# INFLUENCE OF LIGAND EXCHANGE ON COPPER REDOX SHUTTLES IN DYE-SENSITIZED SOLAR CELLS

Ву

**Eric James Firestone** 

# A DISSERTATION

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#### ABSTRACT

Dye-sensitized solar cells (DSSCs) are recognized as a promising, eco-friendly alternative to traditional photovoltaics, characterized by their unique light-harvesting capabilities and potential for enhanced efficiency and stability in renewable energy applications. In this study, the focus is on the development of copper redox complexes, which exhibit varying responses to ligand exchange upon the introduction of 4-tertbutylpyridine (TBP), a critical factor influencing electron transfer processes and the overall performance of DSSCs. Three copper complexes, copper(II/I) N,N'-Dibenzyl-N,N'-bis(6-methylpyridin-2-ylmethyl)ethylenediamine triflate, [Cu(dbmed)]OTf<sub>1/2</sub>, copper(II/I) 2,6-bis[1,1-bis(2-pyridyl)ethyl]pyridine triflate, [Cu(PY5)]OTf<sub>1/2</sub> and copper(II/I) 6,6'bis(1,1-di(pyridine-2-yl)ethyl)-2,2'-bipyridine bistriflimide, [Cu(bpyPY4)]TFSI<sub>1/2</sub> were investigated, with synthetic and electrochemical methodologies, including UV-Vis spectroscopy, NMR, and cyclic voltammetry, being utilized to examine the redox behavior and ligand exchange phenomena. The performance of DSSC devices with each redox mediator was measured to be 4.32%, 2.01%, and 1.23% respectively. Methodology developed in this study, which involves using redox potential as an indicator to predict ligand exchange events, represents an expansion and refinement of existing concepts found in the literature. By building on prior research, this approach not only deepens the understanding of copper complex behaviors in DSSCs but also offers a more nuanced perspective for enhancing the design and efficiency of these innovative solar cells.

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## **Chapter 1 – Introduction**

#### 1.1 Motivations in solar energy

Energy is a cornerstone of modern society, and its consumption has profound implications on our environment, most notably in the form of increasing  $CO_2$  emissions. Data from the past decade, specifically between 2010 and 2022, highlights a rise in  $CO_2$  emissions by 1.0% annually, amounting to roughly  $9.9 \pm 0.5$  GtC yr<sup>-1</sup>. This has resulted in an atmospheric  $CO_2$  concentration 51% higher than pre-industrial levels.<sup>1</sup> An alarming 82% of these emissions can be traced back to fossil fuel consumption.<sup>2</sup> This rapid surge in energy use, particularly from fossil fuels, has resulted in energy-related  $CO_2$  emissions surging to record highs, further underscoring the urgent need for carbon-neutral energy sources.

If current trends in emission mitigations and renewable energy adoption persist, projections suggest a 3°C global temperature rise from pre-industrial levels by 2100.<sup>3</sup> This potential escalation intensifies the imperative for a shift toward carbon-neutral energy solutions. Solar energy, boasting an overwhelming theoretical potential of approximately 173,000 TW, dwarfs the current global demand of 2.9 TW and outpaces potential outputs from other renewable sources like wind and hydro.<sup>4,5</sup> Although renewable energy's contribution to global power reached a commendable 12.8% in 2022,<sup>5</sup> broader adoption is constrained by factors such as generation costs and fabrication complexity.



Figure 1.1: The 1.5 AM solar spectrum which represents the average amount of light that reaches the surface of the Earth across the continental United States.<sup>6</sup>

Solar cells present a promising avenue in this regard. Their rising prevalence, combined with declining costs due to the SunShot Initiative, signifies the growing feasibility of solar energy. The SunShot Initiative is a DOE program with the goal to reduce the cost of solar energy by 75%, meeting the 2020 goal by 2017.<sup>7</sup> While the reduction in fabrication costs of traditional silicon solar cells has played a role in this price drop, further reductions face challenges chiefly due to stringent fabrication requirements. The quest for more cost-effective solar solutions necessitates the exploration of alternative photovoltaics with simpler fabrication processes, reduced energy input, and the use of readily available materials.

Dye-Sensitized Solar Cells (DSSCs) emerge as a frontrunner in this category. Their potential affordability stems from their straightforward fabrication and the utilization of earth-abundant materials. However, to truly position DSSCs as a game-changer in the renewable energy landscape, research must intensify around enhancing their efficiency and trimming material costs, thereby ensuring their economic viability and widespread adoption.<sup>8</sup>

# 1.2 History of DSSCs

The legacy of DSSCs is based on the development of the theory of photoelectrochemistry, which can be traced back to Edmond Becquerel's groundbreaking work in 1839.<sup>9</sup> Since the discovery of photoelectrochemistry, it has been used to develop methods of generating clean energy.

Semiconductors are materials with specific bandgaps that can absorb photons of suitable energy. When they absorb these photons, they generate electron-hole pairs that can separate within the semiconductor and participate in redox reactions on different surfaces. Utilizing this idea, in 1873 and 1887 respectively, Vogel and Moser independently explored "sensitization" using silver halides mixed with visible-light-absorbing dyes.<sup>10</sup> The theory was further elucidated almost a century later, in 1969, by Gerischer, who detailed how excited state dissolved dyes could inject electrons into ZnO semiconductor crystals.<sup>11</sup> Further advancements were made with the anchoring of ruthenium and quinone sensitizers by two researchers, Weber and Matsumura in 1979 and 1980, respectively.<sup>12,13</sup>



Figure 1.2: The composition of a DSSC.

Grätzel and his team exponentially enhanced current generation using polycrystalline anatase TiO2 films and the iodide/triodide redox shuttle.<sup>14</sup> By 1993, they achieved a 10% power conversion efficiency (PCE), thanks to refined TiO<sub>2</sub> electrodes and expanded light-harvesting sensitizers.<sup>15</sup> However, with minimal improvements beyond 10% PCE the progress plateaued until 2010 when outer-sphere redox shuttles became prevalent in DSSCs.<sup>16</sup> The subsequent decade saw organic sensitizers paired with outer-sphere redox shuttles, pushing PCEs to 15%.<sup>17–20</sup> In the ensuing sections, the intricate operations of the dye-sensitized solar cell will be delved into, followed by a discussion on the factors limiting the PCE of these devices.

DSSCs are a unique type of photovoltaic that distributes charge separation and collection over multiple components, in contrast to conventional crystalline semiconductor photovoltaics. In a

DSSC, a dye or sensitizer is anchored to semiconductor nanoparticles, usually acting as the primary light absorber. When this dye absorbs a photon, an electron is excited to a state where it can be injected into the semiconductor's conduction band. The role of the semiconductor, often materials like TiO<sub>2</sub>, is to transport these electrons to an FTO substrate (fluorine-doped tin oxide). However, for the dye to continue absorbing light, it needs another electron. This is where a redox shuttle, dissolved in the electrolyte, comes into play. It diffuses to the dye's surface, donating an electron and ensuring the dye's readiness for subsequent photon absorptions. The oxidized redox shuttle then moves to the counter electrode to accept an electron, completing the circuit.

The efficiency of a DSSC in converting sunlight to electrical power depends on several factors. The excited dye must have sufficiently negative potential to inject its electron into the semiconductor. The injection must be faster than excited dye decays or recombines with the semiconductor's electrons. The rate of dye regeneration should outpace its recombination rate. Furthermore, electrons in the semiconductor need to be collected quickly to prevent their recombination with the oxidized redox shuttles. The interplay of these processes largely determines the DSSC's power conversion efficiency.

#### 1.3 Redox Shuttles in DSSCs

DSSCs draw their essence from the ability to regenerate continually. Central to this regenerative ability is the redox couple. Predominantly found in a liquid electrolyte form, the redox couple—both in its reduced and oxidized states—acts as the linchpin, bridging conductivity between the photoanode and the counter electrode.

For the dynamic to work efficiently, the reduced form of the redox couple necessitates a relative negative reduction potential compared to the dye in its ground state. Once the dye molecule

dispatches an electron to the semiconductor, it undergoes oxidation. This is where the reduced redox couple, acting as an electron donor, plays its part. It regenerates the oxidized dye, priming it for the next photon absorption. The pace at which this regeneration occurs is paramount—it contributes to the photocurrent's magnitude. Once it donates its electron, the reduced redox species becomes oxidized, primarily found near the photoanode. Through liquid electrolyte diffusion, this oxidized form drifts to the counter electrode to reclaim an electron from a catalyst surface, completing the cycle.

Not only do redox couples play a vital kinetic role, but their potential also shapes the DSSC's photovoltage output. The open-circuit voltage ( $V_{oc}$ ) is defined by the energy difference between the Fermi level of the semiconductor and the solution potential of the redox shuttle. The Fermi level of a semiconductor is defined by the equation

$$E_F = E_c - \frac{k_B T}{e} ln \frac{n_C}{N_C} \quad (1.1)$$

where  $E_c$  is the energy of the conduction band minimum,  $k_B$  is the Boltzmann constant, T is the temperature in Kelvin, e is the elementary charge of an electron,  $n_c$  is the density of conduction band electrons, and  $N_c$  is the density of states in the conduction band.<sup>21</sup> The Fermi level is influenced by both the influx of electrons into the conduction band and the rate at which electrons exit the conduction band, whether through recombination or charge separation. By deploying diverse redox couples, one can skillfully modulate  $V_{OC}$ , providing avenues for enhanced cell performance.

The equilibrium potential of the liquid electrolyte at the counter electrode sets the cathode's energy level. A redox couple with a more positive redox potential increases the cell's V<sub>oc</sub>, with a limit of the dye's ground state potential. In order to efficiently regenerate the dye, some energy, acting as a driving force for electron transfer, is inevitably lost. If the electron acceptor (the oxidized form of the redox couple) in the electrolyte has a more positive potential than the Fermi Level, it can lead to electron recombination. According to Marcus theory, faster electron transfer rates occur with larger driving forces in the normal region. However, redox couples that transfer electrons rapidly and have a higher potential often face electron recombination, reducing the electron flow under equilibrium. Thus, adjusting the redox properties of the couple is crucial for enhancing solar cell performance.

Triiodide/iodide redox couple's pioneering endeavors set a robust foundation for DSSC efficiency. These couples, due to their superior electron transfer kinetics, became instrumental in ensuring high photocurrent outputs. Studies, notably by Boschloo, delved deep into their mechanisms.<sup>22</sup> Here, the iodide ion would regenerate the dye, subsequently generating the diiodide radical. This radical undergoes rapid disproportionation, yielding triiodide and iodide. The more positive reduction potential of triiodide results in a reduction of electron recombination, thereby increasing the cell's current output. But this comes at a price: energy loss.

Despite their prowess, the intricacies of triiodide/iodide electron transfer mechanisms remain complex, prompting researchers to explore alternate redox couples. Outer-sphere one electron transition metal redox couples offer a more straightforward electron transfer mechanism, sidestepping the complexities seen in iodide/triiodide couples. An example is the cobalt(III/II) tri(2,2'-bipyridine) couple, which has gained immense traction.<sup>23</sup> Their potential is exemplary, but

challenges persist, particularly in low electron transfer rates which leads to high driving force to regenerate the dye.

In summary, redox couples not only act as the heartbeat of DSSCs but also offer a rich tapestry of variables for researchers to manipulate. Balancing energy loss with efficient regeneration and electron transfer remains the ever-present challenge, pointing towards a promising avenue of future exploration.

Recent advancements in solar cell technology have spotlighted the promise of copper(II/I) redox couples. Following several years of research, the efficiency of solar cells featuring copper(II/I) complexes has soared, positioning itself among the elite. Leading to the current highest efficiency DSSC devices to utilize copper(II/I) redox complexes.<sup>20</sup> Remarkably, cells employing these couples consistently demonstrate an open-circuit voltage (V<sub>OC</sub>) exceeding 1 V, a notable leap from cells using cobalt complexes, which exhibit less positive redox potentials.

Historically copper complexes were studied due to their role in electron transfer processes, both biologically and inorganically. Earlier studies gravitated towards understanding copper's role within metalloproteins.<sup>24</sup> These proteins, often sizable and challenging to study, necessitated the exploration of small molecule analogs. This eventually propelled studies into the redox chemistry of copper(II) coordination complexes. In this context, the so-called "blue-copper" Type I protein garnered significant attention due to its distinctively positive reduction potentials, which hinted at the protein's utility in natural electron transport systems.<sup>25</sup> Intriguingly, these properties also align perfectly with the requisites for solar energy conversion, paving the way for their adoption in this realm.

The initiation of this paradigm shift can be attributed to Hattori in 2005, who introduced the potential of copper complexes in DSSCs.<sup>26</sup> The study delineated three diverse redox couples, all with unique ligand environments, and their compatibility with the N719 dye. Of particular interest was the [Cu(SP)(mmt)]<sup>0/-</sup> complex, which mimicked blue-copper proteins. This seminal work laid the groundwork for subsequent researchers to unravel the intricacies of copper redox couples, ultimately culminating in Bai's breakthrough in 2011 that showcased a marked efficiency leap from 1.4% to 7.0%, by pairing a copper redox couple with an organic dye bound to the semiconductor.<sup>27</sup>

As researchers delved deeper into the interplay between dyes and copper redox couples, more nuanced findings emerged. Colombo's exploration with bulky asymmetric phenanthroline copper(II/I) complexes, for instance, highlighted the importance of careful electrolyte composition.<sup>28</sup> By 2016, a flurry of research showcased high-efficiency DSSCs using copper redox couples, with Cong's and Freitag's works standing out. Both explored different ligands and preparation methods, yet achieved efficiencies hovering around 9%.<sup>29,30</sup> Saygili's 2016 study further propelled the field, achieving over 10% efficiency with various copper bipyridyl redox couples.<sup>31</sup>

The pace of advancement in this domain did not abate, with Hu's 2018 study introducing a stable tetradentate copper(II/I) redox couple, which achieved an impressive efficiency of 9.2%.<sup>32</sup> As of the current research landscape, the copper redox mediator copper(II/I) 4,4',6,6'-tetramethyl-2,2'-bipyridine, [Cu(tmpy)<sub>2</sub>]<sup>2+/+</sup>, and the organic dye 3-{6-{4-[bis(2',4'-dihexyloxybiphenyl-4-yl)amino-]phenyl}-4,4-dihexyl-cyclopenta-[2,1-b:3,4-b']dithiphene-2-yl}-2-cyanoacrylic acid, Y123, combination remains at the pinnacle of DSSC performance.<sup>20</sup> However, the quest for perfection

continues, as researchers strive to grasp the intricacies of electron transfer processes within these couples, all in a bid to optimize dye regeneration and electron recombination kinetics.

Base additives in DSSCs, such as pyridines and imidazoles, play a critical role in enhancing redox mediator performance.<sup>33,34</sup> Lewis bases such as 4-tert-butylpyridine (TBP) are used as additives in DSSCs to increase the performance of the DSSC devices.<sup>35–37</sup> This increase is attributed to a shift in the titania conduction band edge to a more negative potential and a reduction in recombination from the titania surface by adsorbing to the titania.<sup>33,34</sup> These additives can undergo an interaction with copper complexes upon oxidation, leading to the formation of new complexes with altered properties.<sup>38</sup> It is currently being investigated as to the extent of the interaction between the base additives and the copper complexes but there are two prevailing theories. The first is that a ligand substitution can occur, where, upon oxidation of the copper complex, the base additives will displace the ligand bound the copper complex forming a copper-base complex.<sup>39</sup> Through either path the presence of these additives can modify the redox potential, stability, and kinetics of copper-based redox mediators.

The interaction between base additives and copper redox mediators can significantly impact DSSC performance. Ligand substitution reactions can influence the energetics of electron transfer processes, affecting charge injection, recombination, and overall cell efficiency.<sup>33,34,38</sup> Understanding these effects is essential for optimizing DSSC design and operation.

Previous research has demonstrated that ligand substitution reactions can either enhance or hinder DSSC performance, depending on the specific copper complex and base additive

involved.<sup>38</sup> Studying the factors that govern these outcomes provides valuable insights into the underlying mechanisms and informs the rational design of more efficient redox mediators.

Developing a predictive model for ligand substitution reactions is essential for advancing the design and optimization of copper-based redox mediators in DSSCs. Such a model would enable researchers to predict the outcomes of different ligand substitution scenarios and guide the selection of base additives and copper complexes to achieve desired performance enhancements. In this thesis, a comprehensive exploration of copper redox mediators in dye-sensitized solar cells (DSSCs) is undertaken, focusing on their interactions with base additives and the consequent implications for DSSC performance. The intricate interplay between copper complexes and base additives is thoroughly examined, with the goal of contributing to the fundamental understanding of ligand substitution processes and developing a predictive model to aid in the rational design of efficient DSSCs.

