THE PENNSYLVANIA STATE UNIVERSITY
SCHREYER HONORS COLLEGE

DEPARTMENT OF CHEMISTRY

A BIOMIMETIC APPROACH TO IMPROVE ELECTRON TRANSFER IN THE OXIDATION HALF CELL OF A PHOTOLYTIC WATER-SPLITTING SYSTEM

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Abstract

Photolytic water-splitting has been called a “holy grail” of chemistry due to the opportunities it presents as a route to clean hydrogen fuel. Currently, a major challenge to achieving adequate efficiency is electron transfer within the oxidative half-cell. A synthetic route to a novel bipyridyl dye modeled on the tyrosine residue mediator in Photosystem II was designed. Progress towards this synthesis was achieved, with the synthesis of the fourth intermediate, 4,4’-diamino-5,5’-dinitro-2,2’-bipyridine in an overall yield of 3.5%.

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I. Introduction

A. History and Relevance of the Photochemical Water Splitting Cell

Photochemical water splitting is an enduring unsolved challenge in chemical research.[1-3] A "holy grail", as it has been sometimes been called, that researchers in this field seek is an efficient, long-lasting system for splitting water into its constituent elements, H_2 and O_2, using light with the intensity and spectral character of the sun (Equation 1).[2] The hydrogen produced could then be used as a "clean" fuel, one produced and combusted without direct production of pollutants or greenhouse gases (Equation 2). It is becoming increasingly clear that developing viable energy alternatives to fossil fuels is crucial for avoiding the adverse effects of global climate change. Additionally, while predictions vary, experts agree that the supply of fossil fuels is dwindling, new sources will be more expensive to tap, and eventually the supply will decrease and finally disappear. Additionally, climate change and the end of fossil fuel supplies come at a time when world energy consumption is increasing and expected to continue to do so, as shown in Figure 1.[4] With the sun providing the Earth's surface with far more energy than even the highest predicted demand in the

$$H_2O + 2\ h\nu \rightarrow H_2 + \tfrac{1}{2}\ O_2 \qquad (1)$$

$$H_2 + \tfrac{1}{2}\ O_2 \rightarrow H_2O + \text{energy} \qquad (2)$$

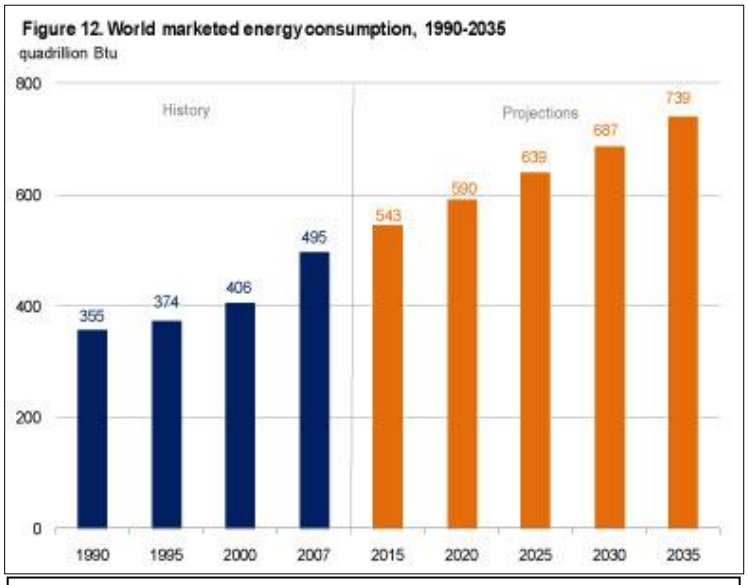

Figure 1: Past and projected marketed world energy consumption[4]

near future, harnessing its power for electricity and fuels is a daunting challenge of great worth to science and society.

The photocatalytic water splitting cell my project involves has its background in two related solar cells, one type pioneered by Michael Gratzel and another by Fujishima Akira and Honda Kenichi. Systems known as dye-sensitized solar cells (DSSCs) were first developed by Gratzel and are now considered to be one of several types of organic solar cells. The Gratzel cell[5-6] (Figure 2) is composed of a photosensitive dye on a porous TiO_2 semiconducting cathode along with a platinum anode. Absorbed sunlight excites the dye, which injects an electron into the TiO_2. The electrons then travel through an external load, after which they are injected back into the dye via an I^-/I_3^- redox couple. Graetzel cells absorb very efficiently in the visible range, but poorly in the infrared. The rate of electron injection from the I/I_3^- redox couple is very fast, thus preventing undesirable back electron transfer.

