dCl-q)_1 , Zn(dCl-q)_2) in an appropriate volume for that data point. For each photoluminescence measurement a new aliquot of the appropriate stock solution was taken and the desired amount of TEA was added. Samples were purged in MeCN-saturated argon for 5 minutes prior to photoluminescence measurement.

Photoluminescence was measured on a Fluorolog-3 equipped with dual monochromators and a photomultiplier tube at right angle geometry. Values given in Figure 3-12 were corrected for the slight dilution of the quinolate stock solution by the addition of the variable amount of TEA.

Catalyst Degradation ^1H NMR study – Samples were prepared on a half scale relative to standard conditions in deuterated acetonitrile. Two vials were prepared each with 210 mg ZnCl_2 , 300 μM dCl-Hq, 4.5 ml $\text{d}_3\text{-MeCN}$, and 0.5 ml TEA. The samples were set up according to the general procedures outlined earlier. After 96 hr of illumination time, samples were removed from light and the contents were allowed to settle. A syringe with a 4 inch needle was used to draw some of the supernatant photoreaction solution from the vial, which was then transferred to an NMR tube. A Bruker 500 MHz NMR Spectrometer was employed in this study.

Initial Rate Kinetics – Zinc Chloride study – All ZnCl_2 was massed directly into the photoreaction vials. Each vial contained 9 ml MeCN, 1 ml TEA, 300 μM dCl-Hq, and ZnCl_2 . The samples were set up and worked up after 1, 2, 4, and 8 hr according to the general procedures outlined earlier. At each time interval, one sample at each mass concentration of ZnCl_2 employed was measured for yields of zinc metal.

Initial Rate Kinetics – dCl-Hq study- Aliquots were taken from a stock solution of dCl-Hq in acetonitrile to ensure accurate concentrations in each photoreaction vial. Each vial also contained 9 ml MeCN, 1 ml TEA, and 420 mg ZnCl_2 . The samples were set up and worked up after 1, 2, 4, and 8 hr according to the general procedures outlined earlier. At each time interval, one sample at each concentration of dCl-Hq employed was measured for yields of zinc metal.

Kinetics – Catalyst Decay study - dCl-Hq was aliquotted from a stock solution to each vial for a concentration of 300 μM . Each photoreaction vial also contained 9 ml MeCN, 1 ml TEA, and 420 mg ZnCl_2 . The samples were set up and one was worked up after the appropriate time interval according to the general procedures outlined earlier.

Results and Discussion

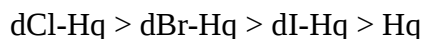
Photocatalyzed Reduction of Zn(II) by Quinolates

The production of zinc metal was observed when ZnCl_2 was added to solutions of TEA and 8-hydroxyquinoline (Hq) in acetonitrile and exposed to visible light under argon. The omission of light, TEA, 8-hydroxyquinoline, or argon all inhibited the generation of zinc metal. 8-hydroxyquinoline was only required in catalytic quantities, whereas stoichiometric amounts of TEA (and ZnCl_2) were necessary. Given the known chelation of Zn(II) and other metals by 8-hydroxyquinoline ligands, the formation of a zinc quinolate species appeared likely. This was confirmed by the discovery of a mono-substituted zinc quinolate to be the active catalyst, which is discussed at length later in this chapter. Although the quenching of zinc quinolates by TEA is previously undocumented, a reductive quenching mechanism similar to that documented for Ir(III)

photocatalysts in chapter 2 is likely. Solid state electron transfer reactions between amines and excited zinc quinolates has already been established in OLEDs. In such OLEDs, a zinc quinolate (eg. Znq₂) serves as the electron transporting material and cycles between its excited state, ground state, and reduced state. Tertiary aromatic amines such as polyvinyl carbazole and triphenylamine derivatives are common hole transporters in these OLEDs.^{90,91} Anhydrous ZnCl₂ was ineffective in affording any zinc metal photoproduct. This indicates that water from the ZnCl₂ crystal lattice is used as the oxygen source in the oxidation of TEA to acetaldehyde, as was the case in chapter 2.

Various ligands with the basic 8-hydroxyquinoline architecture were evaluated as precatalysts for Zn(II) photoreduction. The basic Hq architecture was varied primarily by incorporating electron withdrawing groups (EWGs) at the 7, 5, and 2 positions, which are labeled as R₂, R₁, and R₃ respectively in Figure 3-2. Unlike with the iridium(III) photocatalysts, noticeable structure-activity relationships were observed for the 8-hydroxyquinoline precatalysts. It was found that the addition of electron withdrawing substituents on the phenol ring at the 5 and 7 positions generally resulted in a higher yield of zinc metal. Complete results of this study are given in Figure 3-3. Exceptions to this trend can largely be attributed to solubility. To illustrate, the sulfonic acid moiety on 5-sulfonic acid-8-hydroxyquinoline (5-SO₃H-Hq) is very electron withdrawing, but the ligand had poor solubility in the reaction mixture, which may have contributed to its low yields of Zn⁰. It is also worth considering that the substituents of some of these ligands may also have an affinity for Zn(II). The coordination of such a quinoline ligand at this auxiliary site would alter the electron density of the ligand and have effects on photocatalytic performance that are difficult to predict.

When these factors are controlled for, increasingly electronegative substituents at the 5 and 7 positions of the Hq ligand clearly increase the yields of zinc metal photoproduct. The halide substituted 8-hydroxyquinoline ligands are an excellent representative example of this trend. All the halogenated Hq ligands employed in this study had similar solubility as the unsubstituted Hq in 9 MeCN : 1 TEA. Additionally, the halogenated quinoline ligands have no metal binding sites beyond the imine and hydroxyl groups common to all Hq derivatives. For the halogenated 8-hydroxyquinolines, it was found that stronger electron withdrawing groups resulted in higher yields of zinc metal. Among all ligands tested, 5,7-dichloro-8-hydroxyquinoline (dCl-Hq) was the most effective and was used in subsequent experiments throughout this chapter. The di-halogenated ligands can clearly be ranked by yield of zinc metal as follows:



The degree of substitution also had a similar effect. The chlorinated 8-hydroxyquinolines can be ranked by yield of zinc metal as follows:

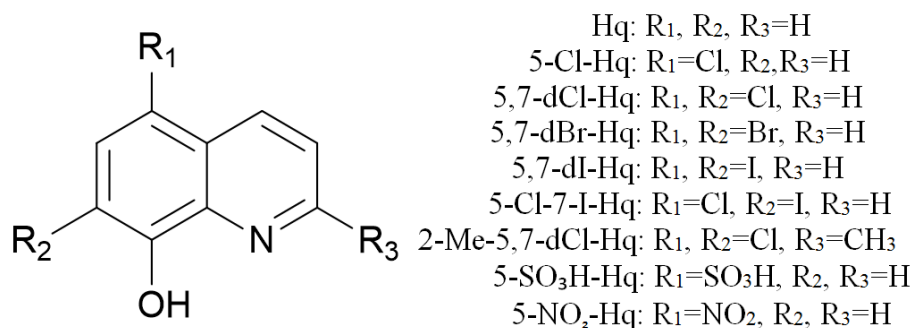
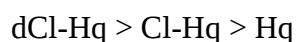


Figure 3-2 – The structure and abbreviations of the 8-hydroxyquinoline ligands tested as precatalysts in Figure 3-3.

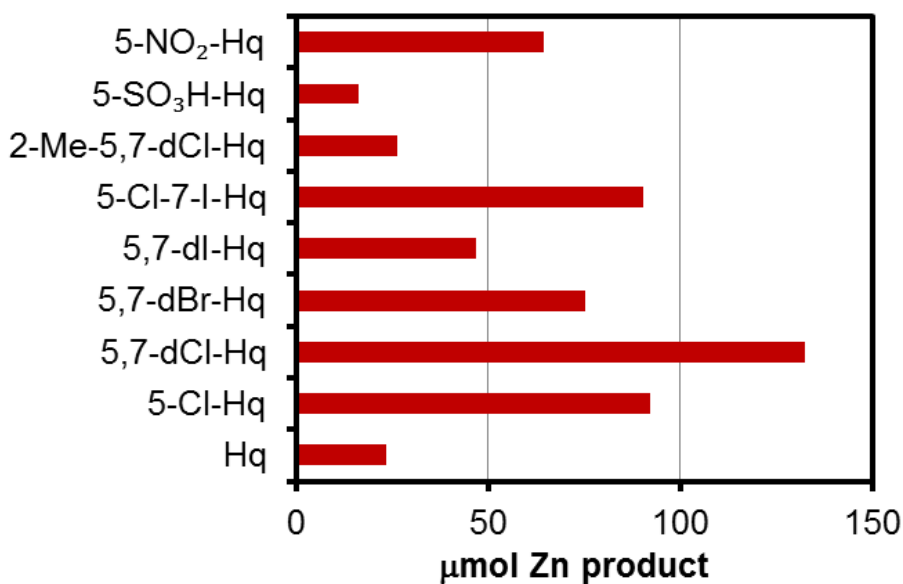


Figure 3-3 – The yields of zinc metal afforded by various 8-hydroxyquinoline precatalysts after 68 hr of illumination under otherwise standard conditions.

Both the HOMO and LUMO of Znq₂ are ligand centered so it is expected that alterations to the Hq structure would impact both participating orbitals in this π to π^* excited state transition. However, because the HOMO is located primarily over the phenol of Znq₂ and derivatives, the EWGs at the 5 and 7 positions of Hq are expected to stabilize the HOMO to a greater degree. A larger drop in the HOMO energy level is expected thus expected to be accompanied by a lower drop in the energy level of the LUMO. A slight blue shift should result, which has been empirically verified in the literature. Depending on the excitation wavelength, the peak luminescence of Znq₂ occurs at either 535 or 567 nm.⁹⁰ The peak photoluminescence intensity of Zn(dCl-q)₂ is blue shifted less than 20 nm to 528 and 545 nm respectively.^{89,143}

Optimization of Reaction Conditions

Reaction conditions of photocatalyzed Zn(II) reduction were optimized by similar experiments to those performed in chapter 2. Several aspects of the mechanism postulated in chapter 2 were found to be independent of the catalyst identity. These mechanistic details include: the coordination of free Zn(II) by MeCN, the reduction of insoluble zinc salts, and the more effective stabilization of a Zn(I) intermediates by zinc halides than other zinc salts. In order to substantiate these hypothesis it must observed MeCN is the preferred solvent, insoluble ZnCl₂ is necessary to generate zinc metal, and that zinc halides afford more zinc metal than other zinc salts regardless of photocatalyst used. In accord with this requirement, these same experiments that were performed using Ir(ppy)₂(dtbbpy)⁺ in chapter 2 were performed using dCl-Hq as the precatalyst.

Zinc generating photoreactions using dCl-Hq as the precatalyst were set up in various organic solvents. Similar to chapter 2, acetonitrile was the best solvent. After 68 hours of illumination, 131 μmol of zinc metal were produced in acetonitrile under standard conditions (see experimental methods for standard conditions). When acetonitrile was completely replaced in the 9 MeCN : 1 TEA reaction solvent by an alternative organic solvent, yields were much lower. Under otherwise identical conditions, 9 μmol of zinc metal were produced in toluene, which was the next higher performing solvent. However, the addition of MeCN in 10% v/v to these poorer performing solvents again dramatically increased yields of zinc metal in photoreactions. These results are displayed in Figure 3-4. This result supports the parallel experiment and supporting electrochemistry conducted in chapter 2 which revealed that MeCN is needed to positively shift the onset potential of Zn(II) reduction. This positive shift increases the

thermodynamic driving force for electron transfer to Zn(II) from the reduced photocatalyst, which results in the higher yields of zinc metal in MeCN seen in Figure 3-4.