#### Chapter 2 – Investigation of [Cu(dbmed)](OTf)<sub>1/2</sub>

#### 2.1 Introduction

The demand for carbon-neutral energy generation has accelerated the development of renewable technologies, particularly in the domain of solar energy. Within this realm, dye-sensitized solar cells (DSSCs) have been identified for their cost efficiency and photon-to-current conversion capabilities across diverse lighting conditions.<sup>8</sup>

A standard DSSC consists of a chromophore anchored to a semiconducting mesoporous metal oxide surface. Upon photoexcitation, an electron is injected into the semiconductor's conduction band. The oxidized chromophore is then regenerated by a redox shuttle present in the solution. This electron, after traversing an external circuit, is eventually received by the counter electrode. Here, the oxidized redox shuttle is reduced, completing the current circuit.

Historically, the iodide/triiodide ( $I^{-}/I^{3-}$ ) redox shuttle system was predominantly used but presented challenges such as corrosiveness, non-tunability, and competitive absorption in the visible spectrum. Additionally, the two-electron redox process of the  $I^{-}/I^{3-}$  system restricted the theoretical maximum photovoltage of DSSC devices.<sup>22</sup> Co(III/II)-based redox shuttles presented their own set of limitations, primarily due to the significant inner-sphere reorganization energy during the electron transfer process, which affected dye regeneration kinetics.<sup>23</sup>

Copper-based redox shuttles have been explored as an alternative due to their reduced innersphere reorganization energies for electron transfer. The geometrical adaptability of copper complexes, influenced by their oxidation state and ligand environment, is of significant interest. While many DSSCs with copper have primarily utilized bidentate ligands such as bipyridine or phenanthroline, there has been a shift towards tetradentate Cu(II/I) redox shuttles, resulting in

improved stability and reduced photovoltage losses.<sup>40,41</sup> Innovations by Freitag and associates, where a tetradentate Cu(II/I) redox shuttle was integrated into DSSCs, have exhibited enhanced stability and reduced photovoltage losses.<sup>42</sup> The rigidity of these tetradentate ligands can further lower reorganization energies, optimizing DSSC performance metrics.

However, DSSC additives like TBP and N-methylbenzimidazole (NMBI), known to enhance cell performance, have demonstrated interactions with copper-based redox shuttles. Specifically, TBP has been observed to coordinate with Cu(II) species, leading to the displacement of bidentate ligands.<sup>38</sup> This interaction impacts the redox potential, electron transfer kinetics, and achievable photovoltage. Given these observations, there's an ongoing investigation into the potential of tetradentate ligands to provide stability in the face of these challenges.

In this chapter, the focus will be on the interactions and stability of copper-based redox mediators in DSSCs, particularly in the presence of base additives, and the potential advantages offered by increased ligand denticity.

#### 2.2 Experimental Details

All NMR spectra were taken on an Agilent DirectDrive2 500 MHz spectrometer at room temperature and referenced to residual solvent signals. All NMR spectra were evaluated using the MestReNova software package features. Cyclic voltammograms were obtained using µAutolabIII potentiostat using BASi glassy carbon electrode, a platinum mesh counter electrode, and a fabricated 0.01 M AgNO<sub>3</sub>, 0.1 M TBAPF<sub>6</sub> in acetonitrile Ag/AgNO<sub>3</sub> reference electrode. All measurements were internally referenced to ferrocene/ferrocenium couple via addition of ferrocene to solution after measurements or run in a parallel solution of the same solvent/electrolyte. UV-Vis spectra were taken using a PerkinElmer Lambda 35 UV-Vis

spectrometer using a 1 cm path length quartz cuvette at 480 nm/min. Elemental analysis data were obtained via Midwest Microlab. For single-crystal X-ray diffraction, single crystals were mounted on a nylon loop with paratone oil using a Bruker APEX-II CCD diffractometer. Crystals were maintained at T ¼ 173(2) K during data collection. Using Olex2, the structures were solved with the ShelXS structure solution program using the Direct Methods solution method. Photoelectrochemical measurements were performed with a potentiostat (Autolab PGSTAT 128N) in combination with a xenon arc lamp. An AM 1.5 solar filter was used to simulate sunlight at 100 mW cm<sup>-2</sup>, and the light intensity was calibrated with a certified reference cell system (Oriel Reference Solar Cell & Meter). A black mask with an open area of 0.07 cm<sup>-2</sup> was applied on top of the cell active area. A monochromator (Horiba Jobin Yvon MicroHR) attached to the 450 W xenon arc light source was used for monochromatic light for IPCE measurements. The photon flux of the light incident on the samples was measured with a laser power meter (Nova II Ophir). IPCE measurements were made at 20 nm intervals between 400 and 700 nm at short circuit current. TEC 15 FTO was cut into 1.5 cm by 2 cm pieces which were sonicated in soapy DI water for 15 minutes, followed by manual scrubbing of the FTO with Kimwipes. The FTO pieces were then sonicated in DI water for 10 minutes, rinsed with DI water, and sonicated in isopropanol for 15 minutes. The FTO pieces were dried under a stream of air then immersed in an aqueous 40 mM solution TiCl<sub>4</sub> solution for 30 minutes at 70 °C. The water used for the TiCl<sub>4</sub> treatment was preheated to 70 °C prior to adding 2 M TiCl<sub>4</sub> to the water. The 40 mM solution was immediately poured onto the samples and placed in a 70 °C oven for the 30-minute deposition. The FTO pieces were immediately rinsed with 18 M $\Omega$  water followed by isopropanol and were annealed by

heating from room temperature to 500 °C, holding at 500 °C for 15 minutes. A 0.36 cm<sup>2</sup> area was

doctor bladed with commercial 30 nm TiO<sub>2</sub> nanoparticle paste (DSL 30NRD). The transparent films were placed in a 100 °C oven for 30 minutes. The samples were annealed in an oven that was ramped to 325 °C for 5 minutes, 375 °C for 5 minutes, 450 °C for 5 minutes, and 500 °C for 15 minutes. The 30 nm nanoparticle film thickness was 8.2  $\mu$ m. After cooling to room temperature, a second TiCl<sub>4</sub> treatment was performed as described above. When the anodes had cooled to room temperature, they were soaked in a dye solution of 0.1 mM Y123 in 1:1 acetonitrile:tertbutyl alcohol for 18 hours. After soaking, the anodes were rinsed with acetonitrile and were dried gently under a stream of nitrogen.

The PEDOT counter electrodes were prepared by electrodeposition in a solution of 0.01 M EDOT and 0.1 M LiClO<sub>4</sub> in 0.1 M SDS in 18 M $\Omega$  water. A constant current of 8.3 mA for 250 seconds was applied to a 54 cm<sup>2</sup> piece of TEC 15 FTO with predrilled holes using an equal size piece of FTO as the counter electrode. The PEDOT electrodes were then washed with DI water and acetonitrile before being dried under a gentle stream of nitrogen and cut into 1.5 cm by 1.0 cm pieces. The working and counter electrodes were sandwiched together with 25  $\mu$ m surlyn films by placing them on a 140 °C hotplate and applying pressure. The cells were then filled in a nitrogen filled glove box with electrolyte through one of the two predrilled holes and were sealed with 25  $\mu$ m surlyn backed by a glass coverslip and applied heat to seal with a soldering iron. The electrolyte consisted of 0.25 M Cu(I), 0.065 M Cu(II), 0.1 M Li(Counter-ion), in acetonitrile with either no 4tert-butylpyridine or 0.5 M 4-tert-butylpyridine added. All batches were made with at least 10 cells per batch. Contact to the TiO<sub>2</sub> electrode was made by soldering a thin layer of indium wire onto the FTO.

Synthesis of N,N'-Dibenzyl-N,N'-bis(6-methylpyridin-2-ylmethyl)ethylenediamine (dbmed):

2-(Chloromethyl)-6-methylpyridine hydrochloride (0.5300g, 3.0 mmol) and benzyltriethylammonium chloride (0.0121 g, 0.05 mmol) were added to 20 mL dichloromethane and stirred until fully dissolved. N,N'-Dibenzylethylenediamine (0.35 mL, 1.48 mmol) was then added to the solution, after which a cloudy white solution was formed. Meanwhile sodium hydroxide (20.1807 g, 500 mmol) was added to 20 mL of water which was then added to the dichloromethane solution and stirred vigorously. After 2 hours the organic solution became clear and the aqueous solution turned white. The solution was then allowed to reflux overnight. After refluxing additional water was added to the solution to allow the layers to fully separate then the organic layer was then separated from the aqueous layer. The aqueous layer was then extracted with dichloromethane two times and all the organic layers were combined, and dried with magnesium sulfate. Then the solvent was removed under low vacuum. The crude solid was then recrystallized in acetonitrile and dried to obtain the product (0.4270 g, 60.1% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 500 MHz) δ 2.50 (s, 6H), 2.67 (s, 4H), 3.56 (s, 4H), 3.67 (s, 4H), 6.96 (d, 2H), 7.25 (m, 12H), 7.45 (t, 2H). Matching the data of the compound made by Hu et al.<sup>40</sup>

Synthesis of [Cu(dbmed)]OTf:

Copper(I) tetrakisacetonitrile triflate (0.1123 g, 0.30 mmol) was dissolved in minimal dry acetonitrile. Meanwhile dbmed (0.1487 g, 0.33 mmol) was dissolved in minimal dry dichloromethane. The dbmed solution was added dropwise to the copper solution, turning the solution a bright yellow color. Reaction was stirred overnight then precipitated with dry ether and filtered. The solvent was then removed via vacuum and the Cu(I)dbmed product was collected (0.1876 g, 94.9% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 500 MHz)  $\delta$  2.67 (s, 2H), 2.72 (s, 6H), 2.82 (s, 2H), 3.57 (s,

2H), 3.74 (s, 2H), 3.85 (s, 2H), 4.16 (s, 2H), 7.20 (m, 4H), 7.29 (m, 8H), 7.43 (d, 2H), 7.83 (t, 2H). Matching the data of the compound made by Hu et al.<sup>40</sup>

Synthesis of Cu(II)dbmed:

Copper(II) triflate (0.808 g, 2.23 mmol) was dissolved in minimal dry acetonitrile. Meanwhile, dbmed (0.1030 g, 2.29 mmol) was dissolved in minimal dry dichloromethane. The dbmed solution was added dropwise to the copper solution, turning a deep blue color. Reaction was stirred overnight then precipitated with dry ether and filtered. The solvent was then removed via vacuum and the Cu(II)dbmed product was collected (0.1596 g, 87.9% yield). Matching the data of the compound made by Hu et al.<sup>40</sup>

## 2.3 Results and Discussion





The ligand, N,N'-Dibenzyl-N,N'-bis(6-methylpyridin-2-ylmethyl)ethylenediamine (dbmed), and the copper ligand complexes, [Cu(dbmed)]OTf and [Cu(dbmed)]OTf<sub>2</sub> were synthesized following a previously reported protocol.<sup>32</sup> A crystal was grown of the copper(I) form, the copper center is coordinated to the two amine and two pyridyl nitrogen's, resulting in a tetrahedral geometry which is common for copper(I) complexes. This crystal matched the crystal shown in the literature.<sup>40</sup> Attempts at growing a crystal of the copper(II) form did not work out, forming an oil instead of crystals. However, it has been previously shown that the copper(II) form is in the

distorted tetrahedral geometry due to strain caused by the methyl groups on the 6 position of the pyridine.<sup>40</sup> It is also noted that the copper(II) complex is air stable, but the copper(I) is not, it oxidizes over the course of a few hours in solution or a few days in the solid state. The dbmed ligand was characterized via <sup>1</sup>H-NMR and both copper complexes were characterized via <sup>1</sup>H-NMR, and elemental analysis, matching previous reports, shown in Figures 2.1A, 2.2A, and 2.3A. The effect of TBP on the [Cu(dbmed)]<sup>2+/+</sup> redox couple was evaluated in the presence of different concentrations of the Lewis base. TBP was added in excess of at least 15 equivalents relative to [Cu(dbmed)](OTf)<sub>2</sub> in solution to match the conditions used in the devices.



Figure 2.3: UV-Vis spectra of 2.14 mM [Cu(dbmed)]OTf<sub>2</sub>, pale green, with increasing concentrations of TBP added, from 0 mM to 53.5 mM with the darker green being higher concentration of TBP added, compared to a spectra of 2.14 mM [Cu(TBP)<sub>4</sub>]OTf<sub>2</sub> in acetonitrile, purple.

The effect of TBP was evaluated using UV–vis spectroscopy, containing 2 mM of  $[Cu(dbmed)](OTf)_2$ , where spectra were recorded as a function of added TBP. As TBP was added to a solution of  $[Cu(dbmed)]OTf_2$  and monitored using UV-Vis spectroscopy. It can be seen that the absorbance of the peak at ~650 nm decreases in intensity and blueshifts slightly. However

even at 25 equivalents of TBP added to the solution the spectra does not match that of  $[Cu(TBP)_4]OTf_2$ .



Figure 2.4: Cyclic voltammogram of 1.6 mM [Cu(dbmed)]OTf<sub>2</sub> in acetonitrile containing 0.1 M LiOTf using a glassy carbon working electrode and a platinum mesh counter electrode and a scan rate of 100 mV/s. Increasing concentrations of TBP were added from 0 mM to 38 mM, the darker green the higher the TBP concentration. The results were compared with the cyclic voltammogram of 2.0 mM free dbmed ligand in red.

As a follow up experiment, the addition of TBP to a solution of [Cu(dbmed)]OTf<sub>2</sub> was monitored via cyclic voltammetry. As it can be seen in Figure 2.2, the cathodic peak of [Cu(dbmed)]OTf<sub>2</sub>, at -0.050 V vs ferrocene decreases in intensity and a second cathodic wave around -0.250 V vs ferrocene grows in as TBP is added to the solution. While the cathodic peak is undergoing a drastic change, the anodic peak does not experience significant change nor shift in potential. Additionally, a peak appears to be growing in around 0.600 V vs ferrocene which corresponds to the redox potential of the free ligand. This observation suggests that dbmed is displaced by TBP upon oxidation, forming [Cu(TBP)<sub>4</sub>]OTf<sub>2</sub>. However, upon reduction, the process reverses: TBP is displaced by the dbmed ligand, reforming [Cu(dbmed)]OTf. This demonstrates that the ligand

substitution is fully reversible. This indicates that that as TBP is added to the solution some of the previously bound dbmed ligand is being released from copper and is able to be oxidized.



Figure 2.5: <sup>1</sup>H-NMR of 9.85 mM [Cu(dbmed)]OTf<sub>2</sub>, black, in deuterated acetonitrile with a known amount of dichloromethane added. Various concentrations of TBP were added, 18 mM, in grey, 50 mM, in purple, and 100 mM, in green. The spectra were compared to a spectra of free dbmed ligand, red.

To determine the extent of the displacement of dbmed unambiguously and quantitatively by TBP, proton NMR spectra were taken of [Cu(dbmed)]OTf<sub>2</sub> in deuterated acetonitrile without and with the addition of TBP. Because [Cu(dbmed)]<sup>2+</sup> is paramagnetic, the proton signals of the dbmed ligands coordinated to the copper(II) center show very different chemical shifts than free dbmed ligands in the solution. The sample was measured with up to 100 equivalents of TBP added, however as the concentration of TBP was added to the solution there were issues with the

shimming due to the high intensity of the methyl group on the TBP, as a result the data shown is limited to 50 equivalents of TBP added and lower. As TBP is added to the solution, four new peaks appear in the NMR spectra between 2.4 and 3.8 ppm. These peaks match with the peaks of unbound dbmed ligand. By utilizing an internal standard of a known amount of DCM, the amount of free ligand in solution can be quantitatively determined. Using this method, it was found that the [Cu(dbmed)](OTf)<sub>2</sub> had not fully undergone ligand substitution by the time 50 equivalents of TBP was added to the solution.



Figure 2.6: J–V curves for the [Cu(dbmed)]<sup>2+/+</sup> DSSC devices, with TBP, dark green, and without TBP light green.

Table 2.1: A summary of D	SSC device performance	metrics for those devices
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	η (%)	Jsc (mA*cm- 2)	Voc (V)	FF
Cu(dmbpy)	0.85(±0.35)	2.19(±0.77)	0.58(±0.02)	0.66(±0.05)
Cu(dmbpy) with TBP	4.32(±0.64)	7.19(±1.24)	0.89(±0.02)	0.67(±0.05)

DSSC devices were fabricated using  $[Cu(dbmed)]^{2+/+}$  as the redox shuttle in conjunction with a poly(3,4-ethylenedioxythiophene) (PEDOT) counter electrode, and the commercially available dye Y123 was used as the light-harvesting component. The devices were constructed as described previously. The devices with TBP added to the solution yielded a respectable performance with a J<sub>SC</sub> of 7.19(±1.24) mAcm<sup>-2</sup> and an overall PCE of 4.32(±0.64) as shown in Table 2.1. However, in the absence of TBP the performance was significantly worse, with a J<sub>SC</sub> of only 2.19(±0.77) mAcm<sup>-2</sup> and an overall PCE of 0.85(±0.35). This indicates that TBP is still performing a pivotal role in increasing the current of the devices.