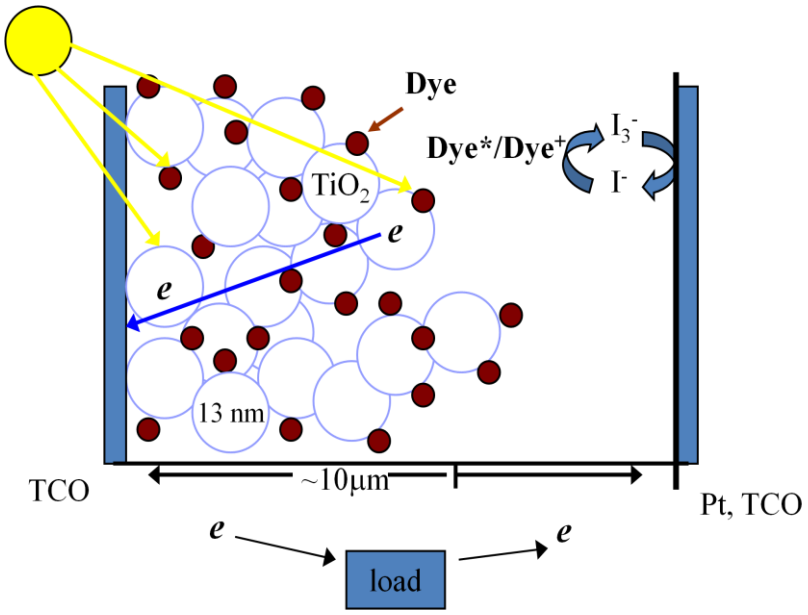

Figure 2: Schematic of a Gratzel solar cell

The water-splitting Fujishima-Honda cell, on the other hand, uses UV light not to directly produce electricity, but instead to split water into its constituent elements, hydrogen and oxygen.

Titanium dioxide is used as a photocatalyst for hydrolysis, and a small applied voltage is also required to achieve reduction of H_2O to H_2. The wide band gap of TiO_2 is sufficient to drive the four-electron oxidation of H_2O to O_2 without the need for a sacrificial redox couple, but precludes the use of visible light.[7-8]

Our cell combines aspects of the Gratzel and the Fujishima-Honda cells to achieve visible-light driven water photolysis based on dye-sensitizing molecules, semiconducting TiO_2, and iridium oxide nanoparticles as water oxidation catalysts (Figure 3).[9] The oxygen-evolving half-cell, which is the focus of this paper, consists of dye-sensitized, hydrated iridium oxide nanoparticles adsorbed onto a nanoparticulate titanium (IV) oxide photoanode. When a photon is absorbed by the ruthenium polypyridyl dye, the resulting excited state of the dye is quenched by electron transfer to the TiO_2. This is followed by electron transfer from the catalytic IrO_2 to the photo-oxidized dye, thus driving the four-electron oxidation of water to molecular oxygen.[9-11] Recent advances in the field include the development of improved water oxidation catalysts with higher site turnover rates;[12-14] the kinetics and the mechanism of water oxidation are also becoming better understood.[15-16] Already, high quantum yields are routinely obtained for some molecular charge systems, such as simple dye sensitized solar cells and sacrificial water oxidation and reduction.[17-19] This shows that individual components of the system, including the colloidal catalysts and dye-

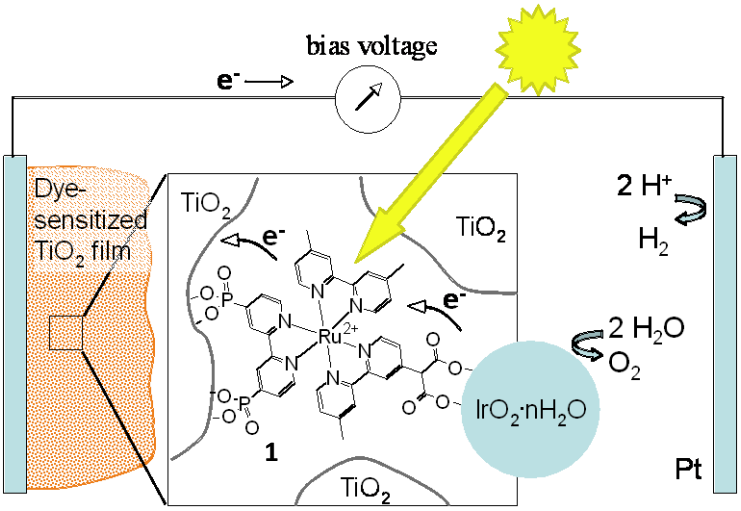

Figure 3: Schematic of dye-sensitized water-splitting solar cell[9]

sensitizer diads, are already available. At this point, therefore, the major task of this overall endeavor is to create the appropriate architectures that will kinetically favor forward over back electron transfer.

B. Current Kinetics of Dye Sensitized Water Splitting Solar Cells

There are only a few recent examples of photoelectrochemical water splitting systems in which visible-light absorbing molecules mediate electron transfer between a TiO_2 electrode and a water oxidation catalyst.[9,20,21] Quantum yields in the neighborhood of 1% have been reported, and so far, there are no other molecule-based systems outside of natural photosynthesis that perform overall water splitting or the more challenging reaction of reducing carbon dioxide while oxidizing water to oxygen using visible light. With the proper understanding of the details of charge separation and recombination and their relation to structure, however, it should be possible to re-design current systems for higher efficiency.

While there are a number of factors that contribute to losses in artificial photosythesis, the most important one is the low quantum yield that results from fast back electron transfer reactions. Back electron transfer in even the simplest systems of this kind (e.g., a sensitized oxide semiconductor particle, loaded with a hydrogen evolving catalyst and linked through a sensitizer molecule to an oxygen evolving catalyst) can occur through many pathways, as shown by the dotted lines in Figure 4. These pathways are typically more energetically favorable than forward electron transfer. Specifically in this system, the electron transfers which contribute the most to inefficiency are quenching of the sensitizer excited state by the IrO_2 clusters and fast backward transfer from TiO_2 to the dye.