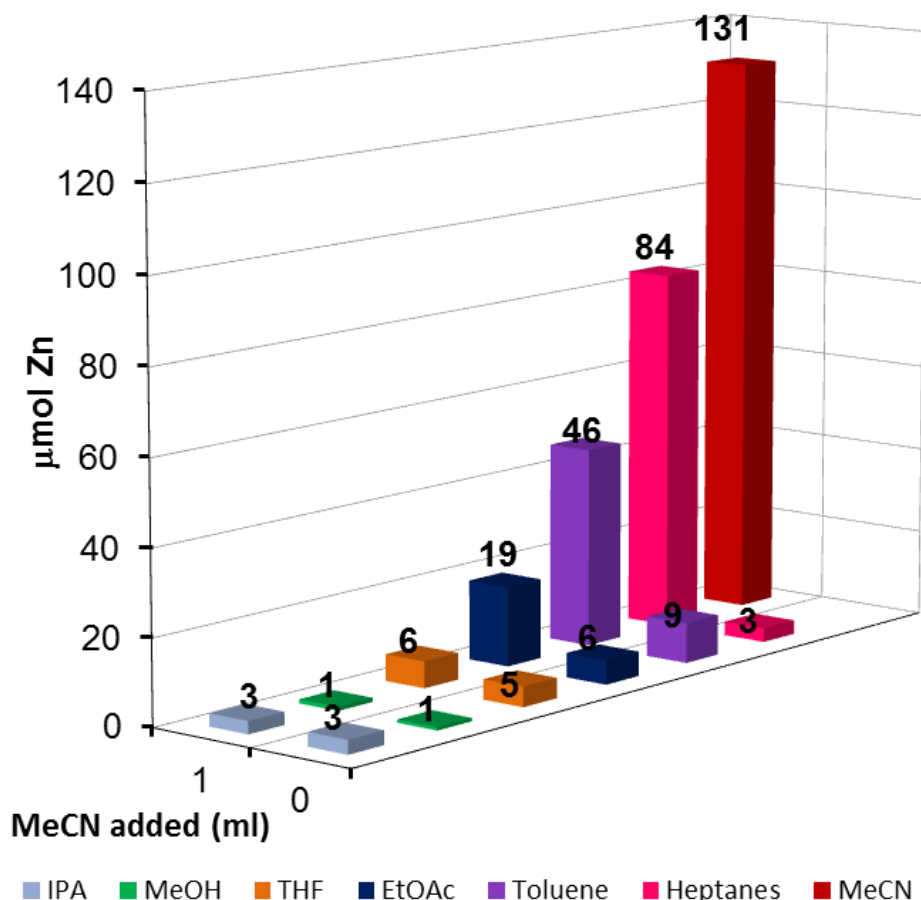


Figure 3-4 – Yields of photoreduced zinc metal in various solvents after 68 hr illumination under otherwise standard conditions.

Additionally, it can also be observed that among the other solvents evaluated, less polar solvents produce higher yields of photoreduced zinc metal when 10% v/v MeCN is added. This trend, which was not observed in chapter 2, is likely due to the difference between the catalysts. $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+$ complexes are very stable in their octahedral conformation and have no additional open binding sites. The active catalyst, which is demonstrated later in this chapter to be a monosubstituted zinc quinolate, has several open coordination sites. Therefore, when MeCN is in excess due to its use as a solvent, it

likely coordinates the active photocatalyst, as well as free Zn(II). The coordination of MeCN to the active photocatalyst is supported by the effectiveness of nonpolar solvents in 10% MeCN. The coordination sphere of the active photocatalyst should not vary significantly in acetonitrile or nonpolar solvents such as heptanes and toluene with 10% MeCN added. The coordination of MeCN to the active catalyst also explains the general greater proportional decline in zinc metal production in other solvents relative to MeCN than the decline that was observed in chapter 2 using $\text{Ir(ppy)}_2(\text{dtbbpy})^+$.

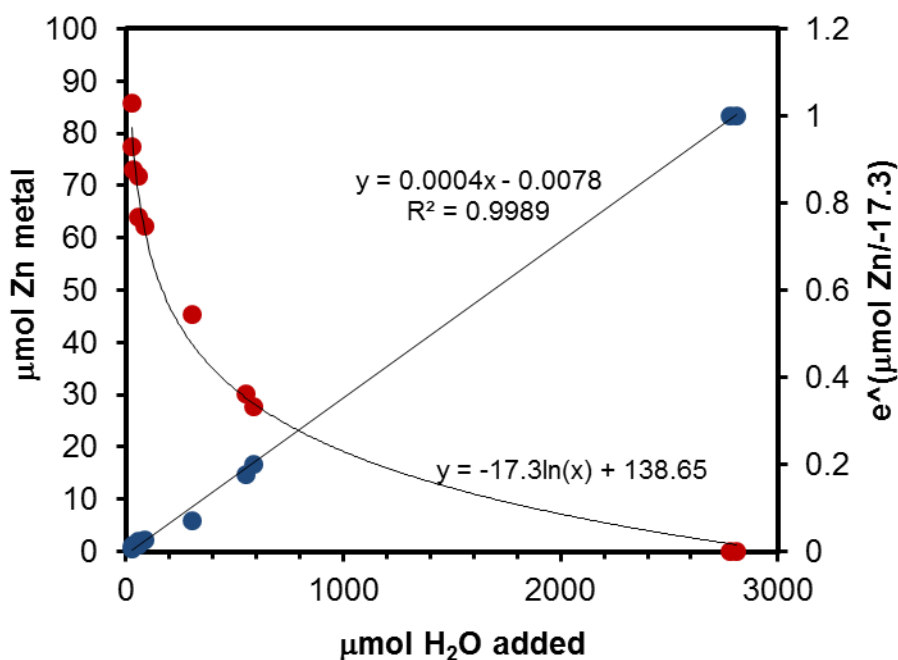


Figure 3-5 – The effects of the addition of water to dried ZnCl_2 on the yields of zinc metal after 44 hr under otherwise standard conditions.

The effect of water on the photocatalyzed reduction of Zn(II) by dCl-Hq as the precatalyst was evaluated as well. In contrast to chapter 2, the ZnCl_2 was dried in a vacuum oven prior to the start of the experiment. EDTA titrations were then performed on the initial and dried ZnCl_2 to determine the degree of hydration of each. Xylenol orange was used as an indicator. Approximately half the water was removed by drying; the results are given in Table 3-1. The dried ZnCl_2 was then used as the Zn(II) source in

Figure 3-5, which depicts the change in yields of zinc metal photoproduct upon the addition of water. Water was shown to noncompetitively inhibit Zn(II) photoreduction by a zinc quinolate formed in situ. A logarithmic decay function was fitted to the dependence of zinc metal yields on H₂O added. This effect of water is similar to that observed in chapter 2. Again, water is likely to react with any Zn(I) intermediate, resulting in the observed inhibition.

	MW (g/mole)	X
Dried ZnCl ₂ · X H ₂ O	146	0.56
ZnCl ₂ · X H ₂ O, as received	157	1.17

Table 3-1 – Degree of ZnCl₂ hydration before and after drying, as determined by EDTA titrations.

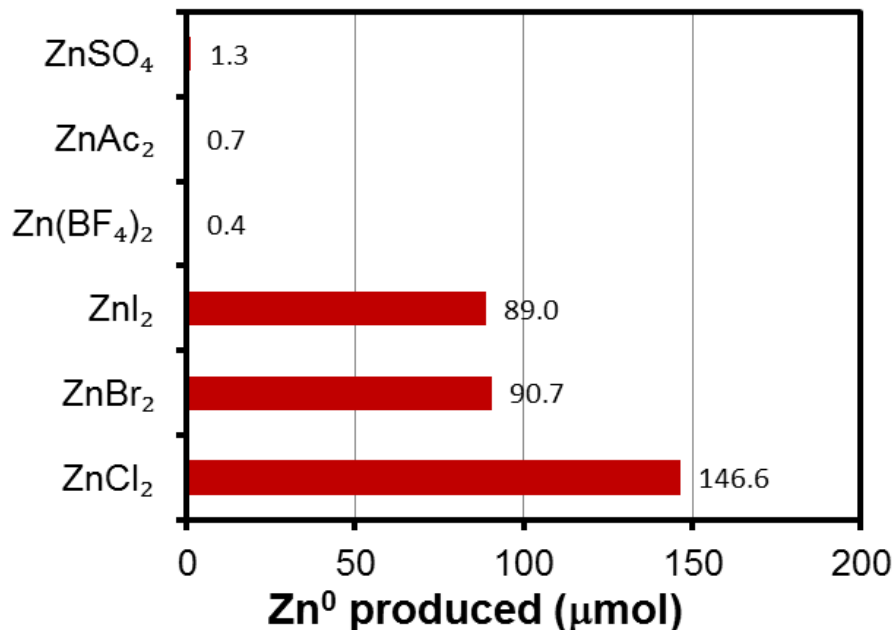


Figure 3-6 – Zinc metal produced after 3 days of illumination using different zinc salts.

5,7-dichloro-8-hydroxyquinoline was evaluated as a precatalyst for the photocatalyzed reduction of various zinc salts. When equal molar quantities (2.01 mmol) of various zinc salts were used in otherwise identical photoreactions, it was again found that zinc halides afforded the most zinc metal. Neither solubility nor hydration of the salt

correlated with the yields of zinc metal photoproduct obtained by the use of different zinc salts. Electronegativity of the anion also did not appear to affect yields of zinc metal. Instead, the most noticeable trend was again the success of the zinc halides. The highest yields of zinc metal were again obtained by the use of ZnCl_2 ; 147 μmol of zinc metal was generated after 3 days, equivalent to 49 TONs. These results can be observed in Figure 3-6. The results in Figure 3-6 are consistent the similar experiment performed in chapter 2 using $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ in lieu of dCl-Hq. This supports the hypothesized role of zinc halides stated earlier that the halide anions help stabilize a $\text{Zn}(\text{I})$ intermediate because this effect should be and is observed regardless of the photocatalyst employed.

Identification of the Active Catalyst

Due to its importance in the reaction mechanism, the identity of the active quinolate catalyst and its mechanism of in situ formation were investigated. Solutions of protonated dCl-Hq in acetonitrile were faint yellow-green, almost colorless. The addition of TEA to such solutions changed the solutions to bright yellow. UV-Vis spectra of dCl-Hq in MeCN and in MeCN with 10% TEA are much different. When TEA is added, a peak in the visible region centered at 407 nm appears and there is a red shift in the original peak from 314 to 345 nm. Figure 3-7 shows the two spectra. This color can be attributed to the deprotonation of the hydroxyl group on the quinoline by the basic nitrogen of TEA, which significantly alters the electron configuration of the ligand. Deprotonated dCl-q⁻ has extended conjugation and additional resonance structures relative to dCl-Hq.

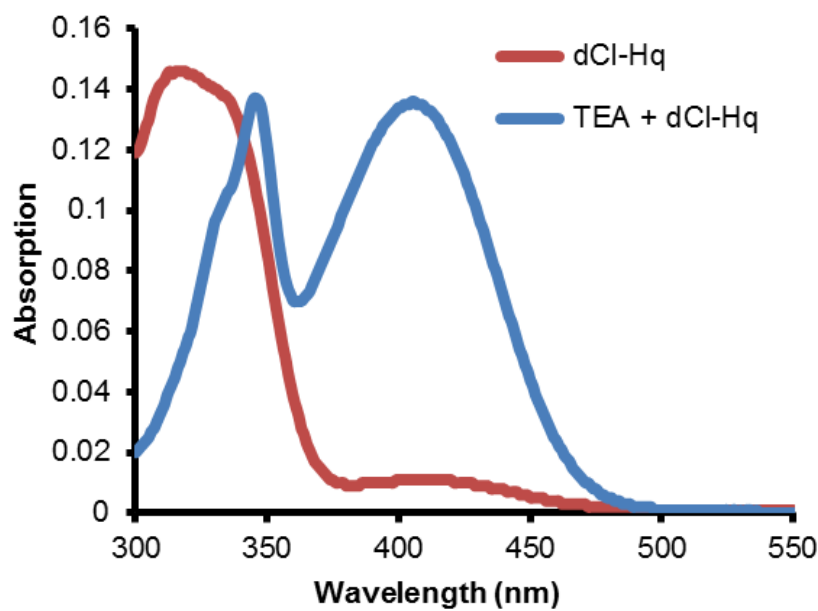


Figure 3-7 – UV-Vis spectra of dCl-Hq in MeCN with and without 10% TEA

Proton NMR spectra were also taken of dCl-Hq in d_3 -MeCN with and without TEA to confirm deprotonation of the Hq hydroxyl group. Lower concentrations of TEA were used so the proton signals of dCl-Hq could be observed at reasonable intensity. The ^1H NMR spectra of dCl-Hq displayed shifted aromatic peaks upon the addition of TEA, as well as the absence of a hydroxyl proton signal. Figure 3-8 shows these spectra. The use strongly basic potassium t-butoxide in place of TEA and subsequent evaporation of the butanol produced showed the same ^1H NMR and absorption spectra, which confirms that dCl-Hq is deprotonated by TEA. However, the addition of ZnCl_2 dCl-Hq solution in MeCN that already contained 10% TEA, did not result in any further color change and the UV-Vis spectra changed minimally. The lack of color change is consistent with expectations because the frontier orbitals of Znq_2 are ligand centered. The maximum absorption wavelength of the visible peak shifted between 407 and 413 nm depending on ZnCl_2 concentration. For the solutions of some more strongly acidic quinoline ligands such as dCl-Hq, a yellow color was observed when ZnCl_2 was added even in the absence

of TEA. For less acidic ligands such as Hq, ZnCl_2 was insufficient to cause such a color change. This indicates that ZnCl_2 is a strong enough lewis acid to deprotonate some hydroxyquinoline ligands but not others.