Table 2.2: Comparison of the solution potential and the predicted Nernstian potential of the electrolyte solution used in each DSSC device set.

	E <sub>1/2</sub> of [Cu(dbmed)]OTf <sub>1/2</sub> / V	Nernst equation / V	Solution potential /V	E <sub>f</sub> Level / V
dbmed	-0.005	-0.023	-0.053	-0.633
dbmed with TBP	-0.005	-0.023	-0.260	-1.150



Figure 2.7: A plot of the electron lifetime vs potential plot for DSSC devices using [Cu(dbmed)]OTf<sub>1/2</sub> (green), with (pale color) and without (dark color) the addition of TBP. By investigating the solution potential of electrolyte compositions, it is observed that the solution potential becomes about 200 mV more negative with the addition of TBP to the electrolyte. Even though there was a negative shift in solution potential, there was a 300 mV increase in the open circuit voltage, indicating that the fermi level of the semiconductor increased by around 500 mV with the introduction of TBP to the devices. This is a further indicator of ligand substitution occurring and forming a more negative redox couple in solution. Furthermore, the electron lifetime also significantly increases with the addition of TBP, to the extent that it is hard to compare the results since there are no overlapping measured potentials that the timescale of the experiment. This drastic increase in potential and electron lifetime can be attributed to the addition of TBP, more specifically both the properties of Lewis bases in DSSC electrolyte (shifting the conduction band potential and reducing recombination) and ligand exchange occurring and forming a  $[Cu(TBP)_4)]OTf_{1/2}$  complex which has very poor electron kinetics.<sup>33,34</sup>

# 2.4 Conclusion

In this study, the [Cu(dbmed)]OTf<sub>2</sub> complex was found to be susceptible to ligand substitution in the presence of TBP, without measurable full ligand substitution occurring when up to 50 equivalents of TBP were added to the solution. Interestingly, this ligand substitution was observed to be reversible upon reduction of the complex. Despite the occurrence of ligand exchange, the addition of TBP notably enhanced the efficiency of the DSSC devices. Allowing for dbmed to continue to be a viable ligand for copper redox shuttles in DSSCs in the future. The underlying cause of this ligand substitution was determined to be the steric strain imposed by the methyl groups on the pyridines of the complex, which effectively outcompetes the thermodynamic stability usually conferred by the increased denticity of the ligand.

#### Chapter 3 – Investigation of [Cu(bpyPY4)](TFSI)<sub>1/2</sub>

#### 3.1 Introduction

The necessity for carbon-neutral energy generation has driven the advancement of novel technologies that exploit renewable sources, notably wind and solar energy.<sup>43,44</sup> By harnessing sunlight for solar-to-electrical energy conversion, photovoltaic cells offer a promising solution.<sup>45–47</sup> A special subset of these, dye-sensitized solar cells (DSSCs), are recognized for their cost-effective nature and their impressive photon-to-current conversion efficiencies under diverse lighting conditions.<sup>20,48–52</sup> A typical DSSC consists of a chromophore anchored to a semiconducting mesoporous metal oxide surface. When subjected to photoexcitation, an electron is injected into the semiconductor's conduction band. Subsequently, the oxidized chromophore (or dye) is regenerated by a redox shuttle present in the solution. This injected electron, having traversed an external circuit, reaches the counter electrode. There, the oxidized redox shuttle undergoes reduction, completing the circuit.<sup>20,47,53</sup>

However, the traditionally employed iodide/triiodide ( $I^{-}/I^{3-}$ ) redox shuttle system exhibits several drawbacks, including corrosiveness, lack of tunability, and competitive absorption in the visible spectrum by the triiodide ion.<sup>54–57</sup> Notably, the  $I^{-}/I^{3-}$  redox couple's two-electron redox process often leads to reduced theoretical maximum photovoltage output from DSSC devices, especially when compared to one-electron redox processes.<sup>57,58</sup> Co(III/II)-based redox shuttles, on the other hand, are accompanied by a significant inner-sphere reorganization energy during the electron transfer process.<sup>59,60</sup> This energy hinders dye regeneration kinetics due to its limited availability for electron transfer. Copper-based redox shuttles, however, have demonstrated parity with the classical  $I^{-}/I^{3-}$  and Co(III/II)-based redox shuttles. Their success is often attributed to the

minimized inner-sphere electron transfer reorganization energies. The ability of copper complexes to adopt various geometries based on their metal oxidation state and ligand setting is noteworthy.<sup>61–63</sup> The majority of copper redox shuttles employed in DSSCs thus far have relied on bidentate bipyridine or phenanthroline-based ligands.<sup>64</sup> An approach which utilizes bulky groups adjacent to nitrogen donors to diminish structural shifts between Cu(II) and Cu(I) redox states. Recent reports also suggest that rigid tetradentate ligands can further optimize Cu(II/I) redox shuttles by promoting even lower inner-sphere reorganization energies, thus resulting in heightened short-circuit current densities and reduced V<sub>oc</sub> losses.<sup>65</sup>

Lewis bases, such as TBP and N-methylbenzimidazole (NMBI), are frequently incorporated additives in DSSC devices.<sup>35–37</sup> These compounds have been shown to improve the overall cell performance. Such enhancements are often associated with the ability of these bases to negatively shift the titania conduction band edge and suppress the interfacial charge recombination rates through surface adsorption.<sup>36,66–68</sup> Notably, when most copper-based redox shuttles are investigated, TBP has been observed to coordinate with various Cu(II) species, potentially displacing polydentate ligands.<sup>38,39,41,58,69–72</sup> Such interactions significantly influence the redox potential by generating multiple redox species, which in turn affects the maximum achievable photovoltage and electron transfer kinetics. The focal point of this research revolves around exploring the interactions between a copper complex with a hexadentate ligand and TBP, with a primary goal of understanding if ligand substitution occurs upon oxidation.

# 3.2 Experimental Details

All NMR spectra were taken on an Agilent DirectDrive2 500 MHz spectrometer at room temperature and referenced to residual solvent signals. All NMR spectra were evaluated using

the MestReNova software package features. Cyclic voltammograms were obtained using µAutolabIII potentiostat using BASi glassy carbon electrode, a platinum mesh counter electrode, and a fabricated 0.01 M AgNO<sub>3</sub>, 0.1 M TBAPF<sub>6</sub> in acetonitrile Ag/AgNO<sub>3</sub> reference electrode. All measurements were internally referenced to ferrocene/ferrocenium couple via addition of ferrocene to solution after measurements or run in a parallel solution of the same solvent/electrolyte. UV-Vis spectra were taken using a PerkinElmer Lambda 35 UV-Vis spectrometer using a 1 cm path length quartz cuvette at 480 nm/min. Elemental Analysis data were obtained via Midwest Microlab. For single-crystal X-ray diffraction, single crystals were mounted on a nylon loop with paratone oil using a Bruker APEX-II CCD diffractometer. Crystals were maintained at T ¼ 173(2) K during data collection. Using Olex2, the structures were solved with the ShelXS structure solution program using the Direct Methods solution method. Photoelectrochemical measurements were performed with a potentiostat (Autolab PGSTAT 128N) in combination with a xenon arc lamp. An AM 1.5 solar filter was used to simulate sunlight at 100 mW cm<sup>-2</sup>, and the light intensity was calibrated with a certified reference cell system (Oriel Reference Solar Cell & Meter). A black mask with an open area of 0.07 cm<sup>-2</sup> was applied on top of the cell active area. A monochromator (Horiba Jobin Yvon MicroHR) attached to the 450 W xenon arc light source was used for monochromatic light for IPCE measurements. The photon flux of the light incident on the samples was measured with a laser power meter (Nova II Ophir). IPCE measurements were made at 20 nm intervals between 400 and 700 nm at short circuit current. TEC 15 FTO was cut into 1.5 cm by 2 cm pieces which were sonicated in soapy DI water for 15 minutes, followed by manual scrubbing of the FTO with Kimwipes. The FTO pieces were then sonicated in DI water for 10 minutes, rinsed with acetone, and sonicated in isopropanol for 10

minutes. The FTO pieces were dried in room temperature air then immersed in an aqueous 40 mM TiCl<sub>4</sub> solution for 60 minutes at 70 °C. The water for the TiCl<sub>4</sub> treatment was preheated to 70 °C prior to adding 2 M TiCl<sub>4</sub> to the water. The 40 mM solution was immediately poured onto the samples and placed in a 70 °C oven for the 60-minute deposition. The FTO pieces were immediately rinsed with 18 M $\Omega$  water followed by isopropanol and were annealed by heating from room temperature to 500 °C, holding at 500 °C for 30 minutes. A 0.36 cm<sup>2</sup> area was doctor bladed with commercial 30 nm TiO<sub>2</sub> nanoparticle paste (DSL 30NRD). The transparent films were left to rest for 10 minutes and were then placed in a 125 °C oven for 30 minutes. The samples were annealed in an oven that was ramped to 325 °C for 5 minutes, 375 °C for 5 minutes, 450 °C for 5 minutes, and 500 °C for 15 minutes. The 30 nm nanoparticle film thickness was approximately 8  $\mu$ m. After cooling to room temperature, a second TiCl<sub>4</sub> treatment was performed as described above. When the anodes had cooled to 80 °C, they were soaked in a dye solution of 0.1 mM Y123 in 1 : 1 acetonitrile : tert-butyl alcohol for 18 hours. After soaking, the anodes were rinsed with acetonitrile and were dried gently under a stream of nitrogen.

The PEDOT counter electrodes were prepared by electropolymerization in a solution of 0.01 M EDOT and 0.1 M LiClO<sub>4</sub> in 0.1 M SDS in 18 M $\Omega$  water. A constant current of 8.3 mA for 250 seconds was applied to a 54 cm<sup>2</sup> piece of TEC 8 FTO with predrilled holes using an equal size piece of FTO as the counter electrode. The PEDOT electrodes were then washed with DI water and acetonitrile before being dried under a gentle stream of nitrogen and cut into 1.5 cm by 1.0 cm pieces. The working and counter electrodes were sandwiched together with 25  $\mu$ m surlyn films by placing them on a 140 °C hotplate and applying pressure. The cells were then filled in a nitrogen filled glove box with electrolyte through one of the two predrilled holes and were sealed with 25  $\mu$ m

surlyn backed by a glass coverslip and applied heat to seal with a soldering iron. The electrolyte consisted of 0.10 M Cu(I), 0.05 M Cu(II), 0.1 M Li(Counter-ion), and 0.5 M 4-tert-butylpyridine in acetonitrile. All batches were made with at least 10 cells per batch. Contact to the  $TiO_2$  electrode was made by soldering a thin layer of indium wire onto the FTO.

Preparation of copper(I) 6,6'-bis(1,1-di(pyridine-2-yl)ethyl)-2,2'-bipyridine Bistriflimide ([Cu(bpyPY4)]TFSI:

Copper(I) tetrakisacetonitrile bistriflimide (0.1647 g, 0.43 mmol) was dissolved in minimal dry acetonitrile. Meanwhile 6,6'-bis(1,1-di(pyridin-2-yl)ethyl)-2,2'-bipyridine (bpyPY4) (0.2545 g, 0.49 mmol) was dissolved in minimal dry dichloromethane. The bpyPY4 solution was added dropwise to the copper solution, turning the solution a dark red color. Reaction was stirred overnight then precipitated with dry ether and filtered. The solvent was then removed via vacuum and the Cu(I)bpyPY4 product was collected (0.2829 g, 76.1% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 500 MHz)  $\delta$  2.25 (s, 6H), 7.219 (s, 4H), 7.76 (s, 4H), 8.10 (d, 2H), 8.17 (t, 2H), 8.35 (d, 2H) Elem. Anal. calc. for C<sub>36</sub>H<sub>28</sub>N<sub>7</sub>F<sub>7</sub>O<sub>4</sub>S<sub>2</sub>Cu: C, 50.03; H, 3.27; N, 11.34. Found: C, 50.05; H, 3.73; N, 11.08.

Copper(II) bistriflimide (0.4215 g, 1.16 mmol) was dissolved in minimal dry acetonitrile. Meanwhile BPYPY4 (0.6942 g, 1.33 mmol) was dissolved in minimal dry dichloromethane. The BPYPY4 solution was added dropwise to the copper solution, turning the solution a pale blue color. Reaction was stirred overnight then precipitated with dry ether and filtered. The solvent was then removed via vacuum and the Cu(II)bpyPY4 product was collected (0.7912 g, 63.9% yield). Elem. Anal. calc. for C<sub>38</sub>H<sub>28</sub>N<sub>8</sub>F<sub>12</sub>O<sub>8</sub>S<sub>4</sub>Cu + ether: C, 41.40; H, 3.14; N, 9.20. Found: C, 41.48; H, 3.10; N, 9.13.

All the electrochemical measurements were performed by using  $\mu$ AutoLabII potentiostat or Autolab PGSTAT128N in a home-made electrochemical cell under N<sub>2</sub> atmosphere. Copper complexes were dissolved in dry acetonitrile, the specific concentrations will be specified in the result and discussion section. Also dissolved in the solution was 0.1 M supporting electrolyte, which will be specified in the main text.

For the cyclic voltammetry measurements, glassy carbon disk was used as the working electrode. The reference electrode was a home-made 0.1 M Ag/AgNO<sub>3</sub> reference electrode. A salt bridge was used to prevent the leakage of the silver containing electrolyte in the reference electrode. The CV of ferrocene was measured in the same solvent before and after measuring the sample. The redox potential of ferrocene/ferrocenium was used to correct the potential of the homemade reference electrode. The counter electrode for CV measurement was a platinum mesh. Scan rate was varied and will be specified in the main text. For the titration measurement, different concentrations of TBP were added into the solution containing copper complexes and supporting electrolyte. The solution was stirred and then stabilized before measuring.

The absorption spectra were measured with Lambda 35 (PerkinElmer) spectrometer. Solutions containing copper complexes were prepared in the glovebox under an inert atmosphere with dry acetonitrile. Screw-cap quartz cuvette with 1 cm path length was used for all the absorption measurements in solution. Blank acetonitrile was used as the reference for the absorption. For the titration measurement, a stock solution containing a constant concentration of copper complex was prepared in the glove box. Each sample contains 4 mL of the stock solution and a stoichiometric amount of TBP. The absorption spectra of different samples were measured.
Proton NMR of copper complexes were measured using a J-Young NMR tube under an inert atmosphere with Agilent DDR2 500 MHz NMR spectrometer at room temperature. For the titration measurement, 0.5 mL solution containing a constant concentration of copper complex was prepared in the glove box with deuterated acetonitrile. Dichloromethane was used as a noncoordinating reference proton source to calibrate the proton peak area. After running NMR of the pure copper complex, the tube was brought back into the glove box and another aliquot of TBP was added into the same sample. For each run, the parameters, number of scans, temperature, decay time, and scan range, used for the NMR measurement were kept the same.

## 3.3 Results and Discussion

The synthesis of the ligand, bpyPY4, has been previously reported, wherein 1,1- bis(2pyridyl)ethane underwent deprotonation with n-BuLi before the addition of the electrophile, 6,6'dibromo-2,2'-bipyridine. The metalation was done utilizing two different counter ions, triflate and bistriflimide, in an attempt to overcome solubility limitations. The copper(I) triflate version exhibits a solubility of less than 0.1 M. In contrast, the solubility of the copper(I) bistriflimide version exceeds 1.25 M, leading to the use of bistriflimide versions for all studies on this copper complex system. As depicted in Scheme 3.1, the metalation is carried out using an equimolar ratio of the appropriate copper salt, either [Cu(acetonitrile)<sub>4</sub>](TFSI) or Cu(TFSI)<sub>2</sub> where TFSI = Bistriflimide, with bpyPY4 in acetonitrile to afford [Cu(bpyPY4)](TFSI) or [Cu(bpyPY4)](TFSI)<sub>2</sub>, respectively. The complexes were purified by slow diffusion of diethyl ether into concentrated acetonitrile solutions, and their characterization was accomplished with <sup>1</sup>H-NMR spectroscopy and elemental analysis. Scheme 3.1: Syntheses of the [Cu(bpyPY4)]TFSI<sub>1/2</sub> complexes and crystal structures of the cations of the Cu(I) species (left) and Cu(II) species (right). Depicted ellipsoids are at the 50% probability level. The anions and hydrogens were omitted for clarity.