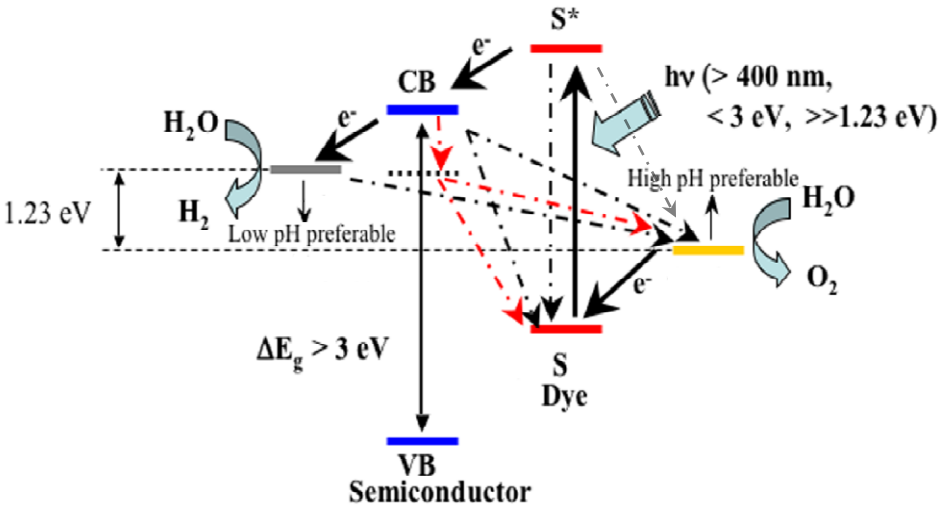

Figure 4: Kinetic scheme illustrating forward electron transfer (solid lines) and possible recombination pathways (dotted lines) in sensitized semiconductor nanosystems containing hydrogen and oxygen evolving catalysts

Understanding and optimizing the kinetics of electron transfer within the cell is an important challenge. Currently, the injection of an electron from the IrO_2 oxygen evolving catalyst to regenerate the dye is between 1-3 orders of magnitude slower than the back electron transfer from the conduction band of TiO_2 to the dye.[12] This decreases efficiency as most of the electrons are not utilized for the oxidation of water. It also promotes degradation of the dye, which occurs on a time scale of seconds without regeneration from injection of an electron.

C. The Role of Tyrosine in Photosystem II

One strategy to address the challenges of the electron transfer kinetics in the oxygen-evolving half cell is to employ a biomimetic design based on a crucial tyrosine residue in photosystem II. Theoretically, positioning a tyrosine mimic between the IrO_2 clusters and the ruthenium dye should increase the rate of forward electron transfer between those two

components. In photosystem II, the tyrosine residue of interest, Tyr_Z, functions as a redox mediator between P680+, the primary electron donor, and the Mn-containing oxygen evolving complex (OEC).[22] Tyr_Z plays a key role in oxygen evolution by acting as a mediator for step-wise electron injection, ensuring that electron transfer occurs at a very fast time scale (Figure 5).[23] The identity and functional role of Tyr_Z was first described by Babcock *et. al.*, and later work has determined both the exact position of Tyr_Z within photosystem II as well as the most likely action of its mechanism.[25-27] Oxidation of Tyr_Z by $P_{680}^{\cdot+}$ is likely achieved with transfer of the phenolic proton to nearby the nearby histidine residue, His190.[26-27] This facilitates fast, efficient electron transfer by poising the redox potential of the tyrosine between that of P680 and the manganese within the oxygen-evolving complex. When tyrosine injects its electron into P680+ to regenerate P680, the proton is transferred back to its original position on the tyrosine oxygen (Figure 6).

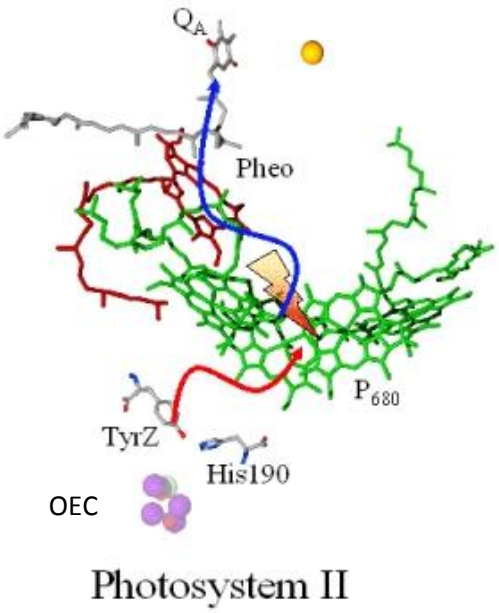

Figure 5: Structure and electron transfer between the oxygen-evolving complex, Tyr_Z, and P_{680} in Photosystem II [24]