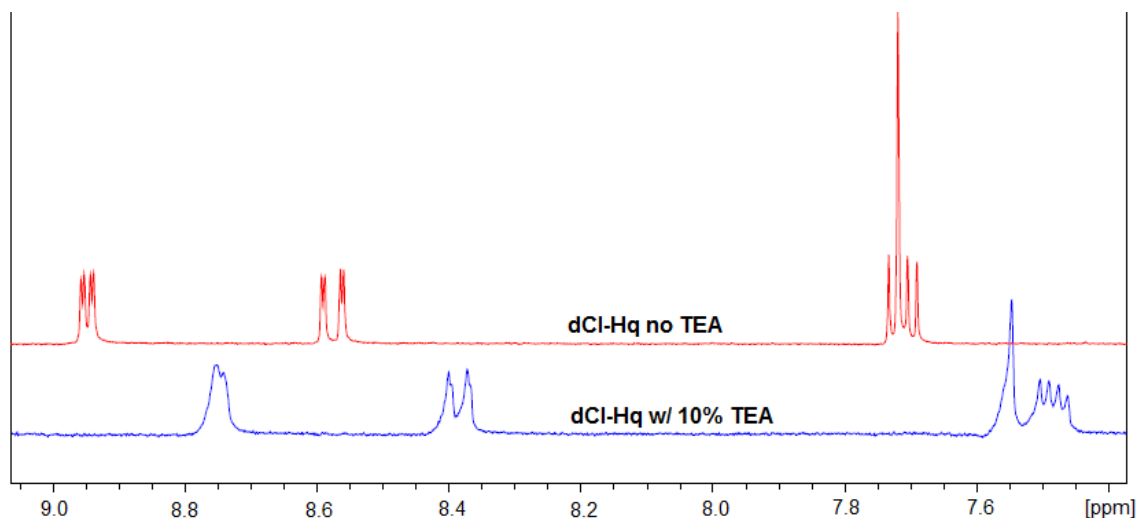


Figure 3-8 – Proton NMR spectra of dCl-Hq in $\text{d}_3\text{-MeCN}$ with and without 1% TEA v/v.

Given the deprotonation of dCl-Hq in the basic photoreaction solution, the formation of a zinc quinolate as the active photocatalyst seemed likely and was investigated. The exact nature of the predominant zinc quinolate formed under photoreaction conditions could not be determined by UV-Vis spectroscopy due to the very similar absorption spectra of q^- , Znq , and Znq_2 . Instead, a ^1H NMR titration was performed. To solutions of ZnCl_2 in $\text{d}_3\text{-MeCN}$, increasing concentrations of dCl-Hq was added and ^1H NMR spectra were taken. The results are given in Figure 3-9. The areas of the non-overlapping peaks were normalized relative to 10% v/v TEA which was used as an internal standard and then plotted as relative concentration against the ligand to ZnCl_2 mole ratio. These results are depicted in Figure 3-10.

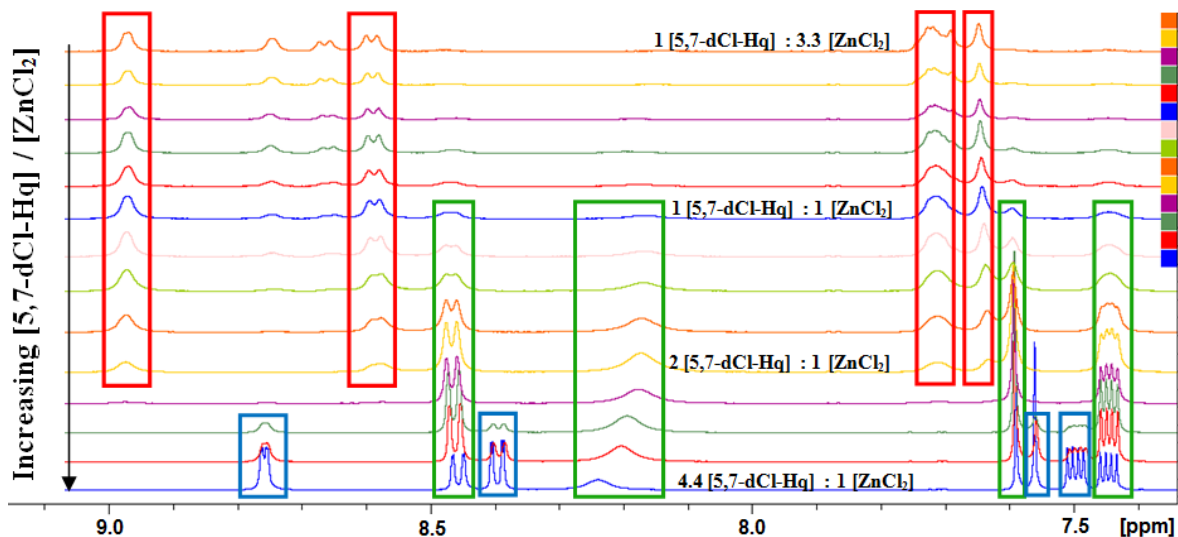


Figure 3-9 – ^1H NMR spectra of ZnCl_2 and dCl-Hq at different ratios relative to each other. Deuterated MeCN with 10% TEA is the solvent is added. Peaks corresponding to the mono-substituted $\text{Zn}(\text{dCl-q})$ are boxed in red, $\text{Zn}(\text{dCl-q})_2$ are boxed in green, and dCl-q- are blue.

The results shown in Figure 3-9 are reversible; the same results are obtained if increasing concentrations of dCl-Hq is added to a solution of ZnCl_2 or vice versa. This indicates that $\text{Zn}(\text{dCl-q})_2$, $\text{Zn}(\text{dCl-q})$, and dCl-q $^-$ are in equilibrium with one another. Mathematica 8 software was employed to perform regression analysis and generate a best fit line for the quinolate concentration data given in Figure 3-10. Because of the excess TEA, it was assumed in the calculation of K values that dCl-Hq is completely and irreversibly deprotonated to dCl-q $^-$. Equilibrium constants (K_{eq}) for the formation of $\text{Zn}(\text{dCl-q})_2$ and $\text{Zn}(\text{dCl-q})$ were found to be 257 M^{-1} and 1026 M^{-1} respectively. Figure 3-11 shows the equilibrium between the zinc quinolates.

Photoluminescence quenching was used to verify the identity of the active catalyst. It can be seen in Figure 3-10 that under typical photoreaction conditions where Zn(II) is in excess of dCl-Hq, the mono-substituted zinc quinolate, $\text{Zn}(\text{dCl-q})$, is the predominant species and therefore the most likely photocatalyst. However, other species

could still possibly be the active catalyst given the equilibrium between the zinc quinolates.

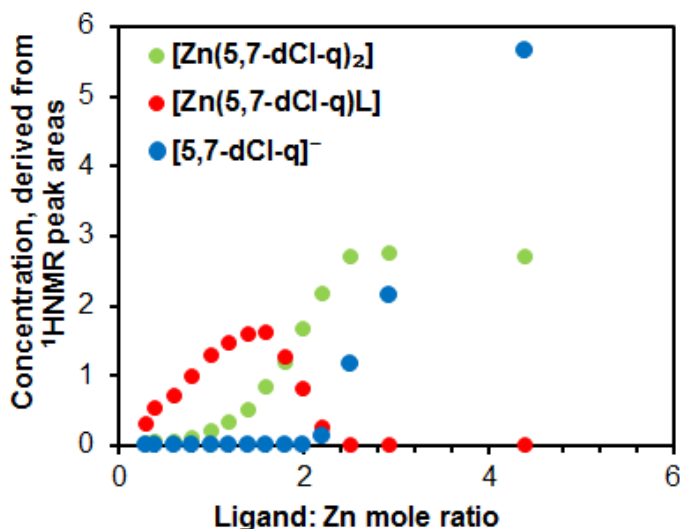


Figure 3-10 – Normalized relative quinolate concentrations derived from ^1H NMR spectra in Figure 3-9.

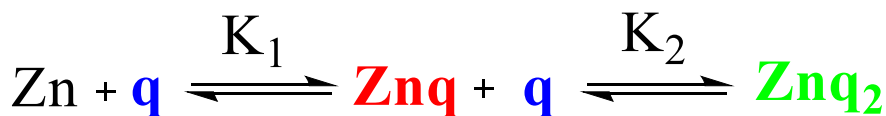


Figure 3-11 – Equilibrium reactions between $\text{Zn}(\text{dCl-q})_2$, $\text{Zn}(\text{dCl-q})$, and dCl-q^- . From Figure 3-10 it was calculated that $K_1 = 257 \text{ M}^{-1}$ and $K_2 = 1026 \text{ M}^{-1}$.

To address this uncertainty, fluorescence quenching experiments were performed; the active catalyst must demonstrate reductive quenching by TEA in order to obtain the necessary electrons to reduce $\text{Zn}(\text{II})$. As such, $\text{Zn}(\text{dCl-q})_2$, $\text{Zn}(\text{dCl-q})$, and dCl-Hq were each titrated with TEA and the photoluminescence intensity of each complex was monitored. $\text{Zn}(\text{dCl-q})_2$ and $\text{Zn}(\text{dCl-q})$ were synthesized in situ using stock solutions of ZnCl_2 and dCl-Hq . It was found that among the three quinolates tested, only the mono-substituted $\text{Zn}(\text{dCl-q})$ was quenched by TEA and was thus confirmed to be the active photocatalyst. The rest of the coordination sphere of $\text{Zn}(\text{dCl-q})$ is undetermined but likely consists of acetonitrile, as postulated earlier, and chloride. The photoluminescence

quenching of Zn(dCl-q) is displayed as a Stern-Vollmer plot in Figure 3-12. It is important to note that in Figure 3-12 the rate of quenching is quickly saturated and thus constant over the relevant range of TEA concentrations employed in photoreactions. Decay of the photocatalytic rate therefore cannot be attributed to a decrease in the rate of photocatalyst quenching.

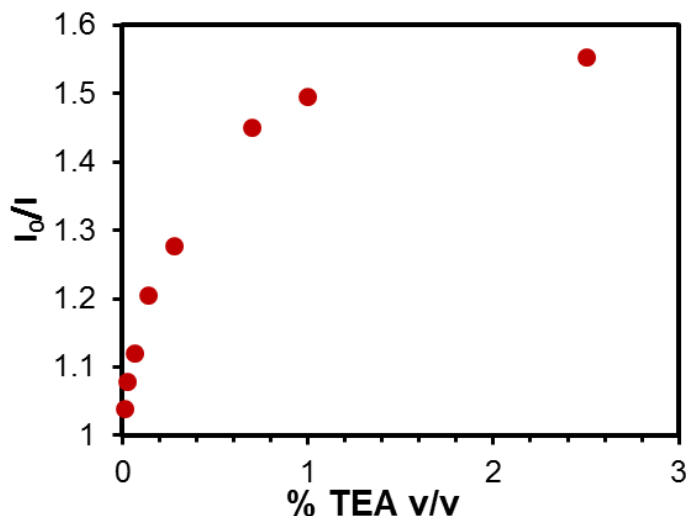


Figure 3-12 - Photoluminescence quenching of Zn(dCl-q) by TEA in MeCN.

Kinetics Studies

The kinetics of photocatalyzed Zn(II) reduction by Zn(dCl-q) formed in situ were also investigated. Similar experiments to those conducted in chapter 2 were performed. The decay in the production of zinc metal over illumination time was measured at 300 μ M dCl-Hq. After ten days the generation of zinc had largely ceased and 242 moles of zinc metal photoproduct were detected. The observed production decay was found to be first order in nature. These results are given in Figure 3-13. The decay of photocatalyzed Zn(II) reduction cannot be attributed to the consumption of ZnCl₂ nor TEA; the concentrations of both TEA and ZnCl₂ remained fairly close to the starting concentrations. If the decay of zinc generation was due to the consumption of a reactant

then zinc production by an Ir(III) photocatalyst would cease after a similar yield of zinc metal. By contrast, zinc production by the Ir(III) photocatalyst in chapter 2 was longer lived, therefore excluding reactant concentration from playing a role in the production decay observed with dCl-Hq as the precatalyst.