Single crystal X-ray diffraction ascertained the solid-state structures of the copper complexes, with details documented in Tables 3.1A and 3.2A. It was observed that the hexadentate ligand formed a five-coordinate geometry around the copper(II) center, binding five out of the six pyridine donors of the bpyPY4. Alternatively, the copper(I) center revealed a four-coordinate geometry with two pyridine donors from bpyPY4 remaining unbound. Geometric indices,  $\tau$ 5 and  $\tau$ 4, are used for five-coordinate and four-coordinate complexes, respectively, to determine how much distortion there is between ideal geometries.<sup>73,74</sup> The  $\tau$  value in each case will have a range from 0 to 1. For five-coordinate complexes, a  $\tau$ 5 value of 0 represents an ideal square pyramidal geometry, and a value of 1 represents an ideal trigonal bipyramidal geometry. For the five-coordinate copper(II) complex, the  $\tau$ 5 value was 0.61, indicative of a distorted trigonal bipyramidal geometry. Within this configuration, the bipyridine fragment of the bpyPY4 ligand

positions itself both axially and equatorially around the copper(II) ion. Notably, the copper(II) ion exhibited a displacement distance of 0.225 Å from the plane defined by the equatorial donors, pointing towards the axial pyridine donor. As a result, the angles involving the axial pyridine nitrogen donor, the copper(II) ion, and the equatorial donors slightly exceed 90°. Moreover, the bipyridine fragment showcases a near-planar orientation, with its pyridine rings forming a torsion angle of 5.0(4)°.

In the case of the copper(I) complex, a four-coordinate complex, an ideal square planar geometry is represented by a  $\tau$ 4 value of 0, and an ideal tetrahedral geometry is represented by a  $\tau$ 4 value of 1.<sup>74</sup> The copper(I) counterpart showcased a  $\tau$ 4 value of 0.63, denoting a highly distorted tetrahedral geometry. In terms of coordination, the bpyPY4 ligand coordinates the copper(I) ion in a manner where the bipyridine unit occupies two of the coordination sites, and the remaining two sites have a pyridine from each of the 1,1-bis(2-pyridyI)ethane fragments bound. The average bond distance between the copper-bipyridine nitrogen stands at 2.082(3) Å, aligning with data from other tetrahedral copper(I) complexes with bipyridine ligands.<sup>75,76</sup> Yet, the copper-pyridine nitrogen bond is slightly shorter, averaging 2.015(2) Å. The bipyridyI segment, in this instance, demonstrates a pronounced distortion, marked by a torsion angle of -18.0(4)° between its pyridine rings.

The <sup>1</sup>H-NMR spectrum of [Cu(bpyPY4)]TFSI, recorded in deuterated acetonitrile at room temperature, integrates to 20 protons. Two broad peaks of equal intensity at  $\delta$  = 7.17 and 7.73 ppm, integrating only to four protons each, combine for eight protons in total. Sharp resonances at  $\delta$  = 810, 8.17, and 8.35 ppm, comprising two doublets and a triplet further downfield in the aromatic spectrum, account for six protons, two protons per peak, and align with the bipyridine

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unit. A sharp singlet at 2.25 ppm accounts for the remaining six protons, representing the two methyl peaks. However, the bpyPY4 framework has 28 protons. Intriguingly, while the bpyPY4 framework boasts 28 aromatic protons, the spectrum under-represents this number by eight protons. Insights from the solid-state structure of the copper(I) complex, depicted in Scheme 3.1, reveal two non-coordinating pyridines, which could account for the eight proton discrepancy. The observable broad peaks at 7.17 ppm and 7.73 ppm suggest a rapid exchange on the NMR timescale between non-coordinated and coordinated pyridine donors.



To delve deeper into this phenomenon, variable-temperature <sup>1</sup>H-NMR spectroscopy was executed, with spectra obtained from –40 to 25 °C consolidated in Figure 3.2. This allows for an interrogation of the solution's dynamic coordination behavior. As the temperature decreased,

new broad peaks emerged by 0°C, yielding eight pronounced peaks by –30°C. Integrating to 16 protons, these peaks originate from the four terminal pyridines, illustrating two distinctive chemical environments. The presumption is that two of these fluctuating pyridines, one from each dipyridylethane "arm", remain uncoordinated, each possessing four distinct aromatic protons. In contrast, the other two are coordinated, accounting for the remaining four peaks. Notably, chemical shifts for non-coordinated pyridines diverge slightly from the free ligand, but such a downfield shift has been documented in prior studies for dissociated heterocycles within a coordinated ligand matrix.<sup>77,78</sup>



Figure 3.2: Variable temperature <sup>1</sup>H-NMR spectra of [Cu(bpyPY4)]TFSI in CD<sub>3</sub>CN.

In anhydrous acetonitrile, the UV-visible spectra of the copper complexes reveal distinct absorption characteristics. The [Cu(bpyPY4)]TFSI complex shows absorption peaks of moderate intensity spanning from 249 to 324 nm, with molar absorptivities ranging from 51,500 to 33,400 M<sup>-1</sup>cm<sup>-1</sup>. The copper(I) complex also displays lower intensity shoulders at 329, 391, and 450 nm, characterized by molar absorptivities of 10000, 6600, and 4100 M<sup>-1</sup>cm<sup>-1</sup>, respectively. A subtle shoulder peak at 538 nm is observed, signifying a metal-to-ligand charge transfer with an extinction coefficient of 2500 M<sup>-1</sup>cm<sup>-1</sup>. The copper(II) complex demonstrates d–d transition bands at 616 and 845 nm, each with extinction coefficients of 270 and 194 M<sup>-1</sup>cm<sup>-1</sup>, respectively.

These characteristics are emblematic of a structure predisposed to a trigonal bipyramidal geometry in solution.



Figure 3.3 UV-visible spectra of the[Cu(bpyPY4)]TFSI complex (yellow) and the [Cu(bpyPY4)]TFSI<sub>2</sub> complex (blue) in anhydrous CH<sub>3</sub>CN.

The cyclic voltammogram of the copper(II) complex revealed a copper(II/I) redox couple at -0.454 V versus the ferrocenium/ferrocene couple as shown in Figure 3.4, with a peak splitting value of 93 mV, indicating that it is quasi-reversible. This redox potential is found to be surprisingly negative relative to most previously reported copper(II/I) redox couples. <sup>79–84</sup>



Figure 3.4: A cyclic voltammogram of 2.00 mM [Cu(bpyPY4)](TFSI)<sub>2</sub> in anhydrous CH<sub>3</sub>CN with 0.1 M TBAPF<sub>6</sub> as a supporting electrolyte, measured at a scan rate of 0.1 V/s on a glassy carbon working electrode.

The interaction of TBP with the [Cu(bpyPY4)]<sup>2+/+</sup> redox couple was probed via cyclic voltammetry at varying concentrations of the Lewis base, with TBP present in an excess of at least 10 equivalents to align with device conditions delineated later. The addition of TBP to the copper complex shows no significant influence on either the cathodic or anodic wave of the copper(II/I) redox couple, indicating there is no reaction between the [Cu(bpyPY4)]<sup>2+</sup> complex and TBP. This observation was further substantiated by UV-Vis spectroscopic analysis, showing that, despite increasing TBP concentrations, the UV-visible absorption spectra remained consistent after being corrected for dilution. This reinforces the finding that TBP remains unbound to the metal center of the redox shuttle. If there was substitution occurring the peak at 845 nm would show a rapid decrease in intensity due to a lack of contribution from the [Cu(TBP)<sub>4</sub>]<sup>2+</sup> complex. Further insight was sought using <sup>1</sup>H-NMR spectroscopy. Titration of the [Cu(bpyPY4)]<sup>2+</sup> sample with TBP unveiled no signals corresponding to free bpyPY4, suggesting an absence of ligand substitution. This behavior is attributed to the transient, non-coordinated pyridines within the hexadentate ligand, which likely occlude any open coordination sites on the metal, precluding the detrimental binding of external Lewis bases.



Figure 3.5: A) Cyclic Voltammogram of 2 mM [Cu(bpyPY4)](TFSI)<sub>2</sub> with 0.1 M TBAPF<sub>6</sub> in anhydrous CH<sub>3</sub>CN with increasing concentration of TBP at a glassy carbon working electrode; scan rate = 100 mVs<sup>-1</sup>. B) UV-Vis absorption spectra of 2 mM [Cu(bpyPY4)](TFSI)<sub>2</sub> in anhydrous CH<sub>3</sub>CN with increasing equivalents of TBP. A spectra of 2 mM [Cu(TBP)<sub>4</sub>]TFSI is shown as a control. C) <sup>1</sup>H-NMR spectra of [Cu(bpyPY4)](TFSI)<sub>2</sub> in CH<sub>3</sub>CN with increasing equivalents of TBP. Unbound bpyPY4 and TBP are shown as controls.

Stopped-flow spectroscopy was utilized to measure the cross-exchange electron transfer rate

constant,  $k_{12}$ , between [Cu(bpyPY4)]<sup>2+</sup> and decamethylferrocene (Fe(Cp\*)<sub>2</sub>).

Scheme 2.2: Reaction followed in stopped-flow experiments.

$$[Cu(bpyPY4)]^{2+} + Fe(Cp^*)_2 \xleftarrow{k_{12}} [Cu(bpyPY4)]^+ + Fe(Cp^*)_2$$

Decamethylferrocene was chosen for the cross-exchange to optimize the driving force and because it has a well-known self-exchange rate constant for electron transfer. Due to the large potential difference between  $[Cu(bpyPY4)]^{2+/+}$  and  $[Fe(Cp^*)_2]^{+/0}$ , it was assumed that the reaction went to completion, with no significant back reaction. Figure 3.6A shows a fit of the absorbance at 450 nm vs time plot, which represents the growth of the  $[Cu(bpyPY4)]^+$  species in solution due to the reduction of  $[Cu(bpyPY4)]^{2+}$  by  $Fe(Cp^*)_2$ , using the following equation:

$$A = A_{\infty} + (A_0 - A_{\infty})e^{-k_{obs}t}$$
(3.1)

For all reactions,  $Fe(Cp^*)_2$  was held in excess to maintain pseudo-first order conditions, allowing  $k_{obs}$  to be represented by:



Figure 3.6: A) An absorbance vs time plot at 450 nm, showing the increase of [Cu(bpyPY4)]TFSI species (black dot) and fitting (red line) for the reduction of [Cu(bpyPY4)]TFSI<sub>2</sub> by decamethylferrocene (Fe(Cp<sup>\*</sup>)<sub>2</sub>). B) The pseudo-first order rate constant, k<sub>obs</sub>, vs the concentration of [Fe(Cp<sup>\*</sup>)<sub>2</sub>] for the reactions of [Cu(bpyPY4)]TFSI<sub>2</sub> and [Fe(Cp<sup>\*</sup>)<sub>2</sub>] in CH<sub>3</sub>CN containing 0.1 M LiTFSI.

A linear fit of the previously fitted  $k_{obs}$  values vs concentration of  $Fe(Cp^*)_2$  provided the value of the cross-exchange rate constant,  $k_{12}$ , from the slope of the line (Figure 3.6B). The initial reaction mixtures and the pseudo-first order observed rate constants can be found in Table 3.1.

Table 3.3: The initial reaction mixture and the observed rate constant, k<sub>obs</sub>, for the cross exchange between [Cu(bpyPY4)]TFSI<sub>2</sub> and [Fe(Cp\*)<sub>2</sub>].

[Cu(bpyPY4)](TFSI) <sub>2</sub> / M	$[Fe(Cp^*)_2] / M$	$k_{obs}$ / $s^{-1}$
	8.59 x 10 <sup>-5</sup>	18.3 (± 6.0)
	1.14 x 10 <sup>-4</sup>	$23.0 (\pm 1.8)$
6.00 x 10 <sup>-6</sup>	1.43 x 10 <sup>-4</sup>	30.0 (± 6.7)
	1.72 x 10 <sup>-4</sup>	35.5 (± 1.5)
	2.00 x 10 <sup>-4</sup>	39.9 (± 5.0)

Using the experimentally determined cross-exchange rate constant from Equation 3.2,  $k_{12}$ , and the previously determined self-exchange constant for  $[Fe(Cp^*)_2]^{+/0}$ ,  $k_{11}$ , the Marcus cross-relation

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12}$$
 (3.3)

was used to calculate the self-exchange rate constant for  $[Cu(bpyPY4)]^{2+/+}$ ,  $k_{22}$ , where  $K_{12}$  is the equilibrium constant,  $f_{12}$  is a nonlinear correction term, and  $W_{12}$  is an electrostatic work term for bringing the reactants into contact. The nonlinear correction term and the work term were calculated (see below for details on the calculation) and determined to be 2.60 and 0.99, respectively (Table 3.3). However, it should be noted that there will be some error in the calculation of the work term since the Debye-Huckel model is not expected to have accurate results when the solution has a high ionic strength, as was the case for this experiment with 0.1 M supporting electrolyte. The equilibrium constant,  $K_{12}$ , was determined using Equation 3.4:

$$nF\Delta E = RTlnK_{12}$$
 (3.4)

where n is the number of electrons transferred, F is Faraday's constant,  $\Delta E$  is the difference in formal potential between the oxidant and reductant in solution, R is the ideal gas constant, and

T is the temperature in Kelvin. The redox potential for  $[Cu(bpyPY4)]^{2+/+}$  was found to be -0.43 V vs ferrocene and the redox potential of  $[Fe(Cp^*)2]^{+/0}$  has been previously determined to be -0.52 V2 vs ferrocene<sup>85</sup>, using cyclic voltammetry which gave a calculated K<sub>12</sub> of 18.4. The self-exchange rate constant for  $[Fe(Cp^*)2]^{+/0}$  was previously identified to be 3.8 × 107 M<sup>-1</sup>s<sup>-1</sup> using NMR techniques.<sup>86</sup> Using these values, the self-exchange rate for the  $[Cu(bpyPY4)]^{2+/+}$  couple was determined to be 8.78 M<sup>-1</sup>s<sup>-1</sup>. The measurement was run multiple times to confirm reproducibility and all samples were within error (see Table 3.2).

Trial	Value / M <sup>-1</sup> s <sup>-1</sup>		
1	9.87 ± 1.22		
2	8.41 ± 1.04		
3	8.07 ± 1.00		

Table 3.4: The self-exchange rate of  $[Cu(bpyPY4)]TFSI_{1/2}$  complex for each trial.

The work required to move the reactant complexes to a distance, r, for the electron transfer reaction was calculated using the Equation 3.5.

$$W_{12} = \exp\left[\frac{-w_{12} + w_{21} - w_{11} - w_{22}}{2R}\right] (3.5)$$
$$w_{ij}(r) = \frac{z_i z_j q^2 N_A}{4\pi\varepsilon_0 \varepsilon r(1+\beta r)} (3.6)$$

Equation 3.6 is used to determine the work associated with the forward and reverse crossexchange reaction, w<sub>12</sub> and w<sub>21</sub> respectively, and the self-exchange reactions, w<sub>11</sub> and w<sub>22</sub>. In this equation z<sub>i</sub> and z<sub>j</sub> are the charges of the interacting complexes, q is the charge of an electron, N<sub>A</sub> is Avogadro's constant,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon$  is the static dielectric of the medium,  $\beta = (\frac{2q^2N_AI}{1000_0\varepsilon k_BT})^{1/2}$ , I is the ionic strength of the solution, and k<sub>B</sub> is the Boltzmann's constant. The calculation has the following assumptions: the work is assumed to be primarily Coulombic, the distance, r, is assumed to be the center-to-center distance between the complexes, and the reactants are assumed to be spherical. The non-linear correction term,  $f_{12}$ , was calculated using the equation

$$lnf_{12} = \frac{1}{4} \frac{\left(ln_{12} + \frac{w_{12} - w_{21}}{RT}\right)^2}{\ln\left(\frac{k_{11}k_{22}}{Z^2}\right) + \frac{w_{11} + w_{22}}{RT}} (3.7)$$

where  $K_{12}$  is the equilibrium constant,  $w_{12}$  and  $w_{21}$  are the work associated with the forward and reverse cross-exchange reaction respectively, R is the ideal gas constant, T is temperature in Kelvin, and Z is the frequency factor, which is assumed to be  $10^{13}$  M<sup>-1</sup>s<sup>-1</sup> due to the larger innersphere contributions to the total reorganization energy.