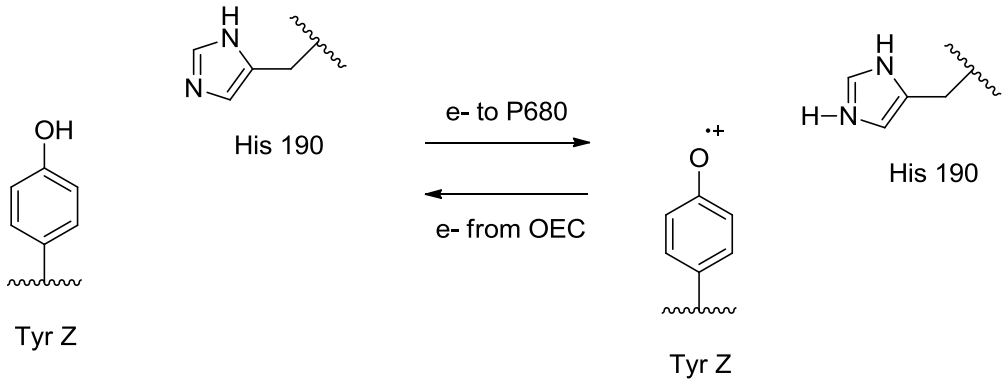

Figure 6: Electron transfer within the Tyr_Z – His 190 diad in photosystem II

D. Design of the Ru-Tyr-IrO_2 Triad

Within our system, a tyrosine mimic poised between the IrO_2 nanoparticles and the dye molecule would ensure that an electron is always available for fast regeneration of the dye molecule on a time scale that could out-compete back electron transfer (Figure 3).

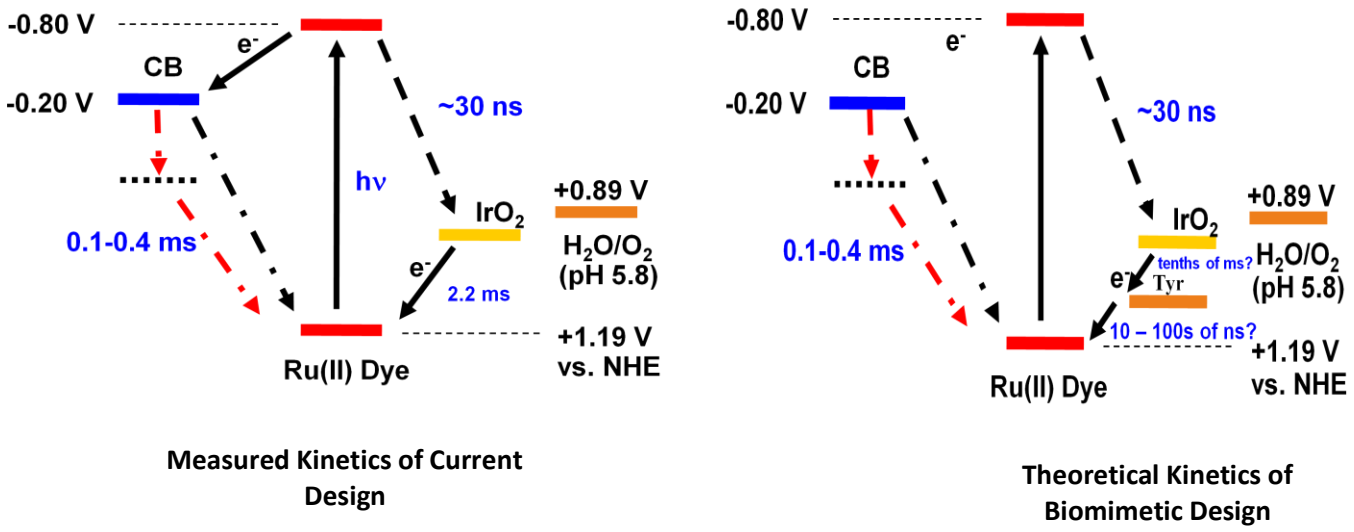

Figure 7: Current measured kinetics of electron transfer within the oxygen-evolving half cell (left side); theoretical kinetics with tyrosine mimic intermediary (right side).

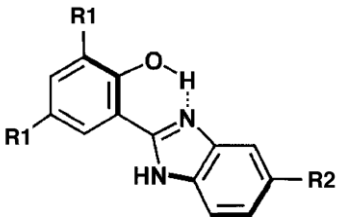

Figure 8: High potential Tyr-His diad mimic

A promising tyrosine mimic has been synthesized and tested by Moore *et al* via the insertion of a high potential mediator (Figure 8) between the sensitizer and the $IrO_2 \cdot nH_2O$ clusters.[28] Studies thus far have shown it to act as a reservoir for electrons and to have a low barrier for electron transfer to a covalently bound porphyrin or ruthenium polypyridyl sensitizer via a proton coupled electron transfer (PCET) mechanism.[28] If this electron transfer is fast, one would expect

significantly improved dye stability because the dye would spend less time in the Ru(III) state. One would also expect improved electron transfer due to the more favorable kinetics of the forward with respect to the back ward electron path.

The internally hydrogen-bonded ortho-phenol/benzimidazole mediator shown in Figure 9, which was determined by the Arizona State group (using R_1 = *t*-butyl, R_2 = H) to be electrochemically reversible with E_0 = +0.95 V vs. SCE in CH_2Cl_2, is a very attractive design in the context of water splitting.[28] This group prepared the benzimidazole as part of a porphyrin ring, but it is theoretically possible to incorporate it into other frameworks such as bipyridyl ligands.