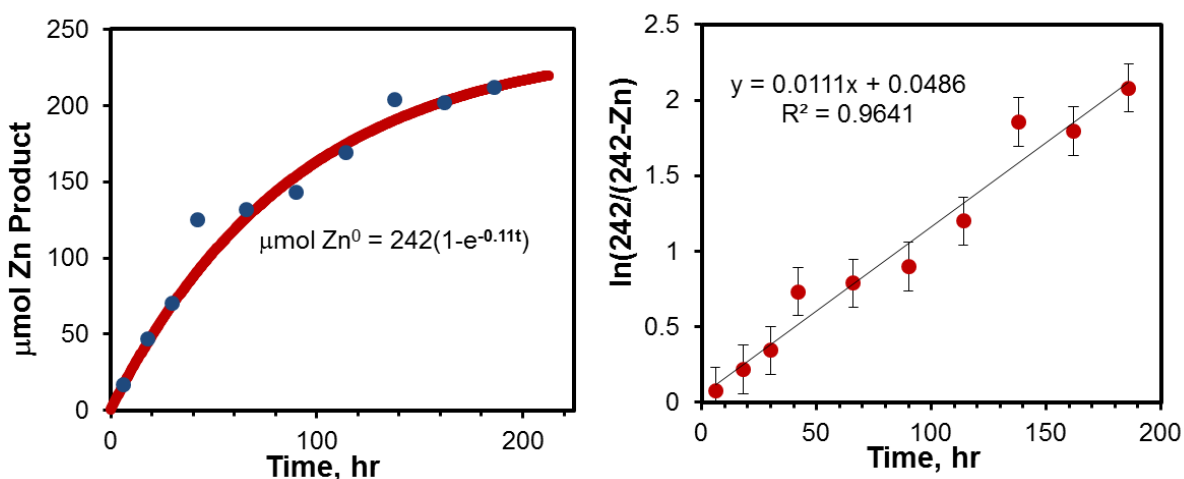


Figure 3-13 – Right: Yield of zinc metal generated over illumination time under standard conditions (blue) and a kinetic fit of the data (red). Left: Linearized first order fit for the production of zinc metal over illumination.

Proton NMR revealed that the decay mechanism stems from the inactivation of the quinolate catalyst itself. ^1H NMR spectra were taken of a photoreaction solution in $\text{d}_3\text{-MeCN}$ before and after 96 hr of illumination. After illumination, the same peaks are present as prior to illumination but three additional peaks can also be observed in the aromatic region, two doublets and a singlet. The identity of this decay product is unclear. The peaks are aromatic or at least conjugated, but it is expected that any side reactions in the highly reducing photoreaction environment, such as a zinc catalyzed hydrogenation, would destroy the aromaticity of the ring. It is possible that the amine radical generated by TEA oxidation plays a role. Figure 3-14 shows these spectra.

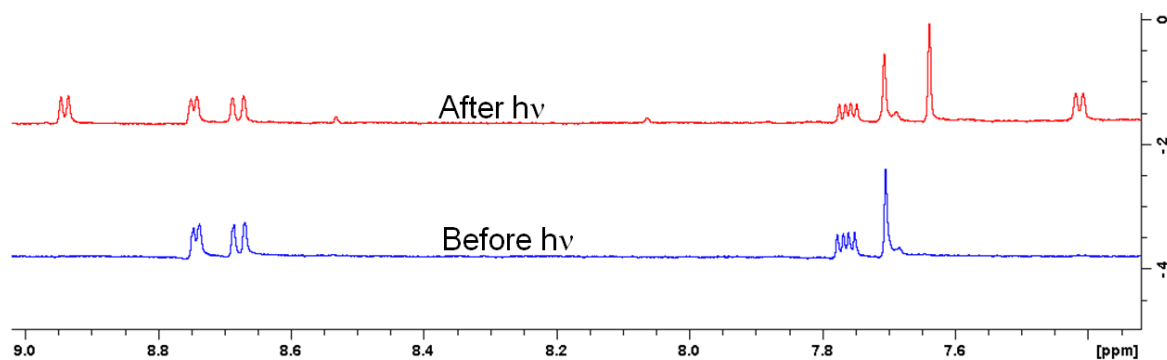


Figure 3-14 – ^1H NMR spectra of the photoreaction solution before and after 96 hr of illumination. Half-scale standard conditions were employed in $\text{d}_3\text{-MeCN}$.

Initial rate kinetics were also investigated for the photocatalyzed reduction of Zn(II) to zinc metal by a zinc quinolate formed in situ. The effect of dCl-Hq concentration on the initial rate of photocatalyzed zinc reduction was first assessed. Concentrations of dCl-Hq evaluated ranged from 50 to 900 μM . Similar to chapter 2, for each concentration of dCl-Hq tested, four identical reactions were set up and worked up after 1, 2, 4, and 8 hrs of illumination time. Zinc metal generated was plotted against illumination time. The slopes of the best fit lines of these plots gave the initial rate of photocatalyzed Zn(II) reduction at different concentrations of dCl-Hq. Then, the initial rate of Zn(II) photoreduction was plotted against concentration of dCl-Hq. The concentrations of dCl-Hq employed were higher than those of $\text{Ir(ppy)}_2(\text{dtbbpy})^+$ in the previous chapter because of the poorer performance of the quinolate photocatalysts. As a result, the plot of initial rate vs [dCl-Hq] is non-linear, and the initial rate fails to increase proportionally with concentration at higher concentrations of dCl-Hq. A first order fit was generated from this data and both plots are shown in Figure 3-15. This first order fit is consistent with the saturation of light absorption at higher concentrations of dCl-Hq. It can also be concluded from the high K value of Zn(dCl-q) formation determined earlier that essentially all of dCl-Hq is converted to Zn(dCl-q) . The concentrations of dCl-Hq

given in Figure 3-15 are essentially equal to the active catalyst concentrations and the results can be interpreted as such.

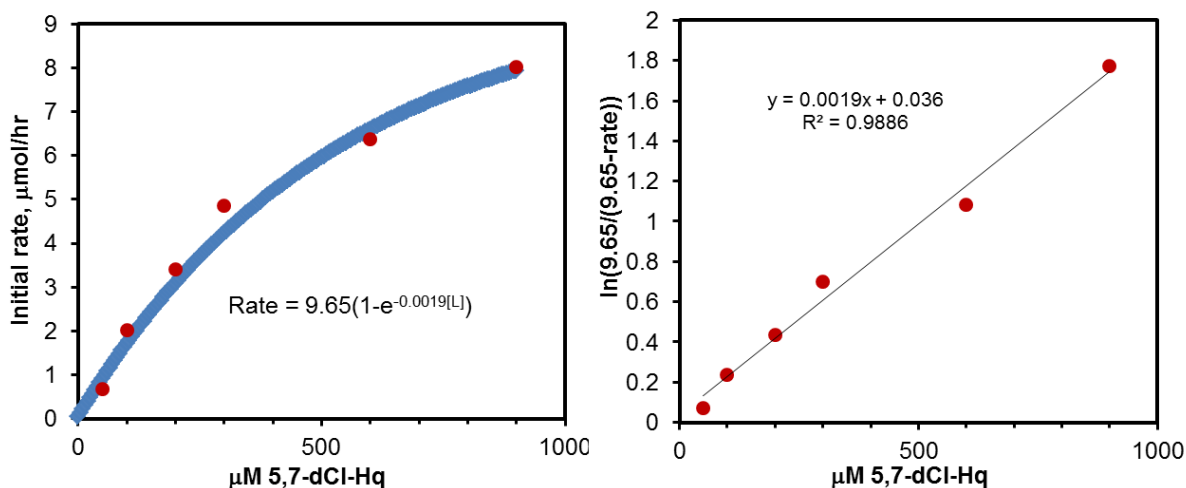


Figure 3-15 – Dependence of the initial rate of Zn(II) photoreduction on [dCl-Hq] under otherwise standard conditions (left). A first order decay fit of the initial rate indicating the saturation of light absorption at higher concentrations of dCl-Hq (right)

Similar experiments were also performed to determine the effect of ZnCl_2 mass concentration on the initial rate of Zn(II) photoreduction by Zn(dCl-Hq) formed in situ. At each mass concentration of ZnCl_2 , which ranged from to mg/10 ml, four identical reactions were set up. After 1, 2, 4, and 8 hr of illumination, one photoreaction vial was worked up at each ZnCl_2 mass concentration tested. The initial rate were determined from the plots of zinc metal produced over time and then plotted against ZnCl_2 mass concentration, in the same approach used for the dCl-Hq concentration study. The results can be seen in Figure 3-16.

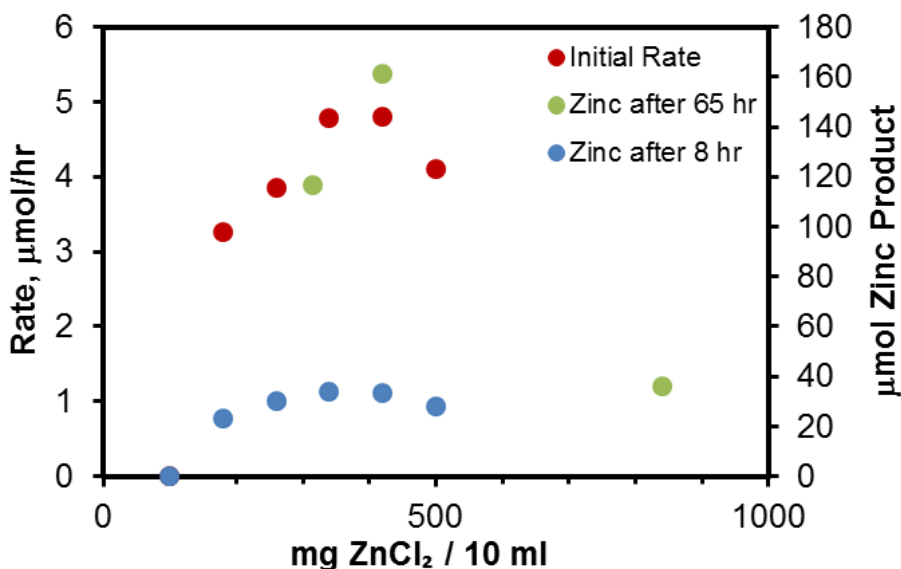


Figure 3-16 – The initial 8 hr rates of zinc production and the yields of zinc metal at various mass concentrations of ZnCl₂ under otherwise standard conditions.

Figure 3-16 shows that with a zinc quinolate catalyst formed in situ there is again a minimum ZnCl₂ mass concentration required for Zn(II) photoreduction. Furthermore, the observed minimum required ZnCl₂ mass concentration is approximately equal to the minimum mass concentration established by similar experiments in chapter 2 using Ir(ppy)₂(dtbbpy)⁺. The catalyst identity thus does not alter this minimum ZnCl₂ mass concentration required for Zn(II) photoreduction, but stays near the solubility limit of ZnCl₂ in 9 MeCN : 1 TEA. This reinforces hypothesis postulated in chapter 2 that insoluble ZnCl₂ is required for successful photocatalyzed reduction of Zn(II) to zinc metal because such a reduction mechanism would be independent of catalyst identity.

Conclusion

This chapter describes the visible photon driven reduction of Zn(II) to zinc metal by a mono-substituted zinc quinolate, Zn(dCl-q), that forms in situ from 5,7-dichloro-8-hydroxyquinoline. It was found that triethylamine is sacrificially oxidized by the excited

photocatalyst, which then transfers its reducing equivalents to Zn(II). The final oxidation of TEA to acetaldehyde and diethylamine requires H₂O from the zinc salt crystal lattice. Several 8-hydroxyquinoline ligands were evaluated for their effectiveness as photocatalyst precursors. It was found that 8-hydroxyquinoline ligands with EWGs, particularly halogens, at the 5 and 7 positions afforded higher yields of zinc metal. Among all ligands tested, 5,7-dichloro-8-hydroxyquinoline was the most effective photocatalyst precursor and was used subsequently throughout this chapter.