The total reorganization energy of the self-exchange reaction was calculated following the equation

$$k_{11} = K_{12} Z \Gamma e^{-(\lambda_{11}/4k_B T)}$$
 (3.8)

where  $k_{11}$  is the previously calculated self-exchange rate,  $K_{12}$  is the equilibrium constant, Z is the frequency factor, same as in Equation 3.7,  $\Gamma$  is a correction for nuclear tunneling, which is assumed to be ~1,  $\lambda_{11}$  is the total reorganization energy of the self-exchange reaction,  $k_B$  is the Boltzmann constant, and T is the temperature of solution. The resulting  $\lambda_{11}$  was found to be 3.15 eV. The outer-sphere reorganization energy for two spherical reactants can be determined using

$$\lambda_{11,o} = \frac{(\Delta zq)^2}{4\pi\varepsilon_0} \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r_{11}}\right) \left(\frac{1}{D_{op,sol}} - \frac{1}{D_{s,sol}}\right) (3.9)$$

where  $\lambda_{11,0}$  is the outer-sphere reorganization energy,  $\Delta z$  is the change in charge of the complex, q is the charge of an electron,  $\varepsilon_0$  is the permittivity of free space,  $a_1$  and  $a_2$  are the atomic radii of the reactants,  $r_{11}$  is the center-center distance between the reactants,  $D_{op,sol}$  is the optical dielectric constant of the medium, which is equal to the square of the refractive index of the medium, and  $D_{s,sol}$  is the static dielectric constant of the medium. The outer-sphere reorganization energy for the self-exchange reaction was calculated to be 0.99 eV. The inner-sphere reorganization energy was determined using  $\lambda_{11,i} = \lambda_{11} - \lambda_{11,0}$  yielding a result of 2.16 eV for the inner-sphere reorganization energy of the self-exchange reaction.

Table 3.5: Summary of the kinetic data used to calculate the self-exchange rate constant of the  $[Cu(bpyPY4)]TFSI_{1/2}$  complex by monitoring the reaction of  $[Cu(bpyPY4)]TFSI_2$  and  $[Fe(Cp^*)_2]$  in  $CH_3CN$  containing 0.1 M LiTFSI at 25°C.

<b>Kinetic Parameter</b>	Values	
K <sub>12</sub>	18.47	
k <sub>12</sub> / M <sup>-1</sup> s <sup>-1</sup>	(1.95 ± 0.24) x10 <sup>5</sup>	
k <sub>22</sub> / M <sup>-1</sup> s <sup>-1</sup>	(3.80 ± 4.00) x10 <sup>7</sup>	
f <sub>12</sub>	0.99	
W <sub>12</sub>	2.60	
k <sub>11</sub>	8.78 ± 0.96	

DSSC devices were fabricated with [Cu(bpyPY4)]TFSI<sub>1/2</sub> as the redox mediator, where poly(3,4ethylenedioxythiophene) (PEDOT) was utilized at the counter electrode and the commercial dye Y123 was used as the light-harvester. The electrolyte consisted of 0.10 M [Cu(bpyPY4)]TFSI, 0.05 M [Cu(bpyPY4)]TFSI<sub>2</sub>, 0.1 M LiTFSI, and 0.5 M 4-*tert*-butylpyridine, 10 equivalents vs the Cu(II) in the electrolyte, in acetonitrile. The constructed devices gave respectable performance with a J<sub>SC</sub> of 4.98(±0.01) mAcm<sup>-2</sup> and an overall power conversion efficiency of 1.23% for the devices with TBP and 4.73(±0.36) mAcm<sup>-2</sup> and an overall power conversion efficiency of 0.21% for the devices without TBP, as shown in Table 3.6.



Figure 3.7: J–V curves for the [Cu(bpyPY4)]TFSI<sub>1/2</sub> based DSSC devices. The devices represented by the black curve contains TBP while the gray curve is without TBP.

Table 3.6: Summary of device performance, parameters represent the average of three devices.

	ŋ (%)	Jsc (mA*cm-2)	Voc (V)	FF
Cu(PY6)	0.21(±0.07)	4.73(±0.36)	0.14(±0.01)	0.32(±0.05)
Cu(PY6) with TBP	1.23(±0.08)	4.98(±0.01)	0.44(±0.01)	0.56(±0.02)

Both sets of devices were affected by mass transport issues which limited their current. Looking at the incident photon-to-current conversion efficiency (IPCE) spectra, which measures the current at various wavelengths to determine how much of the photons absorbed at each wavelength are converted to current. The IPCE in Figure 3.8 shows that as TBP is added there is a slight increase in the photon-to-current conversion between 450 and 650 nm. This increase could be caused by decreased recombination to the redox shuttle as TBP is being added to the solution. The IPCE spectra can also be integrated to determine what the theoretical current of the device, resulting with an integrated current of 7.87 mAcm<sup>-2</sup> for the devices with TBP and 7.77 mAcm<sup>-2</sup> for



the devices without TBP, we can see that roughly 3 mAcm<sup>-2</sup> were lost due to the mass transport limitations.

Figure 3.8: IPCE curves for the [Cu(bpyPY4)]TFSI<sub>1/2</sub> based DSSC devices. The devices represented by the black points and curve contains TBP while the gray points and curve is without TBP. For the IPCE, the points represent IPCE responses while the solid lines represent the integrated photocurrent.

The effect of TBP on the fermi level of the devices was investigated. By knowing the solution potential and the V<sub>oc</sub> of the devices the fermi level could be calculated, which can be determined by adjusting the open circuit voltage (V<sub>oc</sub>) by the solution potential. For both devices with and without TBP the solution potential was roughly the same, at -0.443 V vs ferrocene for the devices without TBP and -0.466 V vs ferrocene for the devices with TBP. However, there was a stark difference in the V<sub>oc</sub> between both sets of devices, devices without TBP having a V<sub>oc</sub> of only 0.14 V vs solution potential where devices with TBP had a V<sub>oc</sub> of 0.44 V vs solution potential. This indicates that the addition of TBP caused the fermi level to undergo a negative shift of roughly 300 mV. Although the [Cu(bpyPY4)]TFSI<sub>1/2</sub> complex does not undergo ligand substitution the

addition of TBP to the electrolyte still drastically increases the electron lifetime, by almost 1000 fold. This indicates that the addition of TBP is still able to reduce recombination in the system, although not as significantly as the [Cu(dbmed)]OTf<sub>1/2</sub> system. This shift in potential could be attributed to the addition of TBP in solution, which can shift the potential of the conduction band of the titania to more negative potentials and reducing recombination by adsorbing to the titania.<sup>33,34</sup>



Figure 3.9: A plot of the electron lifetime vs potential plot for DSSC devices using  $[Cu(dbmed)]OTf_{1/2}$  (green),  $[Cu(bpyPY4)]TFSI_{1/2}$  (red), with (pale color) and without (dark color) the addition of TBP.

## 3.4 Conclusions

This study has demonstrated the complex relationship between ligand design and metal coordination in copper complexes using the bpyPY4 scaffold. The crystallographic analysis revealed that the bpyPY4 ligand can adapt to both five-coordinate and four-coordinate structures

around copper(II) and copper(I) centers. These structures showed significant deviations from ideal geometries, indicating the influence of the bpyPY4 scaffold on how the ligand and metal interact.

The behavior of these copper-ligand interactions was further explored using <sup>1</sup>H-NMR studies, which showed a rapid interchange between pyridine donors that are coordinated and those that are not. The results from variable-temperature NMR spectroscopy highlighted the unstable nature of the copper-pyridine bonds, providing a detailed view of how these bonds behave in solution.

The UV-visible spectroscopic analysis helped improve understanding on the electronic transitions in these complexes, revealing specific absorption patterns that correspond to their structural preferences in solution. The consistent behavior of the [Cu(bpyPY4)]<sup>2+/+</sup> redox couple, even with added TBP, suggests a strong metal-ligand bond, which is promising for applications where interactions with Lewis bases are expected.

The high theoretical current and the negative redox potential make this redox shuttle a candidate for utilization with narrow band gap dyes for high photocurrent DSSC devices. Future studies will focus on utilizing this redox complex with near IR absorbing dyes and developing new ligand designs to vary the energetics and stability of the copper species.

Overall, this comprehensive study not only deepens our understanding of copper complexes with hexadentate ligands but also lays the groundwork for designing new ligands that can control and alter the shapes and reactivities of metal centers. The potential uses of these systems in areas like catalysis and electronic devices are significant, highlighting the value of detailed studies like this one.

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# Chapter 4 – Investigation of [Cu(PY5)]<sup>2+/+</sup>

## 4.1 Introduction

Following Grätzel's seminal 1993 report on dye-sensitized solar cells (DSSCs) achieving 10% efficiency, advancements were hindered by the reliance on the I<sup>3-</sup>/I<sup>-</sup> redox shuttle.<sup>15</sup> The high overpotential required for efficient dye regeneration was a major limitation. Recent progress with outer sphere redox shuttles offers a solution to mitigate this limitation and enhance DSSC performance.<sup>23</sup> Conversely, Co(III/II) based redox shuttles introduce an inner-sphere reorganization energy challenge due to electron transfer transitions between d<sup>7</sup> Co(II) and d<sup>6</sup> Co(III) states. This affects dye regeneration kinetics by limiting the available electron transfer driving force.<sup>23</sup>

The robust performance of copper-based redox shuttles in DSSCs has positioned them as a compelling avenue for overcoming conventional limitations. Their success stems from their remarkable ability to attain efficiencies that surpass previous benchmarks. With an exceptional 15.2% efficiency under standard solar irradiance and an astonishing 34.5% efficiency under indoor fluorescent lighting at 1000 lux intensity, copper-based redox shuttles have firmly established their credentials.<sup>20,87</sup> This achievement can be attributed to their intrinsic advantage of lower inner-sphere electron transfer reorganization energies compared to traditional options. Furthermore, their versatile coordination geometries, witnessed in copper(II) d<sup>9</sup> complexes which frequently adopt six-coordinate, octahedral or tetragonal, five-coordinate, square pyramidal or trigonal bipyramidal, or four-coordinate, tetrahedral or square planar geometries, and copper(I) d<sup>10</sup> complexes which predominantly adopt four-coordinate, tetrahedral or square planar geometries, underscore their adaptability.<sup>60–63</sup> Employing ligands based on bidentate bipyridine

or phenanthroline motifs, augmented with strategically positioned bulky groups, these shuttles can reduce the reorganization energy needed for the transition between Cu(II) and Cu(I) redox states, facilitating more efficient electron transfer processes within the DSSC system.<sup>64</sup> Recent observations have illuminated a critical facet of copper-based redox shuttle performance within DSSCs. Notably, prevalent Lewis base additives, including 4-*tert*-butylpyridine (TBP), have been revealed to coordinate with Cu(II) species.<sup>38</sup> This coordination has potentially adverse impacts on copper redox mediator electrochemistry and, consequently, overall device efficacy. Studies into this phenomenon elucidate that TBP-induced coordination or ligand substitution often involving bipyridyl and phenanthroline ligands—leads to intricate electrochemical changes within the DSSC devices. When the ligand substitution occurs and [Cu(TBP)<sub>4</sub>]<sup>2+</sup> is present in the devices it is accompanied by a substantial negative shift in formal redox potentials, by hundreds of millivolts.<sup>38</sup> This phenomenon limits the attainable photovoltage, exerting a significant constraint on device performance.

Recent strides in copper-based redox shuttle design have been underscored by the efforts of Sun and colleagues, who introduced copper based redox shuttles incorporating pentadentate ligands within DSSC devices.<sup>41</sup> The pentadentate Cu(II) complex was shown to have a resistance to substitution, even when exposed to commonly employed Lewis base additives such as 4-tertbutylpyridine (TBP). This resistance to ligand substitution is attributed to two factors. First, the increased denticity of the ligand translates to a heightened overall stability of the metal complex, owing to the chelating effect. Second, they specifically designed the coordination sphere's steric constraints to shield the copper complexes—particularly their oxidized forms—from TBP

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coordination. Building upon this concept, a copper-based redox shuttle harnessing the potency of a pentadentate ligand, 2,6-bis[1,1-bis(2-pyridyl)ethyl]pyridine (PY5), is presented.

#### 4.2 Experimental Details

All NMR spectra were taken on an Agilent DirectDrive2 500 MHz spectrometer at room temperature and referenced to residual solvent signals. All NMR spectra were evaluated using the MestReNova software package features. Cyclic voltammograms were obtained using µAutolabIII potentiostat using BASi glassy carbon electrode, a platinum mesh counter electrode, and a fabricated 0.01 M AgNO<sub>3</sub>, 0.1 M TBAPF<sub>6</sub> in acetonitrile Ag/AgNO<sub>3</sub> reference electrode. All measurements were internally referenced to ferrocene/ferrocenium couple via addition of ferrocene to solution after measurements or run in a parallel solution of the same solvent/electrolyte. UV-Vis spectra were taken using a PerkinElmer Lambda 35 UV-Vis spectrometer using a 1 cm path length quartz cuvette at 480 nm/min. Elemental Analysis data were obtained via Midwest Microlab. Continuous-wave (Cw) EPR measurements were performed using a Bruker E-680X spectrometer operating at X-band frequencies and equipped with an SHQ-E cavity. EPR samples comprising 0.01 M Cu(II) complexes in acetonitrile or dichloromethane. The liquid solutions were studied in a quartz flat cell. An Oxford ESR-900 cryostat and an ITC-503 temperature controller were used for measurements at 298 K. Cw-EPR simulations were performed with EasySpin 5.2.28, running in MATLAB 2020a. We simulated the solution spectra using the "chili" module from EasySpin. Our simulations varied the coefficients for copper hyperfine coupling, isotropic diffusion correlation time, and intrinsic linewidth. The results are shown as dashed curves offset from the spectra (solid lines). For single-crystal X-ray diffraction, single crystals were mounted on a nylon loop with paratone oil using a Bruker APEX-II CCD

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diffractometer. Crystals were maintained at T ½ 173(2) K during data collection. Using Olex2, the structures were solved with the ShelXS structure solution program using the Direct Methods solution method. Photoelectrochemical measurements were performed with a potentiostat (Autolab PGSTAT 128N) in combination with a xenon arc lamp. An AM 1.5 solar filter was used to simulate sunlight at 100 mW cm<sup>-2</sup>, and the light intensity was calibrated with a certified reference cell system (Oriel Reference Solar Cell & Meter). A black mask with an open area of 0.07 cm<sup>-2</sup> was applied on top of the cell active area. A monochromator (Horiba Jobin Yvon MicroHR) attached to the 450 W xenon arc light source was used for monochromatic light for IPCE measurements. The photon flux of the light incident on the samples was measured with a laser power meter (Nova II Ophir). IPCE measurements were made at 20 nm intervals between 400 and 700 nm at short circuit current.

TEC 15 FTO was cut into 1.5 cm by 2 cm pieces which were sonicated in soapy DI water for 15 minutes, followed by manual scrubbing of the FTO with Kimwipes. The FTO pieces were then sonicated in DI water for 10 minutes, rinsed with acetone, and sonicated in isopropanol for 10 minutes. The FTO pieces were dried in room temperature air then immersed in an aqueous 40 mM TiCl<sub>4</sub> solution for 60 minutes at 70 °C. The water the for the TiCl<sub>4</sub> treatment was preheated to 70 °C prior to adding 2 M TiCl<sub>4</sub> to the water. The 40 mM solution was immediately poured onto the samples and placed in a 70 °C oven for the 60-minute deposition. The FTO pieces were immediately rinsed with 18 M $\Omega$  water followed by isopropanol and were annealed by heating from room temperature to 500 °C, holding at 500 °C for 30 minutes. A 0.36 cm<sup>2</sup> area was doctor bladed with commercial 30 nm TiO<sub>2</sub> nanoparticle paste (DSL 30NRD). The transparent films were left to rest for 10 minutes and were then placed in a 125 °C oven for 30 minutes. The samples

were annealed in an oven that was ramped to 325 °C for 5 minutes, 375 °C for 5 minutes, 450 °C for 5 minutes, and 500 °C for 15 minutes. The 30 nm nanoparticle film thickness was ~8 μm. After cooling to room temperature, a second TiCl<sub>4</sub> treatment was performed as described above. When the anodes had cooled to 80 °C, they were soaked in a dye solution of 0.1 mM Y123 in 1:1 acetonitrile : tert-butyl alcohol for 18 hours. After soaking, the anodes were rinsed with acetonitrile and were dried gently under a stream of nitrogen.

The PEDOT counter electrodes were prepared by electropolymerization in a solution of 0.01 M EDOT and 0.1 M LiClO<sub>4</sub> in 0.1 M SDS in 18 MΩ water. A constant current of 8.3 mA for 250 seconds was applied to a 54 cm<sup>2</sup> piece of TEC 8 FTO with predrilled holes using an equal size piece of FTO as the counter electrode. The PEDOT electrodes were then washed with DI water and acetonitrile before being dried under a gentle stream of nitrogen and cut into 1.5 cm by 1.0 cm pieces. The working and counter electrodes were sandwiched together with 25  $\mu$ m surlyn films by placing them on a 140 °C hotplate and applying pressure. The cells were then filled in a nitrogen filled glove box with electrolyte through one of the two predrilled holes and were sealed with 25  $\mu$ m surlyn backed by a glass coverslip and applied heat to seal with a soldering iron. The electrolyte consisted of 0.10 M Cu(I), 0.05 M Cu(II), 0.1 M Li(Counter-ion), and 0.5 M 4-tert-butylpyridine in acetonitrile. All batches were made with at least 5 cells per batch. Contact to the TiO<sub>2</sub> electrode was made by soldering a thin layer of indium wire onto the FTO.