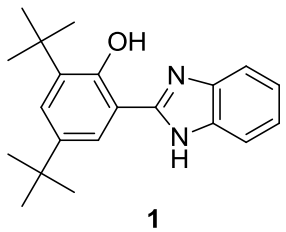

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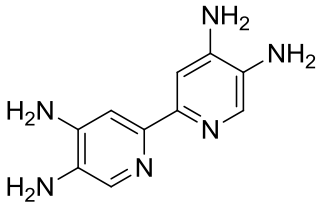
Figure 9: Internally hydrogen-bonded ortho-phenol/ benzimidazole mediator prepared by Moore *et al.*

E. Synthetic Route to Ru(bpy)$_2$(4,4',5,5'-tetraaminobipyridyl)

Our current system design utilizes ruthenium dye functionalized with bipyridyl ligands. One advantage of using the ruthenium dye as a photosensitizer is that up to three different ligands can be attached to the metal center, giving the dye greater functionality and the opportunity to bind to the other constituents of the system. Also, multiple ligands allows for electronic tuning of the sensitizer dye. As such, the major goal of this project was to design and synthesize a novel ligand which covalently links the tyrosine mimic to a ruthenium metal center. This would allow the

tyrosine mimic to be easily incorporated into our current system design. In the previously made system by Moore *et al.,*[28] phenyl 3,5-di-*tert*-butyl-2-hydroxybenzoate was condensed with a diaminophenyl functionality on a zinc porphyrin to create the desired structure. The most obvious strategy is therefore to identify an appropriate bipyridyl ligand which would supply the diaminophenyl group in this reaction.

Over the past twenty years, synthetic routes to a wide variety of functionalized bipyridyl ligands have been developed. A suitable ligand for the purpose of condensation with the hydroxybenzoate molecule is 4,4',5,5'-tetraamino-2,2'-dipyridyl (**2**), the preparation of which was previously described by Balme and Gruffaz.[29] After completion of the synthesis of **2,** it could be condensed with same hydroxybenzoate molecule used in the literature[28] **(3)** with the porphyrin to create the suitable target ligand, shown as structure **4** (Scheme 1). This reaction uses a procedure analogous to that used by Moore *et al* in the synthesis of their porphyrin. It is unknown whether both diamino functionalities would participate in the reaction, or whether only one hydroxybenzoate would attach to each bipyridyl. The answer would likely depend on the stoichiometric ratios employed in the reaction along with steric effects.



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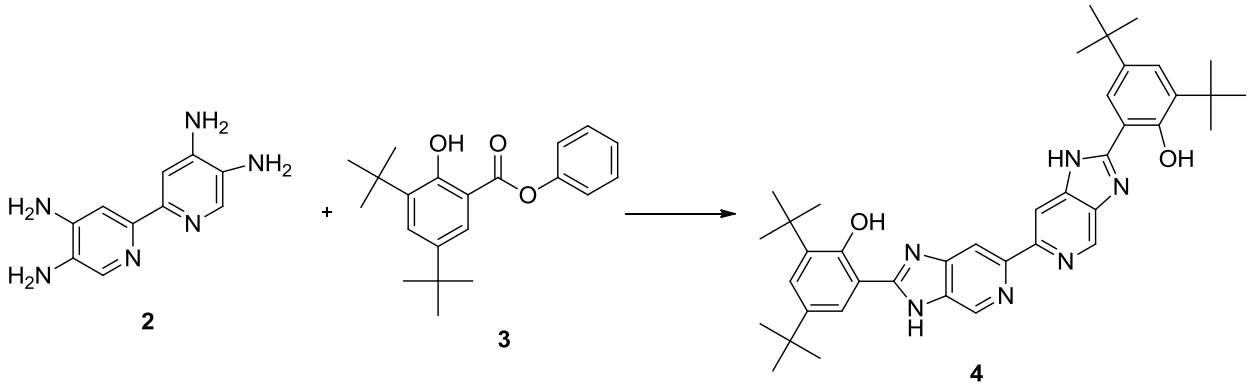
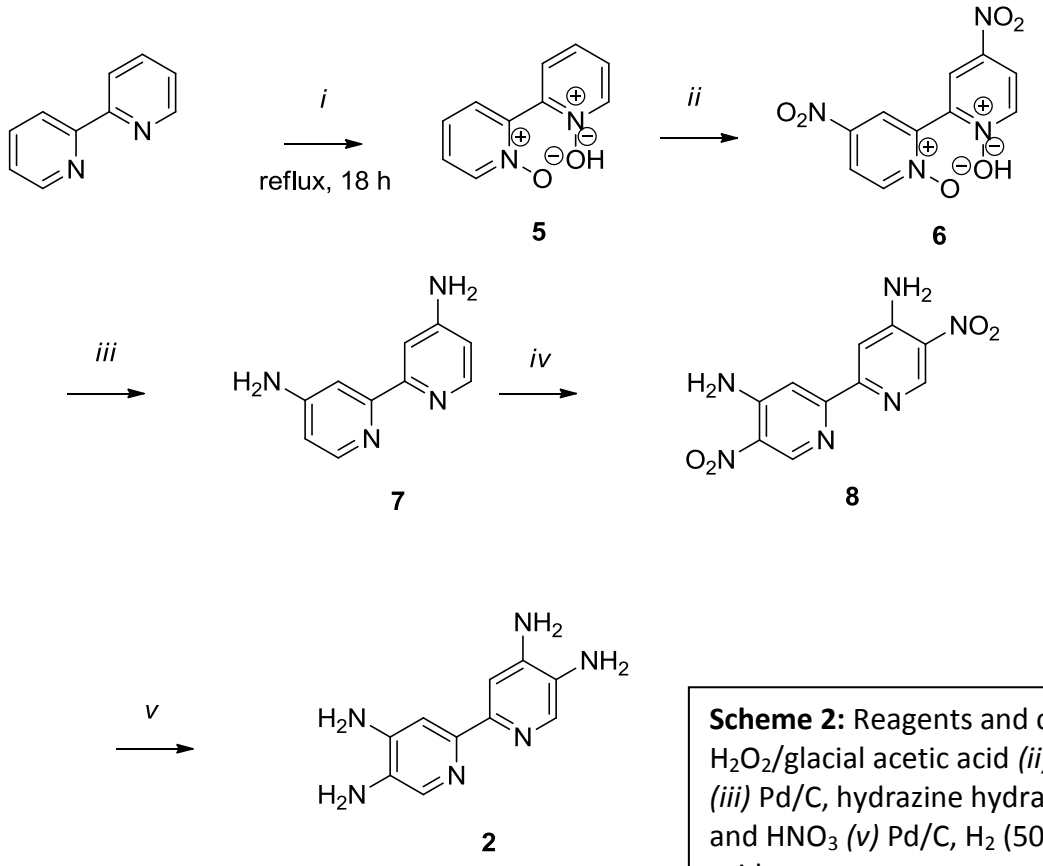