The optimal solvent and zinc salts for the photocatalytic reduction of Zn(II) by zinc quinolates were evaluated in order to substantiate the reaction mechanism proposed in chapter 2. Acetonitrile again proved to be the most effective solvent for the photocatalytic reduction of Zn(II). This result is consistent with the findings of chapter 2 that MeCN is the most effective solvent because it positively shifts the onset potential of Zn(II) reduction. Acetonitrile also likely coordinates one of the open sites on the active catalyst, Zn(dCl-q). ZnCl₂ was dried in order to more rigorously document the inhibitive effect of H₂O on the yields of zinc metal, and a logarithmic relationship was found. In another similarity to the results from chapter 2, higher yields of photoreduced zinc metal were obtained through the use of zinc halides. The success of halides regardless of catalyst supports the hypothesis postulated earlier that Zn(I) intermediates are longer lived in halide salts.

The identity of the active photocatalytic species that forms in situ was also investigated and determined to be a mono-substituted zinc quinolate. Proton NMR and UV-Vis spectroscopy studies revealed that the 8-hydroxyquinoline ligand is deprotonated by triethylamine in the photoreaction solution. An NMR titration study was

conducted in which ^1H NMR spectra were taken of solutions of $\text{d}_3\text{-MeCN}$ with 10% TEA containing ZnCl_2 and dCl-Hq . The ratio of ZnCl_2 to dCl-Hq was varied in this study so that NMR spectra were obtained ranging from 1 ZnCl_2 : 4.4 dCl-Hq to 3.3 ZnCl_2 : 1 dCl-Hq . Three quinolate species, dCl-q^- , Zn(dCl-q) , and Zn(dCl-q)_2 were observed over this concentration range. The normalized area of the peaks from each species was used to plot the relative concentration of each quinolate over the ratio of ZnCl_2 to dCl-Hq . The ensuing plot and demonstrated reaction reversibility permitted the calculation of equilibrium constants for the formation of Zn(dCl-q) and Zn(dCl-q)_2 . It was determined that under photoreaction conditions where ZnCl_2 is in excess, almost all dCl-Hq is converted to Zn(dCl-q) . Photoluminescence quenching experiments revealed that out of the possible quinolates, TEA only quenched Zn(dCl-q) , confirming it as the active photocatalyst.

Kinetics studies similar to those reported in chapter 2 were performed employing dCl-Hq as the precatalyst. After 10 days, 81 catalyst TONs are reported at a concentration of 300 μM dCl-Hq . The decay in zinc production over time was found to be first order in nature, and ^1H NMR revealed that this is due to catalyst degradation. The initial rate of Zn(II) photoreduction was found to have a first order dependence on photocatalyst concentration. Furthermore, it was found again a minimum mass concentration of ZnCl_2 was required for the photocatalytic reduction of Zn(II) to proceed. This observation supported the hypothesis put forth in chapter 2 that the photoreduction of Zn(II) is heterogeneous and that insoluble ZnCl_2 is reduced. A basic mechanism of photocatalysis summarizing the findings of this chapter, including the heterogeneous photoreduction of ZnCl_2 and formation of Zn(dCl-q) in situ, is given in Figure 3-17.

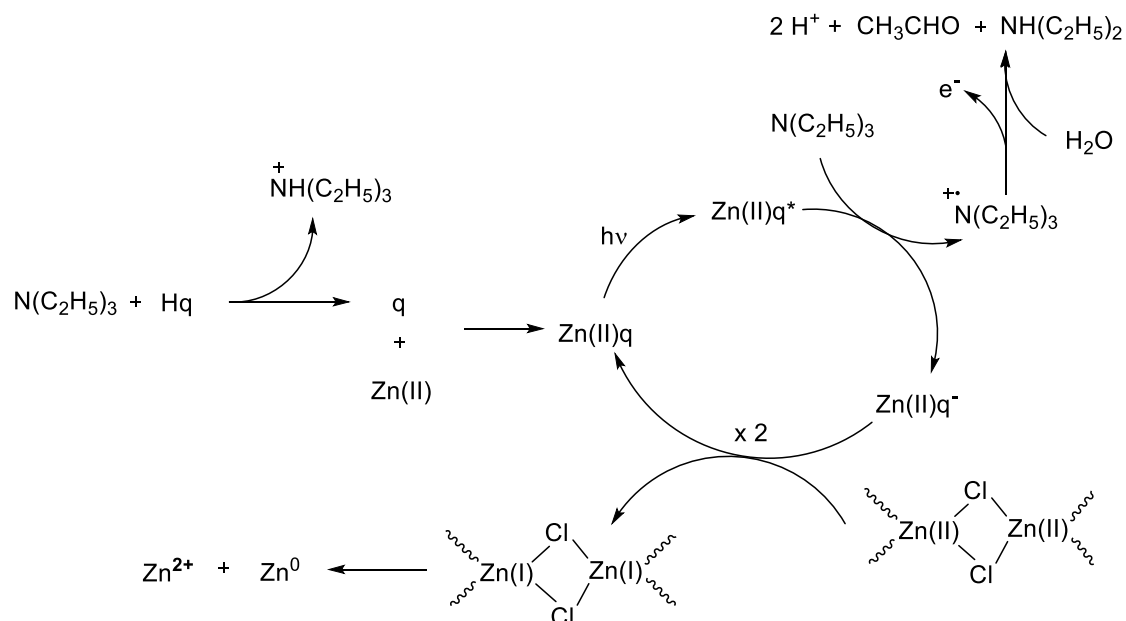


Figure 3-17 – Photocatalyzed reduction of Zn(II) by a zinc quinolate formed in situ. dCl-Hq has been abbreviated to Hq for clarity.

Chapter 4. Organocatalysts with Extended Pi Systems for Zn(II) Photoreduction

Introduction

The in situ formation of a zinc photocatalyst for Zn(II) reduction described in chapter 3 is an approach with significant merits but also drawbacks. One shortcoming is the poor visible absorption of the zinc quinolates documented. For Zn(dCl-Hq), visible absorption onsets at approximately 475 nm, and peaks at 407 nm. As a result, the solar conversion efficiency of a Zn(dCl-q) photocatalyzed system is inherently limited because visible photons with sufficient energy to reduce Zn(II) are not absorbed by the photocatalyst. Using the thermodynamic requisites of photocatalysis discussed in chapter 1, the energy of an incident photon must exceed the energy required to split ZnO by 600 eV. Considering this, the maximum photon wavelength capable of catalyzing complete ZnO splitting is 551 nm (photon energy = $1.65 + 0.6 = 2.25$ eV). It is therefore desirable to shift the onset of photocatalyst absorption approximately 75 nm, in order to successfully convert of photons over this range (475 – 551 nm) and raise the solar conversion efficiency of the photocatalytic system.

The conversion of these wavelengths of light is especially desirable given the great intensity of solar irradiation between 475 and 551 nm. Figure 4-1 shows the AM 1.5 spectrum of solar irradiance at the earth's surface. It can be seen that the maximum solar irradiance occurs at 531 nm; more solar energy is irradiated at this wavelength than any other. The failure to capture and convert photons over this 76 nm range thus results in a steeper drop of solar conversion efficiency than if any other wavelength of light could not be absorbed. Overall, solar irradiance between 475 and 551 nm accounts for

over 10% of total solar irradiance, a huge value over such a short range. The absorption of photons between 475 and 551 nm could thus dramatically improve the solar conversion efficiency of photocatalytic Zn(II) reduction.

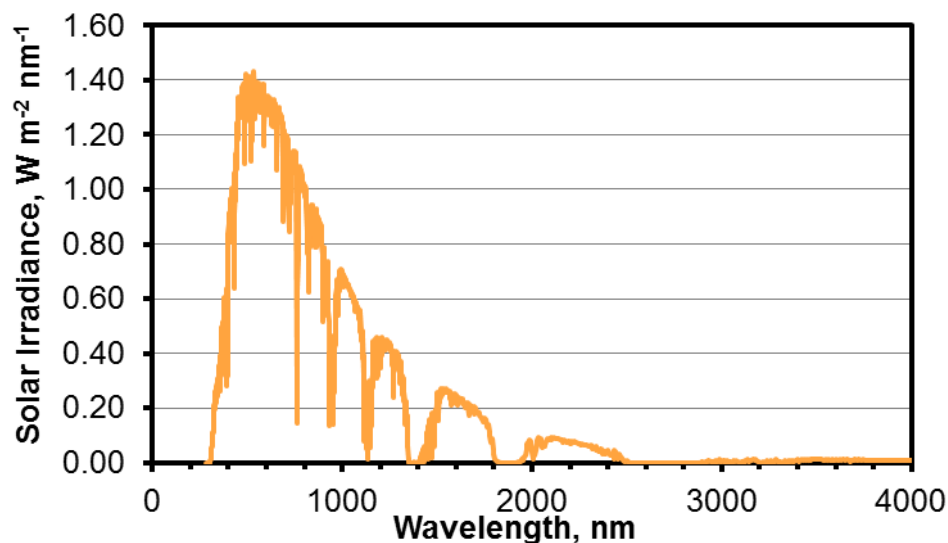


Figure 4-1 – The AM 1.5 Solar Spectrum.

Given the upsides of capturing 475 to 551 nm sunlight, this chapter describes the design, synthesis and testing of alternative precatalyst ligands that could potentially capture these photons. These precatalysts were then evaluated using the same set-up for zinc-generating photoreactions employed earlier. Ligands whose zinc complexes were known to be luminescent electron transporters were pursued, as such traits were indicative of successful catalysts in previous chapters.^{94,144,145} These ligands were also established chelators of Zn(II) in order to preserve the advantages of in situ catalyst formation discussed in chapter 3.^{146–148} The most successful ligands, 10-hydroxybenzo(h)quinoline (Hbq) and 9,7-diiodo-10-hydroxybenzo[h]quinoline, preserved the bidentate aryl-imine and phenol binding sites of Hq, but had extended pi conjugation. The extension of pi conjugation is a common approach used to red shift the absorption of chromophores. This approach has previously been employed successfully

in hydroxyquinolines both through larger fused ring structures and by the addition of free rotating aryl groups.^{144,145,149–151} Figure 4-2 shows dI-Hbq and Hbq.

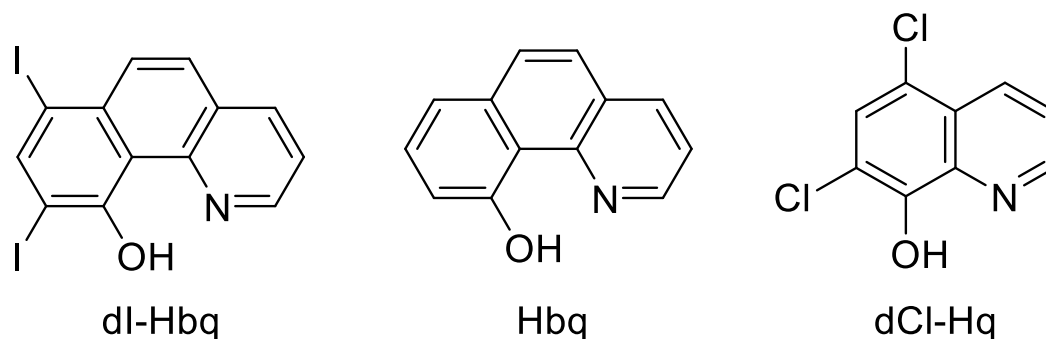


Figure 4-2 – Structures of dI-Hbq and Hbq which were the most successful precatalysts in this chapter, along with dCl-Hq from chapter 3.

Experimental Methods

Materials – All materials were used as received. ZnCl_2 and other zinc salts were purchased from Sigma. TEA was purchased from Acros Organics, and MeCN was purchased from Fisher Scientific. All starting materials and ligands that were not synthesized, including 10-hydroxybenzo[h]quinoline, were purchased from VWR International.

Custom-Built Photoreactor- Ligands were evaluated as precatalysts in the same home-built photoreactor described in chapter 2.

General Procedure for Set-Up of Photoreactions – Photoreactions were set up according to the general procedure outlined in chapter 2. Standard conditions for a photoreaction included 300 μM ligand, 420 mg ZnCl_2 , 9 total ml of MeCN, and 1 ml TEA.

General Procedure for Work-Up of Photoreactions – Zinc generating photoreactions in this chapter were worked up by the same procedure as described in chapter 2.