Acetonitrile, deuterated acetonitrile, dichloromethane, methanol, ethanol, diethyl-ether, deionized water, 1,1-bis(2-pyridyl)ethane, 2,6-difluoropyridine, 2.5 M n-butyl lithium in hexanes, tetrakisacetonitrile copper(I) triflate, copper(II) triflate , silver nitrate, tetrabutylammonium

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hexafluorophosphate, lithium triflate, lithium bistriflimide, silver bistriflimide, copper (I) chloride, copper (I) bistriflimide, and isopropyl alcohol were purchased from Sigma-Aldrich.

Starting material 1,1-Bis(2-pyridyl)ethane, and ligand PY5 were synthesized according to published procedures.<sup>88</sup>

## [Cu(PY5)](OTf)

A mixture of PY5 (74.5 mg, 0.168 mmol) and [Cu(ACN)<sub>4</sub>](OTf) (57.5 mg, 0.153 mmol) in anhydrous acetonitrile was stirred for 30 minutes at room temperature. The solution was precipitated with anhydrous diethyl ether, forming a yellow solid, and the solid was collected. The solid was dried under vacuum. (97.8 mg 97.4% yield) <sup>1</sup>H NMR (500 MHz, acetonitrile-d3):  $\delta$  = 8.53 (d, 4H); 8.04 (t, 1H); 7.92 (d, 2H); 7.77 (t, 4H); 7.37 (d, 4H); 7.26 (t, 4H); 2.20 (s, 6H); 2.18 (1.5 H). Elem. Anal. Calc. for C<sub>30</sub>H<sub>25</sub>CuF<sub>3</sub>N<sub>6</sub>O<sub>3</sub>S C, 54.42; H, 3.98; N, 12.28. Found: C, 54.79; H, 3.91; N, 12.05. TOF-MS-ES+ *m/z* calc. for [Cu(PY5)] C<sub>29</sub>H<sub>25</sub>CuN<sub>5</sub> 506.14; Found, 506.1407.

## [Cu(PY5)](TFSI)

Silver Bistriflimide (47.0 mg, 0.121 mmol) and copper chloride (12.0 mg, 0.121 mmol) was dissolved in minimal anhydrous ACN and was stirred for 30 minutes at room temperature. After mixing, the solid silver chloride was removed from the solution, and the solution was then added to PY5 (52.5 mg, 0.118 mmol) and stirred overnight. The solution was precipitated with anhydrous diethyl ether, forming a yellow solid, and the solid was collected. The solid was dried under vacuum. (90.2 mg 96.9% yield). <sup>1</sup>H NMR (500 MHz, acetonitrile-d3):  $\delta$  = 8.53 (d, 4H); 8.04 (t, 1H); 7.92 (d, 2H); 7.77 (t, 4H); 7.37 (d, 4H); 7.26 (t, 4H); 2.20 (s, 6H); 2.18 (1.5 H). Elem. Anal. Calc. for C<sub>31</sub>H<sub>25</sub>CuF<sub>6</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub> C, 54.42; H, 3.98; N, 12.28. Found: C, 54.79; H, 3.91; N, 12.05. TOF-MS-ES+ *m/z* calc. for [Cu(PY5)], 506.14; Found, 506.14.

[Cu(PY5)](OTf)<sub>2</sub>

A mixture of PY5 (0.2924 g, 0.66 mmol) and Cu(OTf)<sub>2</sub> (0.2210 g, 0.61 mmol) in anhydrous DCM was stirred for 30 minutes at room temperature. The solution was precipitated with anhydrous diethyl ether, forming a blue solid, and the solid was collected. The solid was dried under vacuum. (0.4776 mg 92.5% yield) Elem. Anal. Calc. for  $C_{31}H_{25}CuF_6N_6O_6S_2$  C, 46.24; H, 3.13; N, 7.89. Found: C, 45.93; H, 3.32; N, 8.38.

## [Cu(PY5)](TFSI)<sub>2</sub>

A mixture of PY5 (47.8 mg, 0.108 mmol) and Cu(TFSI)<sub>2</sub> (67.2 mg, 0.108 mmol) in anhydrous DCM was stirred for 30 minutes at room temperature. The solution was precipitated with anhydrous diethyl ether, forming a blue solid, and the solid was collected. The solid was dried under vacuum. Any further purification was done via recrystallization from ACN with diffused ether.(46.3 mg 40.1% yield) Elem. Anal. Calc. for C<sub>35</sub>H<sub>28</sub>CuF<sub>12</sub>N<sub>8</sub>O<sub>8</sub>S<sub>4</sub> C, 37.93; H, 2.55; N, 10.11. Found: C, 37.38; H, 2.31; N, 9.41.

## 4.3 Results and Discussion

The synthesis of the ligand, PY5, has been previously documented, involving the deprotonation of 1,1-bis(2-pyridyl)ethane by n-BuLi followed by the addition of 2,6-difluoropyridine as the electrophile.<sup>89</sup> The copper complexes were synthesized by reacting equimolar ratios of the PY5 ligand with copper precursors in different solvents, leading to the formation of [Cu(PY5)]OTf, [Cu(PY5)]OTf<sub>2</sub>, [Cu(PY5)]TFSI, and [Cu(PY5)]TFSI<sub>2</sub>. The copper(I) bistriflimide was synthesized by combining equimolar amounts of silver bistriflimide and copper chloride. The complexes were purified via recrystallization from acetonitrile for copper(I) and dichloromethane for copper(II) solutions and characterized using <sup>1</sup>H-NMR and elemental analysis.

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Single crystal X-ray diffraction revealed the solid-state structures of the complexes. A geometric index,  $\tau 4$ , can be used for four-coordinate complexes to determine how much distortion there is from ideal tetrahedral or square planer geometries.<sup>74</sup> Where a  $\tau 4$  of 1 represents an ideal tetrahedral geometry and 0 represents an ideal square planer geometry. The [Cu(PY5)]OTf complex exhibited a highly distorted tetrahedral geometry with a calculated  $\tau 4$  value of 0.65. The constrained nature of the ligand led to a significant portion of the copper center being solvent-exposed. The choice of solvent during synthesis played a role in preventing a disproportionation reaction in which the copper(I) form disproportionated to copper metal and a copper(II) complex when the complex was synthesized in dichloromethane. Interestingly when an NMR was taken of the disproportionated copper(II) product, it did not match the synthetic [Cu(PY5)]OTf<sub>2</sub> product.

Acetonitrile was used as the solvent of choice when synthesizing the copper(I) form since it did not cause the copper(I) form to undergo disproportionation.



Figure 4.1: Crystal structures of the cations of the [Cu(PY5)]OTf species (A), and [Cu(PY5)]OTf<sub>2</sub> species (B), and the [Cu(PY5)]TFSI<sub>2</sub> species which was grown in dichloromethane, a non-coordinating solvent (C). Depicted ellipsoids are at the 50% probability level. The non-interacting anions and hydrogens were omitted for clarity.

The solid-state structure of [Cu(PY5)]OTf<sub>2</sub> showed pseudo-octahedral geometry, with the PY5 ligand coordinated at five sites and the acetonitrile, the solvent used for synthesis, coordinated at the sixth site. The average bond length for the PY5 ligand is 2.081 Å, and the bond length between the copper and the nitrogen on the acetonitrile is 2.369 Å, a significantly longer distance.

To investigate changes in a system with a vacant axial site, the crystals were regrown using an innocent solvent, dichloromethane. This process revealed an interaction between one of the oxygens on the trifluoromethanesulfonate counter-ion and the copper center in the axial position. The bond length was measured at 2.453 Å. This copper-counter-ion bond length increases further when the bistriflimide counter-ion is studied, yielding a copper-oxygen bond length of 2.728 Å. Challenges arose in purifying acetonitrile-bound copper(II) complexes due to the lability of acetonitrile, leading to a mixture of copper complexes with and without acetonitrile bound. To ensure accurate measurements, the copper(II) form was synthesized in dichloromethane.

To assess the structural nuances of the copper complex with different counter ions, <sup>1</sup>H-NMR analysis was employed. The <sup>1</sup>H-NMR spectra for both [Cu(PY5)]OTf and [Cu(PY5)]TFSI, shown in Figures 4.1A and 4.4A respectively, were recorded in deuterated acetonitrile at room temperature. Both spectra display an integration for 25 protons. Four peaks representing the pyridine "arms" are observed: one at approximately 8.5 ppm and three others between 7.35 and 7.95 ppm, with each integrating to four protons. Peaks at around 8.00 ppm, integrated to one proton, and 7.25 ppm, integrated to two protons, correspond to the central pyridine. The peak at approximately 2.20 ppm, integrating to six protons, is attributed to the ligand's methyl groups. The copper(II) complex is a paramagnetic compound making it hard to pull any quantifiable information from the spectra, however, it should be noted that the NMR of both of the OTf and TFSI counter ion, irrespective of it they are of the copper(I) or copper(II) complexes, yield similar spectra.



Figure 4.3: A) Cyclic voltammograms of 2 mM [Cu(PY5)]OTf<sub>2</sub>, blue, [Cu(PY5)]TFSI<sub>2</sub>, red, in anhydrous CH<sub>3</sub>CN. B) [Cu(PY5)]OTf<sub>2</sub> in dichloromethane, blue, with 5 equivalents of acetonitrile added to the solution. All samples contained 0.1 M TBAPF<sub>6</sub> as a supporting electrolyte, measured at a scan rate of 0.1 V/s on a glassy carbon working electrode.

To further understand how the electrochemical behavior of the complex was affected by the different counter ions, cyclic voltammetry was conducted. In the [Cu(PY5)]OTf<sub>2</sub> complex, two peaks were observed in the cyclic voltammogram. One peak appeared at -0.372 V vs ferrocene, while the other was observed at -0.662 V vs ferrocene. When the complex was measured in the absence of acetonitrile, using dichloromethane as the solvent, the peak at -0.662 V went away, and when acetonitrile was titrated into the solution, the peak at -0.622 V returned. Which

indicates that the peak at -0.662 V was the acetonitrile bound complex, and the peak at -0.372 V was either triflate bound or a 5-coordinate [Cu(PY5)]OTf<sub>2</sub> complex. When the [Cu(PY5)]TFSI<sub>2</sub> complex was investigated in anhydrous acetonitrile it exhibited a single peak at -0.382 V vs ferrocene, indicating that the acetonitrile was not axially bound in the TFSI version of the complex. This could be due to the increased bulk of the TFSI counter-ion when compared to the OTf counter-ion, the TFSI may be physically blocking the acetonitrile from binding with the copper center. The minimal change in redox potential of the peak around -0.375 V vs ferrocene with various counter ions indicates that the redox couple being measured does not require the presence of acetonitrile, and it is indifferent to the copper center. This suggests that the peak at around -0.375 mV corresponds to a 5-coordinate species where the axial position is vacant.



Figure 4.2: The UV-Vis spectra of the copper(I), A, and copper(II), B, complexes in anhydrous acetonitrile. The triflate complexes are in blue while the bistriflimide complexes are in red.

Shifting our focus to how the different counter ions affect the optical properties of the copper complexes, we examined their UV-visible absorption spectra. The UV-Vis spectra of the copper(I) complexes in acetonitrile displayed peaks below 450 nm which were attributed to  $\pi$ - $\pi$ \* absorptions from pyridine units. Metal to ligand charge transfer bands were observed between

450-500 nm in copper(I) complexes, with no significant difference between the triflate and bistriflimide variants.

The [Cu(PY5)]OTf<sub>2</sub> complex exhibits two d-d transitions, the first at 597 nm, with an extinction coefficient of 79.8 M<sup>-1</sup>s<sup>-1</sup>, and the second at 909 nm, with an extinction coefficient of 13.2 M<sup>-1</sup>s<sup>-1</sup>. The [Cu(PY5)]TFSI<sub>2</sub> complex only exhibits one peak at 598 nm, with an extinction coefficient of 53.0 M<sup>-1</sup>s<sup>-1</sup>, although the tailing on the peak could indicate the overlap of two peaks. The observation of two d-d transitions is indicative of either a Jahn-Teller distorted octahedral complex, or a square pyramidal complex. However, the large difference in wavelengths between the two transitions indicates that this is a square pyramidal geometry. The difference in absorbance of spectra when the counter-ion is changed is most likely due the lack of acetonitrile bound to the axial position in the TFSI version of the complex.



Figure 4.4: Simulated, red, and experimental, black, EPR spectra of 2 mM [Cu(PY5)]OTf2 in either anhydrous acetonitrile, A, or dichloromethane, B. Spectra C shows the difference between the dichloromethane spectra, red, and the acetonitrile spectra, black, when corrected for solvent affects.

Electron Paramagnetic Resonance spectra were taken in an attempt to elucidate the solution geometry of the copper(II) form of the redox couple. Two spectra were taken of the [Cu(PY5)]OTf<sub>2</sub> complex, one of the complex synthesized and measured in acetonitrile and the other in dichloromethane. The EPR showed that in both systems the complex is axially elongated which is indicative of the complex having an elongated octahedral, square pyramidal, or square planer geometry. The two systems have similar g-value but the hyperfine coupling is quite different

between the two, indicating that the complexes are similar in geometry but not identical. When the spectra were adjusted to account for the effects of using two different solvents, it becomes easy to see that the species in solution are not identical. However, it remains unclear what the complex's exact makeup in solution is.

Table 4.1: EPR Parameters of  $[Cu(PY5)]OTf_2$  complexes with liquid solutions in acetonitrile (ACN) or dichloromethane (DCM) at room temperature. All parameters were simulated using MATLAB.

	g parallel	g perpendicular	hyperfine parallel (G)	hyperfine perpendicular (G)
In ACN	2.28	2.04	437	42.6
In DCM	2.30	2.04	372	39.8

To investigate potential interactions between the triflate counterion and the copper center in solution, a variable temperature <sup>19</sup>F-NMR experiment was conducted. The experiment involved cooling the solution from room temperature to -40°C. Upon lowering the temperature, the fluorine peak corresponding to the triflate counterion exhibited a decrease in intensity coupled with an increase in sharpness. This observation suggests that the counter-ion does not undergo exchange with the axial site on the copper center, implying that the counter-ion doesn't interact with the copper center in solution. Such an exchange would typically result in broadening of the peak as the temperature decreases. Notably, this trend remained consistent irrespective of whether acetonitrile or dichloromethane was used as the solvent. When this evidence is compiled with the previous results of the UV-Vis, cyclic voltammetry, and EPR experiments it becomes clear that the solution geometry of the [Cu(PY5)]<sup>2+/+</sup> complexes a square pyramidal where the axial site is vacant.



Figure 4.5: <sup>19</sup>F-NMR spectra of [Cu(PY5)]OTf<sub>2</sub> in anhydrous deuterated acetonitrile at various temperatures, 25°C-red, 0°C-green, -20°C-blue, and -40°C-purple.





In order to understand how the dynamic nature of the interaction with the open axial site the self- exchange kinetics of both systems were investigated. First the [Cu(PY5)]OTf complex was investigated utilizing stopped-flow spectroscopy. Stopped-flow spectroscopy was utilized to measure the cross-exchange electron transfer rate constant,  $k_{12}$ , between [Cu(PY5)]OTf<sub>2</sub> and octamethylferrocene (FcMe8).

$$[Cu(PY5)]^{2+} + FcMe8 \xleftarrow{k_{12}} [Cu(PY5)]^{+} + FcMe8^{+}$$
(4.1)



Figure 4.7: An absorbance vs time plot at 450 nm, showing the increase of [Cu(PY5)]OTf<sub>2</sub> species (black dot) and fitting (red line) for the reduction of [Cu(PY5)]OTf<sub>2</sub> by octamethylferrocene (FcMe8).