2 **3** **4**

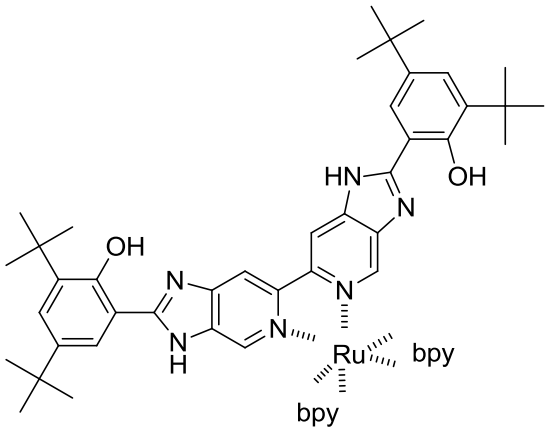
Scheme 1: Condensation of 4,4',5,5'-tetraamino-2,2'-dipyridyl with phenyl 3,5-di-*tert*-butyl-2-hydroxybenzoate to synthesize target bipyridyl ligand **4.**

The synthesis of hydroxybenzoate **3** is relatively straightforward, requiring only one step utilizing 3,5-di-*tert*-butylsalicylic acid and phenol as starting materials.[28] The total synthesis of **2** from 2,2'-bipyridine, in contrast, consists of five separate steps (Scheme 2). The synthesis is based on prior work by a number of laboratories.[30-32] First, 2,2'-bipyridine is reacted with H_2O_2 in acetic acid to form the N-oxide derivative **5.** Symmetric nitro groups are added using fuming HNO_3 under harshly acidic conditions, then reduced using hydrazine hydrate as the electron donor with a Pd/C catalyst. The diamino-bipyridyl compound **7** is then converted to 4,4'-diamino-5,5'-dinitro-2,2'-bipyridine (**8**), again using fuming HNO_3 and concentrated H_2SO_4. Finally, the last pair of nitro groups in compound **8** are reduced with H_2 (40 bar) and catalytic Pd/C to form the final product 4,4',5,5'-tetraamino-2,2'-dipyridyl (**2**).



Scheme 2: Reagents and conditions: (*i)* H_2O_2/glacial acetic acid *(ii)* H_2SO_4 and HNO_3 *(iii)* Pd/C, hydrazine hydrate, EtOH *(iv)* H_2SO_4 and HNO_3 *(v)* Pd/C, H_2 (50 bar), glacial acetic acid

Once tetraamino-bipyridyl compound **2** is synthesized and condensed with hydroxybenzoate **3**, as shown in Scheme 1, and the final target ligand **4** is formed, the desired ruthenium dye can be created. Syntheses of heteroleptic ruthenium dyes are well known,[33-35] and the desired final product **9** can be synthesized in a procedure similar to that used by Freedman *et al*.[33]



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II. Experimental

All chemicals and solvents were obtained from Aldrich (Milwaukee, WI) and used as supplied except where specified. All ^{1}H NMR spectra were recorded on a Bruker DPX-300 multinuclear NMR spectrometer using solvents as stated.

2,2'-Bipyridine-*N,N'*-dioxide, 5. A solution of 25 mL of 30% hydrogen peroxide was added to 2,2'-bipyridine (64 mmol, 10.0 g) in 67 mL of glacial acetic acid. The resulting clear solution was heated and stirred at 80 °C for 15 hours. After cooling to rt, the reaction mixture was added to 800 mL of acetone to precipitate the product as a light yellow solid, which was collected by vacuum filtration

and dried in air. The solid was then recrystallized from hot water to give 9.02 g (48 mmol, 75% yield) of the product as thin, white crystals.

4,4′-Dinitro-2,2′-bipyridine *N*,*N*′-Dioxide, 6. A solution of **5** (26.5 mmol, 4.98 g) in 24 mL of concentrated sulfuric acid was cooled to 0 °C. Fuming nitric acid (8.45 mL) was added dropwise, and the mixture was kept at 0°C for an additional 10 min. The solution was then heated under N_2 at 90-95°C for 12 h, during which time the mixture changed color from clear to bright yellow. After cooling to rt, the reaction mixture was poured over ice and quenched with Na_2CO_3 (~50g). The resulting yellow precipitate was collected with vacuum filtration and dried overnight at 60°C (**6**, yellow powder yield 2.1 g, 7.5 mmol, 28%) 1H NMR (300 MHz; DMSO*d*6; ppm): δ 8.34 (m, 2H), 8.62 (d, 2H), 8.68 (d, 2H).