Synthesis of 2-(2'-hydroxyphenyl)-5-methylpyridine (Hmppy) – A solution of 116 mg (375 μ mol) 1-(2-(2-methoxyphenyl)-2-oxoethyl)pyridin-1-ium bromide and 289 mg (3.75 μ mol) Ammonium acetate in methanol was heated to 70 °C under reflux. A solution of 30.9 μ l methacrolein in methanol was slowly added to the solution under reflux over the course of 75 minutes. The reaction remained on heat for 18 hr. The reaction was cooled to room temperature, and then 3 times excess of water was added. 2-(2'-methoxyphenyl)-5-methylpyridine (OMemppy) was then extracted in chloroform. 30 mg of OMemppy was heated to 125 °C for 8 hr in a solution of 5 ml concentrated HBr and 5 ml glacial acetic acid. The product was cooled to room temperature and neutralized with $\text{Na}_2\text{CO}_3/\text{H}_2\text{O}$ and washed with water. The product was then extracted in chloroform and purified by twice recrystallization in hexanes. **^1H NMR** (CDCl_3 , 300 MHz): δ (ppm) 14.38 (s, 1H), 8.26 (s, 1H), 7.73 (t, 2H), 7.56 (d, 1H), 7.27 (m, 1H), 7.01 (d, 1H), 6.87 (t, 1H), 2.31 (s, 3H).

Synthesis of 2-(2'-hydroxynaphthyl)benzoxazole (HNapOx), 2-(2'-hydroxynaphthyl)benzothiazole (HNapThi), and 2-(2'-hydroxynaphthyl)benzimidazole (HNapIm) –

Polyphosphoric acid (PPA) was made through the slow addition of phosphorous pentoxide to a stirring solution of concentrated phosphoric acid, which was cooled at first in a large tub of water. 20 ml of PPA was added to 564 mg (3 mmol) of 2,3-hydroxynaphthoic acid and an equimolar quantity of the appropriate o-substituted aniline (2-aminothiophenol, p-phenylenediamine, 2-aminophenol). The solution was heated to 115 °C for 6 hr and then poured into 350 ml of cold water after being allowed to cool to room temperature. The resulting precipitate was filtered and washed twice with both $\text{NaHCO}_3/\text{H}_2\text{O}$ and water. HNapOx was purified by sublimation at 180 °C. The crude

HNapThi was almost pure and required only several EtOH rinses. HNapIm was purified by flash chromatography in 5:1 Ethylacetate:Hexanes. **¹H NMR** HNapOx (300 MHz, d₆-DMSO): δ (ppm) 7.41 (t, 1H), 7.54 (m, 4H), 7.82 (d, 1H), 7.90 (t, 1H), 8.06 (d, 1H), 8.76 (s, 1H), 11.04 (s, 1H). HNapThi (300 MHz, d₆-DMSO): δ (ppm) 7.37 (t, 1H), 7.42 (s, 1H), 7.50 (m, 2H), 7.58 (t, 1H), 7.77 (d, 1H), 8.04 (d, 2H), 8.12 (d, 1H), 8.18 (d, 1H), 8.88 (s, 1H), 11.53 (s, 1H). HNapIm (300 MHz, d₆-DMSO): δ 13.43 (1H, s), 13.28 (1H, s), 8.71 (1H, s), 7.89 (1H, d), 7.78 (2H, d), 7.66 (1H, d), 7.51 (1H, t), 7.42 (1H, s), 7.36 (3H, m).

Synthesis of 7,9-diiodo-10-hydroxybenzo[h]quinoline (dI-Hbq)- 546 mg (2.8 mmol) of 10-hydroxybenzo[h]quinoline was dissolved in 2.36 ml of methanol and stirred. A solution of 191 mg (6.16 mmol) I₂ was added over one hour to the methanol solution. The reaction was then heated at 70 °C for 6 hr. The precipitate was removed by filtration, dissolved in CHCl₃, and washed 3 times each with aqueous solutions of Na₂CO₃ and then Na₂S₂O₃. The product was purified by two recrystallizations in acetone. **¹H NMR** (300 mHz, CDCl₃): δ 8.89 (dd, 1H), 8.61 (s, 1H), 8.38 (dd, 1H), 8.13 (d, 1H), 7.8 (d, 1H), 7.69 (dd, 1H).

Synthesis of 7-iodo-10-hydroxybenzo[h]quinoline (I-Hbq) – I-Hbq was synthesized under the same conditions and by the same means as dI-Hbq, only 0.9 molar equivalents of I₂ per equivalent Hbq were used instead of 2.2 to 1. **¹H NMR** (300 mHz, CDCl₃): δ 8.86 (dd, 1H), 8.38 (dd, 1H), 8.06 (d, 1H), 7.77 (dd, 2H), 7.64 (dd, 1H), 7.22 (d, 1H).

Results and Discussion

Given the success of 8-hydroxyquinolines to form photocatalysts in situ capable of Zn(II) reduction, other ligands were pursued for the same purpose. Among the ligands evaluated as precatalysts, 8-hydroxybenzo[h]quinoline was commercially available, and the rest were synthesized. The highest yields of photoreduced zinc metal seen in this chapter were obtained through the use of 7,9-diiodo-benzo[H]quinoline. In general, ligands with expanded conjugated pi systems were more successful.

One family of ligands targeted were 2-(2-hydroxyphenyl)-benzothiazole, -benzimidazole, and -benzoxazole derivatives. The zinc complexes of these ligands, which are shown in Figure 4-3, are commonly used as electron transporters in OLEDs.¹⁵² The hole transporting materials used in tandem with the zinc complexes of these ligands are also used in zinc quinolate-containing OLEDs. It was hoped that the zinc complexes of these ligands in Figure 4-3 could also then be photocatalytically active in the reduction of Zn(II). However, neither 2-(2-hydroxyphenyl)-benzothiazole, 2-(2-hydroxyphenyl)-benzoxazole, nor 2-(2-hydroxyphenyl)-benzimidazole were capable of photocatalyzing the reduction of Zn(II) to zinc metal. This is likely because visible light with a peak intensity of 460 nm was used for these experiments. The solutions of the ligands in MeCN were all clear, and no color change was observed in the solutions of 2-(2-hydroxyphenyl)-benzoxazole and 2-(2-hydroxyphenyl)-benzimidazole when TEA and ZnCl₂ was added. While this does not indicate that chelation of zinc failed to occur, it does suggest that the zinc complexes of these ligands absorb in the UV but not visible region. The solution of 2-(2-hydroxyphenyl)-benzothiazole turned a faint yellow upon exposure to TEA and ZnCl₂ but was also ineffective.

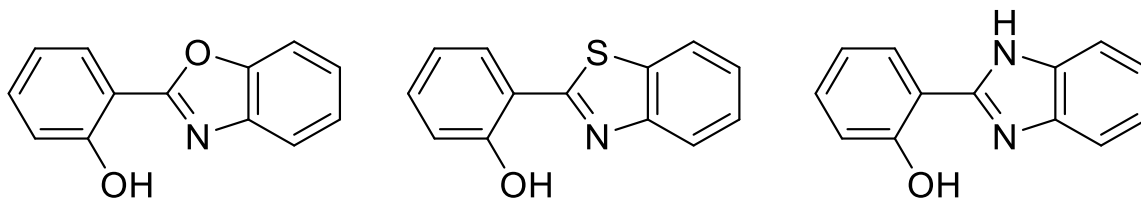


Figure 4-3 – Ligands that were ineffective in the photocatalytic reduction of Zn(II)

Ligands with extended aromatic ring systems were thus targeted as possible photocatalyst precursors whose zinc complexes would have superior visible light absorption. Due to the merits of the ligands in Figure 4-3, similar ligands were synthesized with hydroxyl-naphthene groups instead of phenol groups so to maintain the basic ligand architecture. 2-(2'-hydroxynaphthyl)benzoxazole (HNaPOx), 2-(2'-hydroxynaphthyl) benzothiazole (HNaPThi), and 2-(2'-hydroxynaphthyl)benzimidazole (HNaPIm) were all synthesized in polyphosphoric acid by an established procedure.¹⁵² The synthetic route taken to these compounds is shown in Figure 4-4.

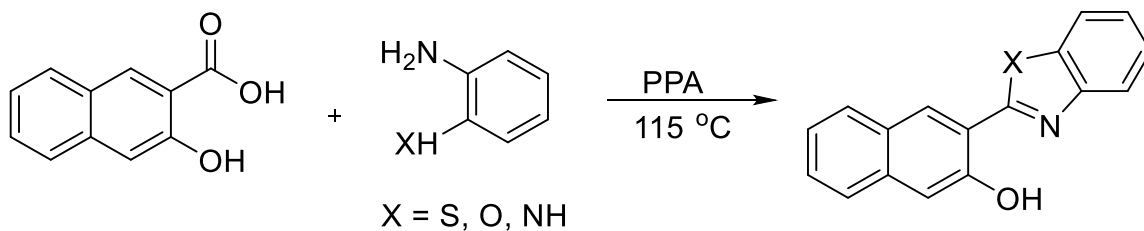


Figure 4-4 – Synthesis of HNaPOx, HNaPThi, and HNaPIm (x = O, S, NH respectively)

Another ligand synthesized for use as a photocatalyst precursor for Zn(II) reduction was 2-(2'-hydroxyphenyl)-5-methylpyridine. Hmppy was synthesized in two steps. First, 2-(2'-methoxyphenyl)-5-methylpyridine was synthesized via a Krohnke reaction under similar conditions to those employed in the synthesis of other phenylpyridine ligands.¹⁵³ Subsequently, the methyl group was cleaved in 1 HBr : 1 acetic acid under reflux to obtain Hmppy. The ¹H NMR spectrum matched that published for Hmppy via an alternative synthetic pathway.¹⁵⁴ The synthesis of Hmppy can be seen

in Figure 4-5. 10-Hydroxybenzo[h]quinoline, which is commercially available, was also identified as a potential precatalyst for Zn(II) photoreduction and is shown in Figure 4-6. Out of the ligands evaluated, Hbq was most similar in structure to Hq, but featured extended aromatic conjugation for increased visible absorption.

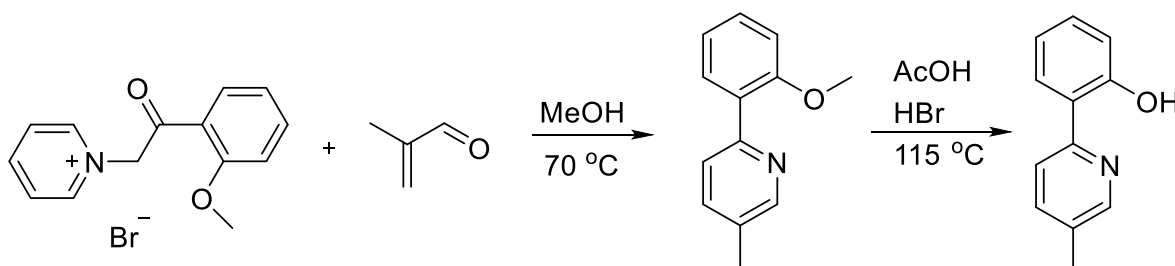


Figure 4-5 – Synthesis of Hmppy

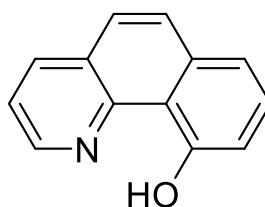


Figure 4-6 - Structure of 10-Hydroxybenzo[h]quinoline.

Hbq and the ligands synthesized in Figures 4-4 and 4-5 were evaluated as precatalysts for Zn(II) photoreduction over 48 hr of illumination under standard conditions. As a direct comparison, dCl-Hq was also included in this study. The results can be seen in Figure 4-7. Among the ligands evaluated, only Hmppy failed to form a zinc complex with visible absorption and was photocatalytically inactive. HNapIm, HNapOx, and HNapThi all formed orange complexes in situ. Hbq was already yellow in MeCN was already yellow, turned bright, more intense yellow upon addition of ZnCl_2 and TEA. The highest yields of photoreduced zinc metal were obtained by Hbq, which

was the only ligand that produced more zinc metal than dCl-Hq.