Octamethylferrocene was chosen for the cross-exchange to optimize the driving force and because it has a well-known self-exchange rate constant for electron transfer.<sup>90</sup> Due to the large potential difference between  $[Cu(PY5)]^{2+/+}$  and  $[FcMe8]^{+/0}$ , it was assumed that the reaction went to completion, with no significant back reaction. Figure 4.7 shows a fit of the absorbance at 450 nm vs time plot, which represents the growth of the  $[Cu(PY5)]^{+}$  species in solution due to the reduction of  $[Cu(PY5)]^{2+}$  by FcMe8, using the following equation:

$$A = A_{\infty} + (A_0 - A_{\infty})e^{-k_{obs}t}$$
(4.2)

For all reactions, FcMe8 was held in excess to maintain pseudo-first order conditions, allowing

 $k_{\rm obs}$  to be represented by:

$$k_{obs} = k_{12}[FcMe8]$$
 (4.3)

A linear fit of the fitted  $k_{obs}$  values vs concentration of FcMe8 provided the value of the crossexchange rate constant,  $k_{12}$ , from the slope of the line. The initial reaction mixtures and the pseudo-first order observed rate constants can be found in Table 4.2.

[Cu(PY5)(OTf) <sub>2</sub> ] / M	[FcMe8] / M
	2.58E-04
	3.10E-04
2.74E-05	3.61E-04
	4.13E-04
	4.65E-04

Table 4.2: The initial reaction mixture and the observed rate constant,  $k_{obs}$ , for the cross exchange between [Cu(PY5)]OTf<sub>2</sub> and FcMe8.

Using the experimentally determined cross-exchange rate constant from Equation 4.3,  $k_{12}$ , and the previously determined self-exchange constant for [FcMe8]<sup>+/0</sup>,  $k_{11}$ , the Marcus cross-relation

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \quad (4.4)$$

was used to calculate the self-exchange rate constant for  $[Cu(PY5)]^{2+/+}$ ,  $k_{22}$ . Where  $K_{12}$  is the equilibrium constant,  $f_{12}$  is a nonlinear correction term, and  $W_{12}$  is an electrostatic work term for bringing the reactants into contact. The nonlinear correction term and the work term were calculated (see below for details on the calculation) and determined to be 2.60 and 0.99, respectively as seen in Table 4.3. However, it should be noted that there will be some error in the calculation of the work term since the Debye-Huckel model is not expected to have accurate
results when the solution has a high ionic strength, as was the case for this experiment (0.1 M supporting electrolyte). The equilibrium constant,  $K_{12}$ , can be determined using Equation 4.5:

$$nF\Delta E = RT lnK_{12} \tag{4.5}$$

where *n* is the number of electrons transferred, *F* is Faraday's constant,  $\Delta E$  is the difference in formal potential between the oxidant and reductant in solution, *R* is the ideal gas constant, and *T* is the temperature in Kelvin. The redox potential for  $[Cu(PY5)]^{2+/+}$  was found to be -0.372 V vs ferrocene<sup>91</sup> and the redox potential of  $[FcMe8]^{+/0}$  has been previously determined to be -0.377 V vs ferrocene, using cyclic voltammetry which gave a calculated  $K_{12}$  of 0.62. The self-exchange rate constant for  $[FcMe8]^{+/0}$  was previously identified to be 2.01 × 10<sup>7</sup> M<sup>-1</sup>s<sup>-1</sup> using NMR techniques.<sup>92</sup> Using these values, the self-exchange rate for the  $[Cu(PY5)]OTf_{1/2}$  couple was determined to be 88.1 (±7.3) M<sup>-1</sup>s<sup>-1</sup>.

The work required to move the reactant complexes to a distance, *r*, for the electron transfer reaction was calculated using the Equation 4.6.

$$W_{12} = \exp\left[-\frac{w_{12} + w_{21} - w_{11} - w_{22}}{2R}\right]$$
(4.6)  
$$w_{ij}(r) = \frac{z_i z_j q^2 N_A}{4\pi\varepsilon_0 \varepsilon r(1+\beta r)}$$
(4.7)

Equation 4.7 was used to determine the work associated with the forward and reverse crossexchange reaction,  $w_{12}$  and  $w_{21}$  respectively, and the self-exchange reactions,  $w_{11}$  and  $w_{22}$ . In this equation  $z_i$  and  $z_j$  are the charges of the interacting complexes, q is the charge of an electron,  $N_A$ is Avogadro's constant,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon$  is the static dielectric of the medium,

 $\beta = \left(\frac{2q^2N_AI}{1000\varepsilon_0\varepsilon k_BT}\right)^{1/2}$ , *I* is the ionic strength of the solution and  $k_B$  is the Boltzmann's constant. The calculation has the following assumptions: the work is assumed to be primarily Coulombic, the

distance, *r*, is assumed to be the center-to-center distance between the complexes, and the reactants are assumed to be spherical.

The non-linear correction term,  $f_{12}$ , was calculated using the equation

$$lnf_{12} = \frac{1}{4} \frac{\left(lnK_{12} + \frac{W_{12} - W_{21}}{RT}\right)^2}{\ln\left(\frac{k_{11}k_{22}}{Z^2}\right) + \frac{W_{11} + W_{22}}{RT}}$$
(4.8)

where  $K_{12}$  is the equilibrium constant,  $w_{12}$  and  $w_{21}$  are the work associated with the forward and reverse cross-exchange reaction respectively, R is the ideal gas constant, T is temperature in Kelvin, and Z is the frequency factor, which is assumed to be  $10^{13}$  M<sup>-1</sup>s<sup>-1</sup> due to the larger innersphere contributions to the total reorganization energy.

Table 4.3: Summary of the kinetic data used to calculate the self-exchange rate constant of the  $[Cu(PY5)]OTf_{1/2}$  complex by monitoring the reaction of  $[Cu(PY5)]OTf_2$  and FcMe8 in acetonitrile containing 0.1 M LiOTf at 25°C.

Kinetic Parameter	Values	
K <sub>12</sub>	0.62	
k <sub>12</sub> / M <sup>-1</sup> s <sup>-1</sup>	4.53E+04	
k <sub>22</sub> / M <sup>-1</sup> s <sup>-1</sup>	2.01E+07	
f <sub>12</sub>	1	
W <sub>12</sub>	2.6	
k <sub>11</sub> / M <sup>-1</sup> s <sup>-1</sup>	88.1	
$\lambda_{se}$ / eV	2.57	
$\lambda_i / eV$	1.55	
$\lambda_o$ / eV	1.02	

The self-exchange of fast exchanging redox complexes can be found by investigating the methyl peaks in the <sup>1</sup>H-NMR spectra of the pure diamagnetic [Cu(PY5)]TFSI complex, the pure

paramagnetic  $[Cu(PY5)]TFSI_2$  complex, and mixtures of the diamagnetic and paramagnetic species. All peaks were fitted to a Lorentzian/Gaussian lineshape. The self-exchange rate constant,  $k_{se}$ , was calculated from

$$k_{se} = \frac{4\pi X_d X_p (\Delta \nu)^2}{(W_{dp} - X_p W_p - X_d W_d)C}$$
(4.9)

where  $W_{dp}$  is the line width (full width at half-maximum) of the mixed species methyl resonance peak,  $W_p$  and  $W_d$  are the line widths of the paramagnetic and diamagnetic peaks, respectively,  $X_p$ and  $X_d$  are the mole fractions of the paramagnetic and diamagnetic species, respectively, C is the total concentration of the exchanging species, and  $\Delta v$  is the observed frequency shift relative to the position of the resonance for the diamagnetic species. The diamagnetic and paramagnetic line widths and the frequency shift are listed in Table 4.4. This analysis produced a  $k_{se}$  of 389 M<sup>-</sup> <sup>1</sup>s<sup>-1</sup> for [Cu(PY5)]TFSI<sub>1/2</sub> in deuterated acetonitrile at 22°C.

Table 4.4: List of parameters used to calculate the self-exchange of [Cu(PY5)]TFSI<sub>1/2</sub>.

W <sub>p</sub>	102.27
W <sub>d</sub>	11.3
X <sub>d</sub>	0.404249
Xp	0.595751
ΔV	22.562
W <sub>dp</sub>	204.66
K <sub>ex</sub>	389.0535

The total reorganization energy for each of the self-exchange reactions was calculated following the equation

$$k_{11} = K_{12} Z \Gamma e^{-(\lambda_{11}/4k_B T)}$$
(4.10)

where  $k_{11}$  is the previously calculated self-exchange rate,  $K_{12}$  is the equilibrium constant, Z is the frequency factor, which is assumed to be  $10^{13}$  M<sup>-1</sup>s<sup>-1</sup> due to the larger inner-sphere contributions

to the total reorganization energy,  $\Gamma$  is a correction for nuclear tunneling, which is assumed to be ~1,  $\lambda_{11}$  is the total reorganization energy of the self-exchange reaction,  $k_B$  is the Boltzmann constant, and T is the temperature of solution in Kelvin. The resulting  $\lambda_{11}$  was found to be 2.57 eV for the OTf complex and 2.41 for the TFSI complex.

The outer-sphere reorganization energy for two spherical reactants can be determined using

$$\lambda_{11,o} = \frac{(\Delta zq)^2}{4\pi\varepsilon_0} \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r_{11}}\right) \left(\frac{1}{D_{op,sol}} - \frac{1}{D_{s,sol}}\right)$$
(4.11)

where  $\lambda_{11,0}$  is the outer-sphere reorganization energy,  $\Delta z$  is the change in charge of the complex, q is the charge of an electron,  $\varepsilon_0$  is the permittivity of free space,  $a_1$  and  $a_2$  are the atomic radii of the reactants,  $r_{11}$  is the center-center distance between the reactants,  $D_{op,sol}$  is the optical dielectric constant of the medium, which is equal to the square of the refractive index of the medium, and  $D_{s,sol}$  is the static dielectric constant of the medium. The outer-sphere reorganization energy for the self-exchange reaction was calculated to be 1.02 eV for the OTf complex and 1.01 eV for the TFSI complex. The inner-sphere reorganization energy was determined using  $\lambda_{11,i} =$  $\lambda_{11} - \lambda_{11,0}$  yielding a result of 1.55 eV for the OTf complex and 1.40 eV for the TFSI complex for the inner-sphere reorganization energy of the self-exchange reaction.



Figure 4.8: A) Cyclic Voltammogram of 2 mM [Cu(PY5)](OTf)<sub>2</sub> with 0.1 M TBAPF<sub>6</sub> in anhydrous acetonitrile with increasing concentration of 4-tert-butylpyridine (TBP) at a glassy carbon working electrode; scan rate = 100 mVs<sup>-1</sup>. B) UV-Vis absorption spectra of 2 mM [Cu(PY5)](OTf)<sub>2</sub> in anhydrous acetonitrile with increasing equivalents of TBP. C) <sup>1</sup>H-NMR spectra of [Cu(PY5)](OTf)<sub>2</sub> in anhydrous acetonitrile with increasing equivalents of TBP. Unbound PY5 and TBP are shown as controls.

Lewis bases such as TBP are used as additives in DSSCs to increase the performance of the DSSC devices.<sup>35–37</sup> Several copper based redox shuttles have been shown to undergo a ligand substitution with the TBP, even polydentate ligands.<sup>38,39</sup> This can have a significant impact on the

redox potential and kinetics of the system as multiple redox systems are present at any given time. Looking at the cyclic voltammetry data, Upon the addition of TBP to the solution containing [Cu(PY5)]OTf<sub>2</sub>, both of the redox waves go away and a new wave grows in at -0.512 V vs ferrocene, indicating that the [Cu(PY5)]OTf<sub>2</sub> complex is reacting with TBP. The new peak continues to grow in as TBP is added until about 10 equivalents relative to the amount of copper(II) in the solution, indicating that whatever the change that occurred has fully stabilized by 10 equivalents added. As such the amount of TBP used in the devices in this study was 10 equivalents, in order to minimize mixed species in solution.

When the addition of TBP is monitored via UV-Vis spectroscopy, there is a noticeable blue shift of 23 nm for the peak at ~600 nm, which also comes with an almost 50% increase in absorbance, and a blue shift of 58 nm for the peak at ~900 nm, with minimal change in absorbance. Once 10 equivalents of TBP is added, relative to the copper(II) in solution, the reaction seems to have reached equilibrium and the peaks no longer shift. This agrees with the previous cyclic voltammetry study indicating that there is a reaction occurring which has reached equilibrium by 10 equivalents of TBP added to the solution. Although it should be noted that when the reaction has stabilized the resulting spectra does not match the spectra of [Cu(TBP)<sub>4</sub>]OTf<sub>2</sub>, meaning that whatever is formed it is not the ligand substituted product.

In an attempt to understand what the interaction of the [Cu(PY5)]OTf<sub>2</sub> complex and TBP was producing, the reaction was monitored via <sup>1</sup>H-NMR. Upon the addition of TBP to the [Cu(PY5)]OTf<sub>2</sub> solution a change in the spectra is seen as soon as a single equivalent of TBP is added. However, after that initial change in the spectra, the only change in the spectra is the broad peaks that seem to correspond to TBP. The broadness of the peaks seems to indicate that

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there is a rapid exchange on the NMR timescale of the TBP and the copper center. However, the spectra show no signs of unbound ligand in the solution as TBP added, suggesting the PY5 ligand remains bound to the copper center. This indicates that the interaction being seen likely stems from TBP displacing the labile axial acetonitrile, resulting in a [Cu(PY5)(TBP)]<sup>2+</sup> copper complex, rather than the displacement of the ligand. It is also worth noting that it has been posited that the interaction of TBP with copper complexes may not necessarily be undergoing a full substitution, instead it may be just a coordination of the TBP to the copper center causing the change in properties, similar to what is being seen with [Cu(PY5)]OTf<sub>2</sub>.<sup>39,93</sup>



Figure 4.9: J–V curves for the [Cu(PY5)]OTf<sub>1/2</sub>, blue, and [Cu(PY5)]TFSI<sub>1/2</sub>, red, based DSSC devices. The devices represented by the pale colored curves contain TBP while the dark colored curves are without TBP.

	η / %	J <sub>sc</sub> / mAcm <sup>-2</sup>	V <sub>oc</sub> / V	FF
CuPY5(OTf)	1.30(±0.25)	8.22(±1.16)	0.26(±0.02)	0.60(±0.01)
CuPY5(OTf) with TBP	1.40(±0.30)	6.22(±1.97)	0.35(±0.05)	0.66(±0.04)
CuPY5(TFSI)	1.01(±0.35)	6.57(±2.18)	0.26(±0.01)	0.59(±0.02)
CuPY5(TFSI) with TBP	1.33(±0.09)	5.84(±0.49)	0.36(±0.03)	0.64(±0.01)

Table 4.5: Summary of device performance of devices comparing [Cu(PY5)]OTf and [Cu(PY5)]TFSI, parameters represent the average of five devices.

DSSC devices were fabricated with the commercial dye, Y123, being used as the light-harvester, and where poly(3,4-ethylenedioxythiophene) (PEDOT) was utilized at the counter electrode. The devices utilized either [Cu(PY5)]OTf<sub>1/2</sub> or [Cu(PY5)]TFSI<sub>1/2</sub> as the redox shuttle used, and for each redox shuttle a batch was fabricated with 10 equivalents of TBP relative to the amount of copper(II) in solution, and another batch without the addition of TBP. The devices yielded statistically similar results for the J<sub>SC</sub>, around 6.71 mAcm<sup>-2</sup>, and efficiencies, around 1.26% for all the batches. The difference between the cells with and without TBP is noticeable in the open circuit voltage (V<sub>oc</sub>) where the devices with TBP have an increase of around 100 mV compared to their counterparts without TBP. While the devices with and without TBP show differences from one another the devices with differing redox mediator showed statistically identical performance when compared, as shown in Table 4.5. This similarity in performance across the different redox shuttles indicates that even though there was a difference in both the redox and kinetic properties of the two versions of the redox shuttle, the choice of counter-ion did not significantly affect device characteristics. When looking at the solution potential of the devices it can be seen that the solution potential is similar between the OTf and TFSI versions of the complex, -0.372 V and -0.398 V vs ferrocene respectively, which for both complexes is slightly negative of the Nernstian potential of -0.357 and -0.365 respectively. The predominate form of the redox shuttle that seems to be controlling the solution potential of the devices is the five-coordinate redox couple represented by the wave at ~-0.375 V vs ferrocene, with minimal contribution from the acetonitrile bound wave at -0.662 V. When TBP is added to the devices the solution potential negatively shifts to -0.496 V and -0.501 V vs ferrocene for the OTf and TFSI complexes respectively, which matches well with the predicted -0.503 V vs ferrocene for the [Cu(PY5)(TBP)]OTf<sub>1/2</sub> complex. This was expected due to the binding of TBP to the copper center, so both versions of the complex would form the [Cu(PY5)(TBP)]<sup>2+</sup> complex. Due to the similarity of the device results between the variations of the complex only  $[Cu(PY5)]OTf_{1/2}$  was used for subsequent experiments.



Figure 4.10: J-V curves of best performing devices containing [Cu(PY5)]OTf<sub>1/2</sub> in dry acetonitrile and 0 M TBP (green), 0.055 M TBP (blue), 0.211 M TBP (gray), 0.526 M TBP (yellow).