4,4′-Diamino-2,2′-bipyridine, 7. A mixture of **6** (5.4 mmol, 1.5 g) and 2.7 g Pd/C (5%) in 160 mL of ethanol was purged with N_2 and heated. When the complex had dissolved, 11.6 mL (373 mmol) of hydrazine hydrate in 40 mL ethanol were added dropwise, and the solution was refluxed for 18 h. When completed, the reaction was filtered hot through a bed of Celite, and the pad was washed with 4 x 50 mL of boiling ethanol. After removal of the solvent under reduced pressure, the yellow precipitate was ground with 50 mL of cold water and left overnight at 2 °C. A white solid separated and was collected by vacuum filtration, washed with cold water, and dried overnight at 60°C (**7**, white crystalline yield 0.35 g, 1.9 mmol, 35%). 1H NMR (300 MHz; DMSO*d*6; ppm): δ 6.60 (m, 2H), 7.17 (d, 2H), 8.04 (m, 2H).

4,4′-Diamino-5,5'-Dinitro-2,2′-bipyridine, 8. A mixture of **7** (0.5 mmol, 93 mg) in 0.5 mL of concentrated sulfuric acid was purged with N_2 and cooled to 0°C. A solution of H_2SO_4/HNO_3 (55 µL/45 µL) was added and mixture kept at 0 °C for an additional 10 min. Mixture was then allowed to warm to rt and stirred for 1 h, during which time the color turned from brown to dark yellow. The solution was then slowly heated to 95-100 °C at a rate which avoided a strong exothermic reaction. Once the reaction had subsided, the mixture was kept at 95-100 °C for 1h, then cooled and poured over ice. Aqueous ammonia (1.4 mL) was added to immediately yield a golden-yellow precipitate, which was collected by vacuum filtration, washed with cold water, and dried overnight at 60°C (**8**, golden-yellow powder yield 65 mg, 0.2 mmol, 47%). 1H NMR (300 MHz; DMSO*d*6; ppm): δ 8.02 (s, 2H), 9.08 (s, 2H).

Phenyl 3,5-di-*tert*-butyl-2-hydroxybenzoate, 3. Under an argon blanket, 3,5-di-*tert*butyl salicylic acid (1.00 g, 4.00 mmol), phenol (414 mg, 4.40 mmol), and N,N'-dicyclohexylcarbodiimide (DCC) (1.19 g, 5.75 mmol) were dissolved in freshly distilled THF (25 mL). The reaction mixture was then stirred under argon for 4 days, after which it was filtered and washed with diethyl ether (3 x 10 mL). The filtrate was concentrated under reduced pressure to yield the impure product as a yellow oil containing both compound **3** and salicylic acid starting material (peaks not listed). 1H NMR (300 MHz; $CDCl_3$; ppm): δ 1.31 (s), 1.42 (s) 7.12-7.50 (m), 7.62 (d), 7.95 (d).

III. Results and Discussion

A. Progress towards 4,4',5,5'-tetraaminobipyridyl

The first four intermediates in the synthetic pathway were successfully synthesized. The yield of 2,2'-bipyridine-*N,N'*-dioxide (**5**) from 2,2'-bipyridine was 75%, and the subsequent nitration of **5** to 4,4'-dinitro-2,2'-bipyridine *N*,*N*'-dioxide (**6**) proceeded with 28% yield. Intermediate **6** was successfully reduced to give 4,4'-diamino-2,2'-bipyridine (**7**) in a 35% yield, and the final successful reaction to yield 4,4'-diamino-5,5'-dinitro-2,2'-bipyridine (**8**) was completed with 47% yield. These four reactions were all performed twice, with improvements in yield and ease of isolation observed during the second set of reactions. One notable improvement was made to the procedure for the synthesis of the dinitro-bipyridyl compound **6** performed by Kavanagh *et al.*[32] While the literature called for pouring the acidic reaction mixture into water and cooling with liquid N_2, then filtering and washing with water to de-acidify, this was found to lead to lower yields due to the partial solubility of the product in water. To achieve higher yields, the reaction mixture was instead quenched with a stoichiometric amount of Na_2CO_3, a procedure which proved not only more effective, but also much easier.

The characterization by ^{1}H NMR was sufficient to confirm the identity of compounds **5-8** as well as their purity. The spectra of all of the products included the expected peaks and matched the characterization reported in the literature. No other significant peaks were observed besides those attributable to solvents.

The reduction of the two nitro functional groups of **8** to theoretically yield 4,4',5,5'-tetraamino-2,2'-bipyridine (**2**) was also attempted multiple times, although synthesis of a

measurable amount of desired product was never achieved. Instead, synthetic attempts resulted in the re-isolation of starting material **8** at best. In the first attempt, the procedure for the synthesis and isolation of **8** outlined in the patent was followed. In summary, into a steel autoclave were introduced 4,4'-diamino-5,5'-dinitro-2,2'-bipyridine (**8**), glacial acetic acid, and 5% Pd/C. The autoclave was purged with helium, and hydrogen was introduced at a pressure of 40 bars. The mixture was heated to 75°C for 5 hours, then cooled and degassed. It was assumed that the patent procedure employed an industry standard of Pd/C (10%), and the appropriate stoichiometric equivalent of Pd/C (5%) was calculated and used. The lengthy isolation procedure outlined in the patent was attempted, but neither starting material nor product was recovered. Only a small amount of insoluble brown powder was obtained; this was assumed to be a decomposition product.