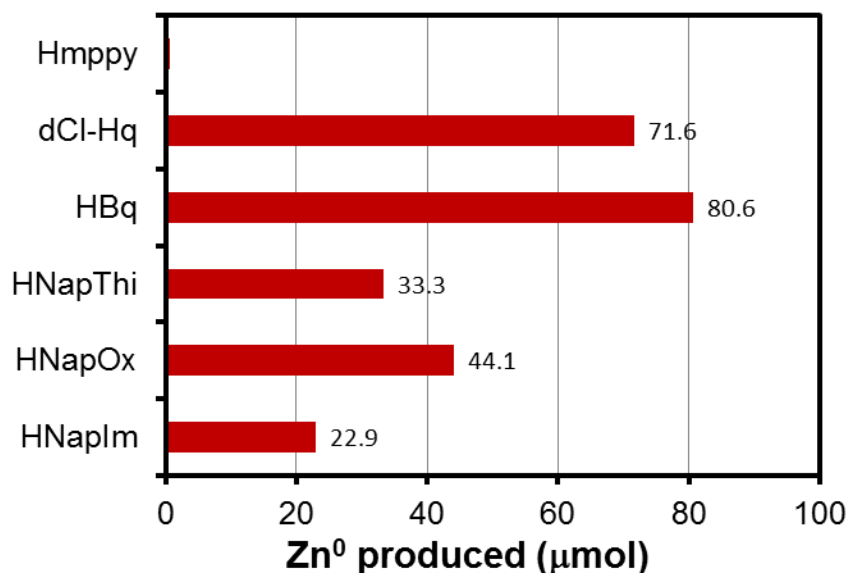


Figure 4-7 – Yields of photoreduced zinc metal afforded by the use of various ligands at 300 μM as photocatalyst precursors after 48 hr under standard conditions.

The success of Hbq in Figure 4-7 prompted the synthesis of halogenated 10-hydroxybenzo[h]quinolones. Recall that in chapter 3 that the use of halogenated 8-hydroxyquinolines as photocatalyst precursors resulted in higher yields of zinc metal relative to Hq. The excited state of Hbq and Hq are similar in that the HOMO is centered over the phenol and the LUMO is centered over the pyridine ring, and it was found that halogenated 8-hydroxyquinolines had higher photocatalytic activities. As a result, it was thought that the halogenation of the Hbq phenol ring at the 7 and 9 positions would stabilize the HOMO and increase yields of zinc metal. The synthesis of chlorinated 10-hydroxybenzo[h]quinolones would be a difficult multistep process that has not been published in the literature, to the best of the author's knowledge. However, the iodination of Hbq is a direct one step process with literature precedent that proceeds under mild conditions. Therefore, both mono- and bis- iodinated 10-hydroxybenzo[h]quinolones

were synthesized to test the hypothesis.¹⁵⁵ Figure 4-8 shows the synthetic route to dI-Hbq and I-Hbq.

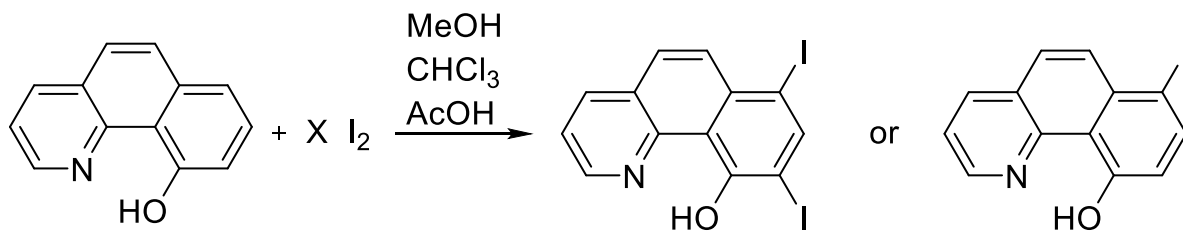


Figure 4-8 – Synthesis of I-Hbq and dI-Hbq. For I-Hbq $x = 0.9$ while for dI-Hbq $x = 2.2$.

The iodinated 10-benzo[h]quinolones were evaluated as precatalysts for Zn(II) photoreduction alongside dCl-Hq, which is the benchmark from the previous chapter. The photoreaction was set up under standard conditions with 300 μM of each ligand for a 17 hr illumination time. It was found that both dI-Hq and I-Hq produced more zinc metal photoproduct, with dI-Hbq affording the highest yields overall. The increase in yields with the increase in halogenation of Hbq was consistent with the results shown earlier in chapter 3, Figure 3-6. The results of this study are given in Figure 4-9. Likely 10-hydroxybenzo[h]quinolones are more effective photocatalysts than 8-hydroxyquinolines because of their extended system of π conjugation. However it is also worth considering that the bond angle between the Zn-N and Zn-O bonds formed by these ligands is greater for 10-hydroxybenzo[h]quinolones than for 8-hydroxyquinolines. This could potentially result in less steric strain on Zn(dI-bq) than Zn(dCl-q), which could contribute to these results.

The photocatalytic capacities of dI-Hbq, Hbq, and dCl-Hq were also evaluated over a longer time period. While the increased initial yields of dI-Hbq as a prephotocatalyst were encouraging, the lifetime of these ligands is also important for their commercial viability. In this study lower concentrations of ligand were used, 50 μM

instead of 300 μM , but otherwise standard conditions were employed. Zinc generated by dI-Hbq, Hbq, and dCl-Hq was measured after 18, 42, 72, and 166 hr of illumination. The results are in Figure 4-10.

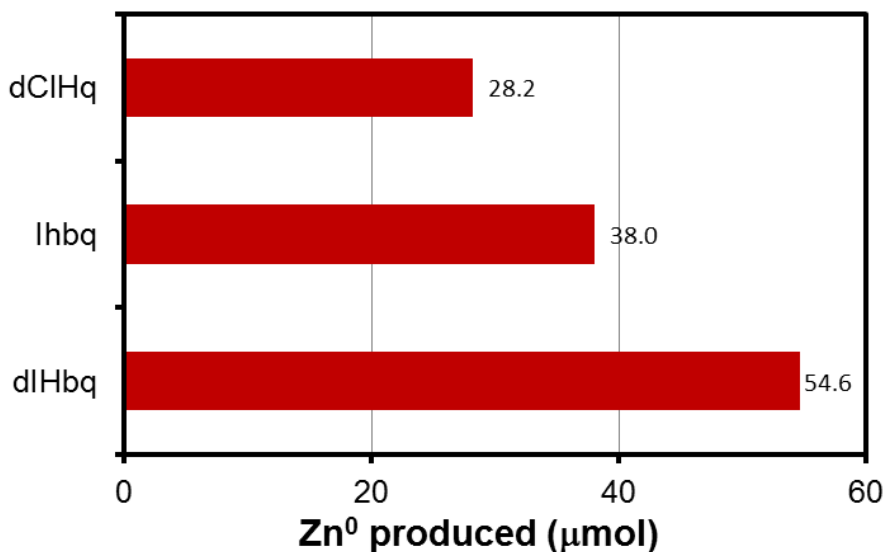


Figure 4-9 - Yields of photoreduced zinc metal afforded by the use of dI-Hq, I-Hq, and dCl-Hq at 300 μM as photocatalyst precursors after 17 hr of illumination under standard conditions.

As expected from the results in Figure 4-9, dI-Hbq has afforded the highest yields of zinc metal photoproduct after 18 hr. After 18 hr, the photoreaction vial containing Hbq produced less zinc metal than dI-Hbq, but more than dCl-Hq. However, the decay in zinc production onsets more quickly for dI-Hbq than the other ligands evaluated. Zinc production by Hbq also decayed, but the use of Hbq still achieved higher yields than by the use of dI-Hbq after 166 hr. While the initial the rate zinc generation by dCl-Hq was the lowest, this photocatalyst was the most effective over the course of the photoreaction. After 166 hr, dCl-Hq achieved 181 TONs, compared to 120 for Hbq and 81 for dI-Hbq. The expanded benzoquinoline aromatic system may be the reason for both the increase in initial rate and faster catalyst decay. Increased light absorption in the visible range and at 460 nm in particular would result in a higher concentration of active catalytic species and

thus a higher initial rate. However, the extended system of pi conjugation also renders dI-Hbq and Hbq more prone to photo-oxidation, which could explain the shorter catalyst lifetimes.

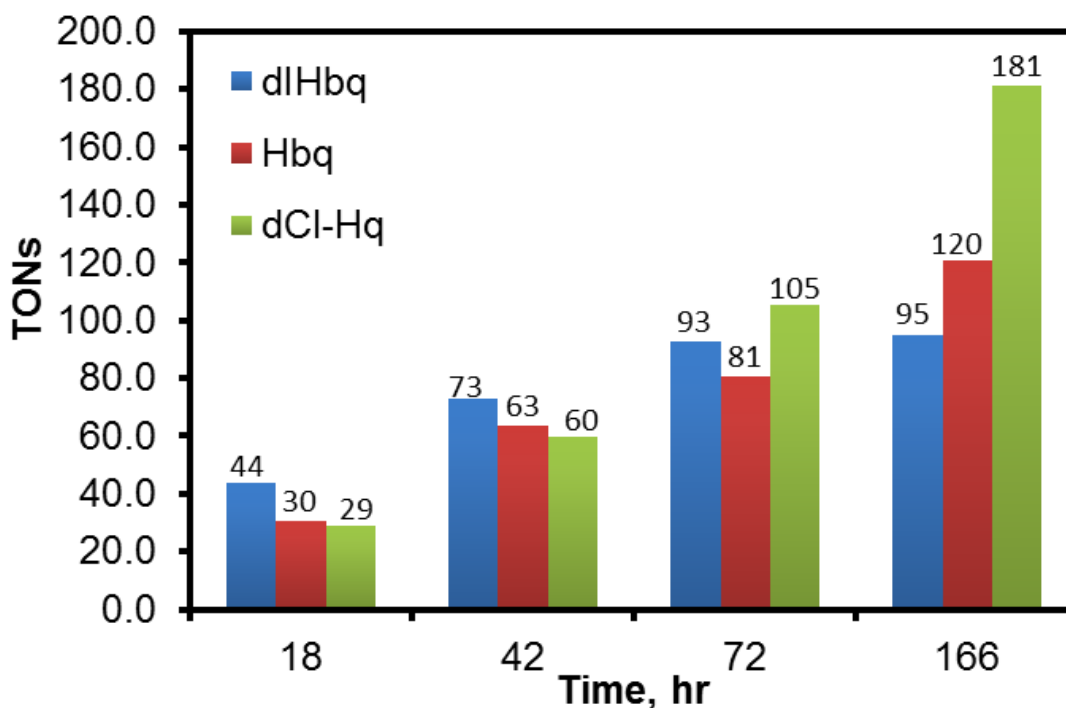


Figure 4-10 – Production of zinc metal by the use of dI-Hbq, Hbq, and dCl-Hq over illumination time. Ligand concentration was 50 μ M under otherwise standard conditions.

Conclusion

This chapter recounts the photocatalyzed reduction of Zn(II) to zinc metal by several ligand precatalysts. The zinc complexes corresponding to these ligands are thought to form in situ and be photocatalytically active. Most ligands used as precatalysts were synthesized; only HbOx, HbIm, HbThi, and Hbq were commercially available. Hmppy was synthesized via a Krohnke reaction and subsequent demethoxylation. The synthesis of HNapIm, HNapOx, and HNapThi occurred via acid catalyzed azole cyclization dehydrogenation. I-Hbq and dI-Hbq were synthesized via the direct iodination

of Hbq. Among the novel ligands evaluated, dI-Hbq, I-Hbq, Hbq, HNapIm, HNapOx, and HNapThi were photocatalytically active. Within the first 42 hr, dI-Hq and Hbq both produced higher yields of zinc metal than dCl-Hq, which was the highest performing ligand precatalyst in chapter 3. However it was found that after 166 hrs of illumination, dCl-Hq was more durable and produced 181 catalytic TONs at 50 μ M, compared to 120 by Hbq and 95 by dI-Hbq. Because of the low concentrations, these are the highest TONs reported in this work for a zinc photocatalyst formed in situ. It was postulated that the improved initial performance of the 10-benzo[h]quinolones is a result of higher absorption at 460 nm. The lower total TON of these novel 10-hydroxybenzo[h]quinoline ligands is likely due to the extended benzoquinoline aromatic systems, which are more prone to photo-oxidation over time.

Chapter 5. Di-Cyano Bipyridine Ir(III) Complexes for Photocatalytic Zn(II) Reduction

Introduction

The success of Ir(III) photocatalysts in chapter 2 prompted the design and synthesis of similar iridium complexes explicitly for Zn(II) reduction. In accord, this chapter describes the synthesis of $[\text{Ir}(\text{C}\wedge\text{N})_2(\text{N}\wedge\text{N})](\text{PF}_6)$ complexes where $\text{N}\wedge\text{N}$ = 4-4'-dicyano-2-2'-bipyridine (dCN-bpy) and the subsequent evaluation of these complexes as photocatalysts for Zn(II) reduction. It was hypothesized that the preservation of the $\text{Ir}(\text{C}\wedge\text{N})_2(\text{N}\wedge\text{N})^+$ architecture and the incorporation of pendant nitrile functional groups would increase photocatalytic activity. Nitrile functional groups were targeted specifically because of the significant solvent effects demonstrated by MeCN in chapters 2 and 3. MeCN positively shifts the onset potential of Zn(II) reduction and its use as a solvent results in much greater yields of photoreduced zinc metal. However, acetonitrile is toxic and the use of any organic solvent for large scale solar fuels generation has detrimental environmental implications. It was thus desirable to achieve this effect in other solvents in the absence of acetonitrile, so nitrile groups were incorporated into the photocatalyst.

The nitrile moiety was also expected to act as a bridging ligand in order to improve the catalytic rate of electron transfer. Literature precedent for bridging ligands serving this purpose can be found in multiple areas of solar energy research. Polydentate ligands capable of binding multiple metals have been used to synthesize combined polynuclear complexes chromophore-catalyst systems with higher rates of water reduction.^{124,156} Improved rates of electron transfer have also been achieved by the

bridging of mononuclear iridium complexes to inorganic substrates. Recent work in the Bernhard group documents $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})](\text{PF}_6)$ complexes with pendant pyridine moieties that effectively bind colloidal platinum WRCs, resulting in higher rates of water reduction.¹²³ It was thus thought that two novel iridium complexes, $\text{Ir}(\text{ppy})_2(\text{dCN-bpy})^+$ and $\text{Ir}(\text{F-mppy})_2(\text{dCN-bpy})^+$, would achieve higher yields of photoreduced zinc metal in the absence of acetonitrile through bridging to the ZnCl_2 substrate.

Experimental Methods

Materials - All materials were used as received. ZnCl_2 was purchased from Sigma. Triethylamine was purchased from Acros Organics, and MeCN was purchased from Fisher Scientific. 4-4'-di-tert-butyl-2-2'-bipyridine and 2-phenylpyridine were purchased from Aldrich while $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Pressure Chemical.

Zn(II) Photoreduction by $[\text{Ir}(\text{ppy})_2(\text{dCN-bpy})](\text{PF}_6)$ and $[\text{Ir}(\text{F-mppy})_2(\text{dCN-bpy})]\text{PF}_6$ - The same photoreactor and procedures for photoreaction set up and work up were employed as in chapter 2. $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ was tested alongside the two novel dCN-bpy iridium complexes over 72 hr of illumination. Each vial contained 420 mg ZnCl_2 , 9 ml MeCN or EtOAc, 1 ml TEA, and 110 μM of the iridium photocatalyst.

Synthesis - dCN-bpy was synthesized according to established procedures.¹⁵⁷

$[\text{Ir}(\text{ppy})_2(\text{dCN-bpy})](\text{PF}_6)$ and $[\text{Ir}(\text{F-mppy})_2(\text{dCN-bpy})]\text{PF}_6$ were both synthesized by modified versions of established procedures for $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+$ complexes.¹²⁸ The original procedure was modified so that cleavage of the $(\text{Ir}(\text{C}^{\wedge}\text{N})_2\text{Cl})_2$ dimer by dCN-bpy was performed under milder conditions, in EtOH under reflux. The entire synthesis is detailed elsewhere.¹⁵⁸

Fluorescence Spectroscopy – The photoluminescence spectrum and lifetime of both $[\text{Ir}(\text{ppy})_2(\text{dCN-bpy})](\text{PF}_6)$ and $[\text{Ir}(\text{F-mppy})_2(\text{dCN-bpy})](\text{PF}_6)$ were measured in MeCN on a Fluorolog-3 equipped with dual monochromators and a photomultiplier tube at right angle geometry. Samples were purged in MeCN-saturated argon for 5 minutes prior to photoluminescence measurement. 50 mM of each complex was used.

Results and Discussion

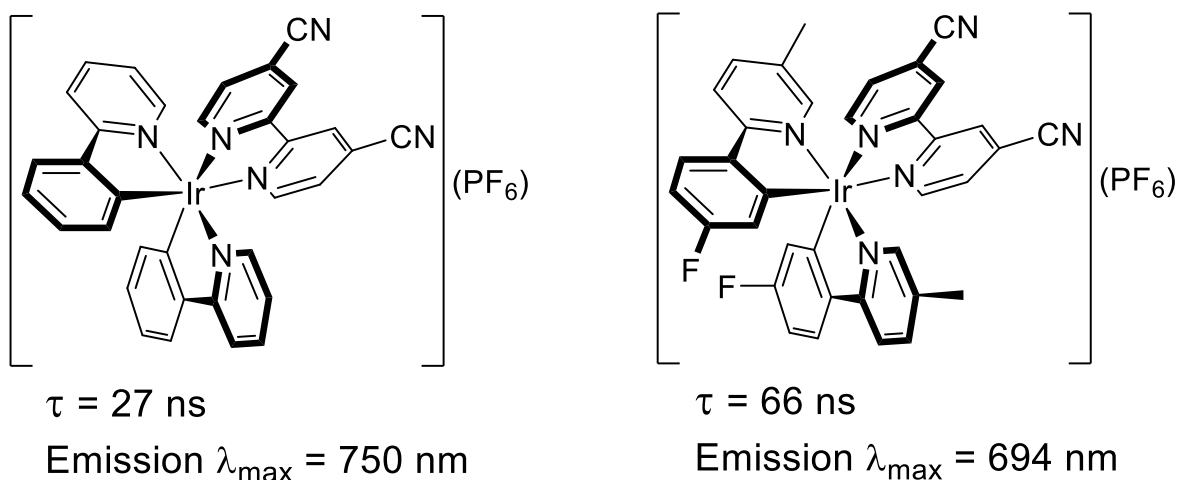


Figure 5-1 – Structures, lifetimes and maximum emission wavelengths of $[\text{Ir}(\text{ppy})_2(\text{dCN-bpy})](\text{PF}_6)$ and $[\text{Ir}(\text{F-mppy})_2(\text{dCN-bpy})](\text{PF}_6)$.

Two novel Iridium complexes, $[\text{Ir}(\text{ppy})_2(\text{dCN-bpy})](\text{PF}_6)$ and $[\text{Ir}(\text{F-mppy})_2(\text{dCN-bpy})](\text{PF}_6)$, were synthesized. The excited state lifetimes and peak photoluminescence wavelengths of these complexes were determined by Fluorescence spectroscopy. This photophysical data and the structures of these complexes can be seen in Figure 5-1. Both $[\text{Ir}(\text{ppy})_2(\text{dCN-bpy})](\text{PF}_6)$ and $[\text{Ir}(\text{F-mppy})_2(\text{dCN-bpy})](\text{PF}_6)$ have drastically shorter lifetimes than their counterparts in which $\text{N}^{\wedge}\text{N}=\text{dtbbpy}$. Typical lifetimes of $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})^+$ complexes exceed 100 ns and are often above 1 μs , so the excited state of these novel complexes is quite short lived by comparison. The emission of these

complexes is also green shifted due to the stabilization of the LUMO by the electron withdrawing nitrile groups on the bipyridine ligand.

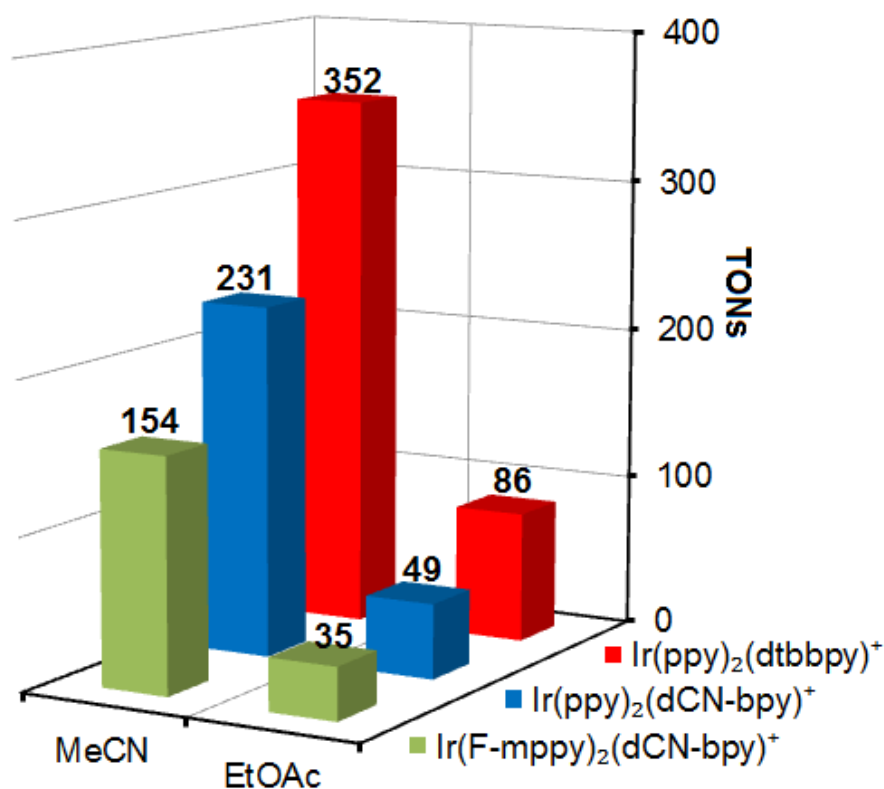


Figure 5-2 – Yields of photoreduced zinc metal afforded by $[\text{Ir(ppy)}_2(\text{dCN-bpy})](\text{PF}_6)$, $[\text{Ir(F-mppy)}_2(\text{dCN-bpy})](\text{PF}_6)$ and $[\text{Ir(ppy)}_2(\text{dtbbpy})](\text{PF}_6)$ in MeCN and EtOAc after 72hr illumination.

These novel complexes and $[\text{Ir(ppy)}_2(\text{dtbbpy})](\text{PF}_6)$ were evaluated as catalysts for photocatalyzed Zn(II) reduction in MeCN and EtOAc. Photoreaction conditions were similar to those described in chapter 2; ZnCl_2 was used as the reagent and TEA as the sacrificial reductant. Zinc metal produced by these complexes was measured after 72 hr of illumination. While it was expected that yields of zinc metal in EtOAc would be higher for the novel dicyano-bipyridine Ir(III) complexes, $[\text{Ir(ppy)}_2(\text{dtbbpy})]\text{PF}_6$ exhibited the highest photocatalytic activity in both MeCN and EtOAc. Figure 5-2 displays these

results. This can be attributed to the absorptivity of the dicyano-bipyridine complexes under the 465 nm blue light employed; future studies should use AM 1.5 solar irradiation for a better direct comparison. In ethyl acetate, the dicyano-bipyridine Ir(III) complexes produced between four and five times less zinc than in acetonitrile, similar to $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$. The pendant nitrile groups alone thus cannot replace the role of acetonitrile in Zn(II) photoreduction. The absence of any relative improvement suggests that the dCN-bpy ligands do not positively shift the onset of Zn(II) reduction in the same manner as MeCN. This may result because the nitriles of dCNbpy are incorporated into the pi system of the ligand, which reduces their capacity as pi acceptors for the $d10$ Zn(II) ion. Alternatively, multiple MeCN ligands may be required to affect the electrochemistry of ZnCl_2 , so one photocatalyst could not duplicate this effect. Different routes must therefore be taken to obtain high photocatalytic activities of Zn(II) reduction in more benign solvents.

Conclusion

This chapter recounts the synthesis and characterization of novel cyclometallated dicyano-bipyridine Ir(III) complexes as well as their evaluation as photocatalysts for Zn(II) reduction. These dCN-bpy iridium complexes exhibited shorter lifetimes and red-shifted emission, and afforded lower yields of photoreduced zinc metal relative to most heteroleptic biscyclometallated Ir(III) complexes. Similar to $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$, yields of zinc metal afforded by $[\text{Ir}(\text{ppy})_2(\text{dCN-bpy})](\text{PF}_6)$ and $[\text{Ir}(\text{F-mppy})_2(\text{dCN-bpy})]\text{PF}_6$ were 4-5 times lower in EtOAc than MeCN. A different approach must be taken

in order to eliminate MeCN from high performance photocatalytic systems for Zn(II) reduction.

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