For subsequent attempted syntheses of tetraamino-bipyridine **2**, a number of procedural modifications were implemented. The H_2 pressure, reaction temperature, and reaction time were increased to align with an alternative procedure mentioned in the literature.[29] Additionally, the lengthy isolation was abandoned in favor of a far simpler approach. After cooling and degassing, the catalyst was removed by filtration through a bed of Celite and aqueous ammonia was added to precipitate the product. In the final attempt, a new catalyst, palladium on charcoal (10%) was utilized to eliminate another potentially significant difference between my reaction and the patent procedure. In all cases, the reaction yielded a yellow-brown precipitate. By ^{1}H NMR in DMSO*d*6, it was determined that the obtained precipitate was starting material; no significant additional peaks were observed. Concentration of the filtrate under reduced pressure yielded only a small additional amount of starting

material as observed by ^{1}H NMR. While several alternative paths to compound **2** were considered, it was determined that the original synthesis was theoretically the simplest and most reliable, and that time constraints prohibited many alternative approaches.

A number of factors could have resulted in the failure to successfully synthesize 4,4',5,5'-tetraamino-2,2'-bipyridine (**2**). Perhaps the reaction is very sensitive to moisture or the presence of oxygen, and the purging procedure was inadequate. Alternatively, the temperature of the oil bath might not accurately reflect the temperature inside of the vessel. Addressing these issues would require use of more sophisticated equipment, such as a glove box and an autoclave whose internal temperature can be measured during the reaction. Another possibility is that an appropriate catalyst has still not been identified. The literature is vague on the exact identity of the catalyst used, and it is possible that different metal loading ratios or slightly different substrates could have differing efficacies for this particular reaction.

B. Progress towards phenyl 3,5-di-*tert*-butyl-2-hydroxybenzoate

The synthesis of phenyl 3,5-di-*tert*-butyl-2-hydroxybenzoate (**3**) was successful, as was shown by the presence of product by 1H NMR. It is expected that the remaining salicylic acid starting material, which was a minority of the obtained solid by rough integration of peaks, would have been successfully removed had column chromatography been performed as was outlined in the literature.[28] This purified compound **3** could then have been condensed with bipyridine **2** to yield the target ligand, had bipyridine **2** been successfully synthesized.

IV. Conclusions

While the ultimate goal of this project, the synthesis of a novel ruthenium dye with a bipyridyl ligand containing a tyrosine mimic, was not completed, significant progress was made along the proposed synthetic route. The first four intermediates towards the synthesis of 4,4',5,5'-tetraamino-2,2'-bipyridine were synthesized in pure form as shown by ^{1}H NMR; the fourth intermediate was formed with an overall yield of 3.5%. The requisite 3,5-di-*tert*-butyl-2-hydroxybenzoate was also synthesized successfully, although it was not purified due to time constraints.

Additionally, the complications that occurred with the final step of the synthesis of 4,4',5,5'-tetraamino-2,2'-bipyridine led to the consideration of many alternative paths forward for the future. One option is to attempt to perform the reduction of the second pair of nitro groups using the same conditions, hydrazine hydrate and Pd/C, as were used for the reduction of the first pair of nitro groups. If that fails, it may also be possible to design a route to a different, but similar biomimetic bipyridyl ligand. For instance, the ortho-diamine functionality could be on a phenyl ring, which is in turn bound to a bipyridyl ring system. Finally, using a phenanthroline instead of a bipyridine as the starting material provides another option to achieve the desired goal.

Once the final biomimetic ligand has been successfully synthesized, further structural characterization, such as ^{13}C NMR and elemental analysis, can be performed to confirm identity and purity. After coordination to the ruthenium to form the heteroleptic ruthenium dye, other characterization techniques can be applied, including transient spectroscopy and oxygen evolution studies using the colloidal water oxidation catalysts and sacrificial electron acceptors.

By comparing the results of these experiments with the results obtained using older designs of the polypyridyl dyes, it will be possible to ascertain the effect of the biomimetic ligand.

The eventual goal, if tests show that the new ligand demonstrates improved electron transfer kinetics and oxygen evolution, that this research leads toward is the engineering of a system architecture which situates the ligand directly between the dye molecules and the colloidal IrO_2 catalyst. This could potentially be achieved through mono or polydentate ligand binding to the IrO_2 colloids, a strategy which has been previously employed to stabilize the nanoparticles. Overall, as greater understanding of the electron transfer mechanisms is gained, the possibilities for targeted improvements to the photolytic water-splitting cell grow. Using this understanding to focus on specifically tailoring the structure of the photolytic cell to meet the desired electrochemical and kinetic parameters is an important step towards the design of more efficient systems.

V. References

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- Improved chromatographic techniques for purification and analysis of metal-ligand structures.
- Developed novel synthetic route to dye-sensitized IrO_2 nanoparticles used as catalysts for colloidal oxidation of water. Achieved significant increase in O_2 production by changing stabilizer:IrO_2 ratio in order to maximize accessible catalytic surface area.
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