Table 4.6: Summary of device performance of devices containing [Cu(PY5)]OTf with various equivalents of TBP added, parameters represent the average of five devices.

	η/%	Jsc / mA*cm <sup>-2</sup>	Voc / V	FF
0 M TBP	2.00(±0.06)	8.40(±0.09)	0.39(±0.00)	0.61(±0.02)
0.055 M TBP	2.12(±0.10)	8.91(±0.39)	0.41(±0.02)	0.58(±0.04)
0.526 M TBP	2.01(±0.24)	7.81(±0.63)	0.45(±0.01)	0.57(±0.03)

The effect of the addition of TBP in the DSSC devices was investigated via fabricating devices with various concentrations of TBP used. All of the devices had an improved power conversion efficiency of around 2.04%, which can be attributed to both an increased short circuit current (J<sub>SC</sub>), around 8.38 mAcm<sup>-2</sup>, and a significantly increased open circuit voltage (V<sub>OC</sub>), which is over 100 mV improved over the previous attempt. However, it can be noted that the current of the devices were hampered by mass transport issues. The incident photon-to-current conversion efficiency (IPCE) spectra was measured, which measures the current at various wavelengths to

determine how much of the photons absorbed at each wavelength are converted to current. The IPCE in figure 4.12 shows that as TBP is added there is a general trend towards an increased photon-to-current conversion between 400 and 650 nm. This increase could be caused by decreased recombination to the redox shuttle as TBP is being added to the solution. The IPCE spectra can also be integrated to determine what the theoretical current of the device is, with the results listed in table 4.7, and all of the devices show higher theoretical current than the measure short circuit current, getting as high as 10 mAcm<sup>-2</sup> when 0.526 M of TBP is added to the solution. The isolution. The high theoretical current and the negative redox potential make this redox shuttle a candidate for utilization with narrow band gap dyes for high photocurrent DSSC devices.



Figure 4.11: IPCE curves for the best performing [Cu(PY5)]OTf<sub>1/2</sub> based DSSC devices with various amounts of TBP added. The devices represented by the green diamonds and curve contain 0 M TBP added, the blue square and curve represent 0.055 M TBP added, the gray triangles and curve represent 0.211 M TBP added, and the yellow circles and curve represent 0.526 M TBP added. The points represent IPCE responses while the solid lines represent the integrated photocurrent.

	Jsc / mA*cm <sup>-2</sup>	Integrated Current /
		mA*cm <sup>-2</sup>
0 M TBP	8.40(±0.09)	8.92
0.055 M TBP	8.91(±0.39)	9.82
0.526 M TBP	7.81(±0.63)	10.64

Table 4.7: The measured current and the integrated current found via IPCE for devices containing [Cu(PY5)]OTf<sub>1/2</sub> and various equivalents of TBP added.

The solution potential of the [Cu(PY5)]OTf<sub>1/2</sub> solution without TBP was -0.374 V vs ferrocene matching well with the calculated Nernstian potential of -0.357 V vs ferrocene. Upon the addition of 0.526 M TBP the solution potential shifted to -0.490 V vs ferrocene as the TBP bound to the copper center, the calculated potential was -0.503 V vs ferrocene. This shift in redox potential and the change in the open circuit potential from 0.39 V to 0.45 V as TBP is added to the solution indicates that the fermi level of the devices increased from -0.764 V vs ferrocene to -0.940 V vs ferrocene. The addition of TBP seems to have shifted the fermi level ~200 mV which is a small shift in the fermi level when compared to the [Cu(bpyPY4)]TFSI<sub>1/2</sub> complex and the [Cu(dbmed)]OTf<sub>1/2</sub> complex. When the electron lifetime is compared to the previous complexes it can be seen that the lifetime of the [Cu(PY5)]OTf<sub>1/2</sub> complex is similar to that of the [Cu(bpyPY4)]TFSI<sub>1/2</sub> complex. The addition of TBP shows an increase in the electron lifetime by a factor of 10. This is likely due to a combination of low driving force for recombination for both the complexes due to their negative redox potential, and their relatively slow electron transfer kinetics.



Figure 4.12: A plot of the electron lifetime vs potential plot for DSSC devices using  $[Cu(dbmed)]OTf_{1/2}$  (green),  $[Cu(bpyPY4)]TFSI_{1/2}$  (red),  $[Cu(PY5)]OTf_{1/2}$  (blue), with (pale color) and without (dark color) the addition of TBP.

# 4.4 Conclusion

A copper-based redox shuttle featuring a pentadentate polypyridyl ligand with a labile axial position was developed for use in DSSC devices. This complex was studied using two different counter ions which provide different redox and kinetic properties for the copper complex, including a 4-fold increase in self-exchange rate. Despite these differences in kinetics and redox behavior, both variants of the copper complex showed identical performance in DSSC applications. In solution, the copper(II) complexes predominantly adopted a five-coordinate geometry with a vacant axial site. Further analysis revealed that while there is an interaction between the copper complex and TBP, this interaction is limited to the substitution at the labile axial position by the base, rather than involving the ligand itself. Notably, the addition of TBP to

the DSSC's electrolyte led to an increase in device performance. This suggests that the presence of a Lewis base, even when reacting with the copper complexes, is beneficial for the overall efficiency of DSSCs.

### Chapter 5 – Developing a model to predict ligand exchange in DSSCs

### 5.1 Introduction

In the wake of Grätzel's pioneering 1993 report on achieving a 10% efficient dye-sensitized solar cell (DSSC) through the use of dye-sensitized photoelectrodes, further advancements in efficiency were hampered by the reliance on the triiodide/iodide ( $I^{3-}/I^{-}$ ) redox shuttle.<sup>15</sup> A primary constraint of  $I^{3-}/I^{-}$  utilization arises from the considerable overpotential required for efficient dye regeneration.

Over the last decade, the adoption of outer sphere redox shuttles has enabled the design of systems that mitigate this overpotential, resulting in performance enhancement.<sup>23</sup> However, the incorporation of Co(III/II) based redox shuttles has encountered challenges due to substantial inner-sphere reorganization energy accompanying electron transfer. This complication, arising from the transition of a high-spin d<sup>7</sup> Co(II) system to a low-spin d<sup>6</sup> Co(III) system, directly affects dye regeneration kinetics by limiting the available electron transfer driving force.<sup>23</sup>

In contrast, there has been a growing interest in copper-based redox shuttles for DSSCs. These shuttles have achieved record efficiencies of 15.2% under 1 sun illumination and an impressive 34.5% under 1000 lux intensity fluorescent lighting.<sup>20,87</sup> The success of copper-based redox shuttles can be attributed to their diminished inner-sphere electron transfer reorganization energies, placing them on par with conventional  $I^{3-}/I^{-}$  and Co(III/II)-based counterparts.

Copper complexes are versatile, adopting diverse geometries influenced by oxidation state and ligand environment. Cu(II) d<sup>9</sup> complexes typically exhibit six-coordinate, octahedral or tetragonal, five-coordinate, square pyramidal or trigonal bipyramidal, or four-coordinate, tetrahedral or

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square planar geometries. Similarly, Cu(I) d<sup>10</sup> complexes predominantly assume four-coordinate, tetrahedral or square planar geometries.<sup>60–63</sup>

Most copper redox shuttles in DSSCs utilize bidentate bipyridine or phenanthroline ligands with bulky flanking groups to minimize structural variation between Cu(II) and Cu(I) states. Notably, recent experimental findings indicate that commonly employed Lewis base additives, like 4-tert-butylpyridine, can coordinate to Cu(II) species, potentially having a detrimental impact on the electrochemical behavior and device performance.<sup>38</sup> This coordination-induced complexity influences redox species and shifts formal redox potentials, limiting photovoltage. However, not all copper redox couples undergo ligand substitution.<sup>39,41,94,95</sup>

The focus of this work lies in harnessing a profound insight contributed by Dr. Rorabacher. Dr. Rorabacher demonstrated a strong correlation between the potential of a copper redox couple and the stability constant of its Cu(II) form.<sup>96</sup> It was found that the Cu(I) form of copper redox shuttles tend to have a similar stability constant, where the stability constant is determined by the steric strain. Dr. Rorabacher was also able to show that, in aqueous solutions, the stability constant of the Cu(II) form was found to be inversely proportional to the redox potential of the Cu(II/I) complex. This relationship was found to be linear, shown in Figure 5.1, with a slope of - 0.059, matching the electrochemical constant of the Nernst equation, which indicates that this is a fundamental property. The trend was tested against a variety of ligand types from cyclic ligands to tripodal ligands, and the trend held true across all the different types. This means that ligands that bind with copper to form complexes with more negative redox potentials should be able to substitute ligands bound to copper complexes with more positive redox potentials. This relationship between redox potential and stability constant presents a novel pathway for

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predicting ligand substitution in copper complexes, specifically in the presence of 4-tertbutylpyridine (TBP).





Building upon Dr. Rorabacher's work, our study delves into the interplay between redox potential

and stability constant. The ability to predict ligand substitution by TBP, a crucial factor in the

electrochemical behavior of copper complexes, opens the door to engineering redox mediators with enhanced performance in DSSCs.

#### 5.2 Experimental Details

All NMR spectra were taken on an Agilent DirectDrive2 500 MHz spectrometer at room temperature and referenced to residual solvent signals. All NMR spectra were evaluated using the MestReNova software package features. Cyclic voltammograms were obtained using µAutolabIII potentiostat using BASi glassy carbon electrode, a platinum mesh counter electrode, and a fabricated 0.01 M AgNO<sub>3</sub>, 0.1 M TBAPF<sub>6</sub> in acetonitrile Ag/AgNO<sub>3</sub> reference electrode. All measurements were internally referenced to ferrocene/ferrocenium couple via addition of ferrocene to solution after measurements or run in a parallel solution of the same solvent/electrolyte. UV-Vis spectra were taken using a PerkinElmer Lambda 35 UV-Vis spectrometer using a 1 cm path length quartz cuvette at 480 nm/min. Elemental Analysis data were obtained via Midwest Microlab.

Synthesis of [Cu(dmbpy)<sub>2</sub>]OTf:

Copper(I) tetrakisacetonitrile triflate (1.0284 g, 2.73 mmol) was dissolved in minimal dry acetonitrile. Meanwhile dmbpy (1.0605 g, 5.76 mmol) was dissolved in minimal dry dichloromethane. The dmbpy solution was added dropwise to the copper solution, turning the solution a red color. Reaction was stirred for 30 minutes then precipitated with dry ether and filtered. The solvent was then removed via vacuum and the Cu(I)(dmbpy)<sub>2</sub>OTf product was collected (1.4716 g, 96.1% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.26 (d, 2H), 8.02 (t, 2H), 7.44 (d, 2H), 2.22 (s, 6H).

Synthesis of [Cu(dmbpy)<sub>2</sub>]OTf<sub>2</sub>:

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Copper(II) triflate (1.0325 g, 2.85 mmol) was dissolved in minimal dry acetonitrile. Meanwhile dmbpy (1.1255 g, 6.11 mmol) was dissolved in minimal dry dichloromethane. The dmbpy solution was added dropwise to the copper solution, turning the solution a dark green color. Reaction was stirred for 30 minutes then precipitated with dry ether and filtered. The solvent was then removed via vacuum and the Cu(II)(dmbpy)<sub>2</sub>(OTf)<sub>2</sub>product was collected (1.7771 g, 85.4% yield). Synthesis of N,N'-Dibenzyl-N,N'-bis(6-methylpyridin-2-ylmethyl)ethylenediamine (dbmed):

hydrochloride 2-(Chloromethyl)-6-methylpyridine (0.5300g, 3.0 mmol) and benzyltriethylammonium chloride (0.0121 g, 0.05 mmol) were added to 20 mL dichloromethane and stirred until fully dissolved. N,N'-Dibenzylethylenediamine (0.35 mL, 1.48 mmol) was then added to the solution, after which a cloudy white solution was formed. Meanwhile sodium hydroxide (20.1807 g, 500 mmol) was added to 20 mL of water which was then added to the dichloromethane solution and stirred vigorously. After 2 hours the organic solution became clear and the aqueous solution turned white. The solution was then allowed to reflux overnight. After refluxing additional water was added to the solution to allow the layers to fully separate then the organic layer was then separated from the aqueous layer. The aqueous layer was then extracted with dichloromethane two times, and all the organic layers were combined and dried with magnesium sulfate. Then the solvent was removed under low vacuum. The crude solid was then recrystallized in acetonitrile and dried to obtain the product (0.4270 g, 60.1% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 500 MHz) δ 2.50 (s, 6H), 2.67 (s, 4H), 3.56 (s, 4H), 3.67 (s, 4H), 6.96 (d, 2H), 7.25 (m, 12H), 7.45 (t, 2H).

Synthesis of [Cu(dbmed)]OTf:

Copper(I) tetrakisacetonitrile triflate (0.1123 g, 0.30 mmol) was dissolved in minimal dry acetonitrile. Meanwhile dbmed (0.1487 g, 0.33 mmol) was dissolved in minimal dry dichloromethane. The dbmed solution was added dropwise to the copper solution, turning the solution a bright yellow color. Reaction was stirred overnight then precipitated with dry ether and filtered. The solvent was then removed via vacuum and the Cu(I)dbmed product was collected (0.1876 g, 94.9% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 500 MHz)  $\delta$  2.67 (s, 2H), 2.72 (s, 6H), 2.82 (s, 2H), 3.57 (s, 2H), 3.74 (s, 2H), 3.85 (s, 2H), 4.16 (s, 2H), 7.20 (m, 4H), 7.29 (m, 8H), 7.43 (d, 2H), 7.83 (t, 2H). Synthesis of [Cu(dbmed)]OTf<sub>2</sub>:

Copper(II) triflate (0.808 g, 2.23 mmol) was dissolved in minimal dry acetonitrile. Meanwhile dbmed (0.1030 g, 2.29 mmol) was dissolved in minimal dry dichloromethane. The dbmed solution was added dropwise to the copper solution, turning the solution a deep blue color. Reaction was stirred overnight then precipitated with dry ether and filtered. The solvent was then removed via vacuum, and the Cu(II)dbmed product was collected (0.1596 g, 87.9% yield).

Synthesis of [Cu(TBP)<sub>4</sub>]OTf:

Copper(I) tetrakisacetonitrile triflate (0.2513 g, 0.67 mmol) was dissolved in minimal dry dichloromethane. 4-*tert*-butylpyridine (0.972 mL, 6.63 mmol) was then added to the solution, turning the solution a bright yellow color. Reaction was stirred overnight then precipitated with dry ether, forming pale yellow crystals, and the solid was filtered. The product was then dried via vacuum and was collected (0.4351 g, 86.% yield). <sup>1</sup>H NMR (500 MHz, acetonitrile-d3)  $\delta$  8.47 (s, 2H), 7.44 (s, 2H) 1.33 (s, 9H).

Synthesis of [Cu(TBP)<sub>4</sub>]OTf<sub>2</sub>:

Copper(II) triflate (0.4135 g, 1.14 mmol) was dissolved in minimal dry acetonitrile. TBP (1.14 mL, 8.00 mmol) was then added to the solution, turning the solution a deep purple color. Reaction was stirred for 2 hours then precipitated with dry ether and filtered. The reaction was then recrystallized using acetonitrile and ether. The product was then dried via vacuum and was collected (0.9043 g, 87.5% yield).

Synthesis of [Cu(bpyPY4)]OTf:

Copper(I) tetrakisacetonitrile triflate (0.1647 g, 0.43 mmol) was dissolved in minimal dry acetonitrile. Meanwhile 6,6'-bis(1,1-di(pyridin-2-yl)ethyl)-2,2'-bipyridine (bpyPY4) (0.2545 g, 0.49 mmol) was dissolved in minimal dry dichloromethane. The bpyPY4 solution was added dropwise to the copper solution, turning the solution a dark red color. Reaction was stirred overnight then precipitated with dry ether and filtered. The solvent was then removed via vacuum and the Cu(I)bpyPY4 product was collected (0.2440 g, 76.1% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 500 MHz)  $\delta$  2.25 (s, 6H), 7.20 (s, 4H), 7.76 (s, 4H), 8.10 (d, 2H), 8.18 (t, 2H), 8.37 (d, 2H)

Synthesis of [Cu(bpyPY4)]OTf<sub>2</sub>:

Copper(II) triflate (0.4215 g, 1.16 mmol) was dissolved in minimal dry acetonitrile. Meanwhile BPYPY4 (0.6942 g, 1.33 mmol) was dissolved in minimal dry dichloromethane. The BPYPY4 solution was added dropwise to the copper solution, turning the solution a pale blue color. Reaction was stirred overnight then precipitated with dry ether and filtered. The solvent was then removed via vacuum and the Cu(II)bpyPY4 product was collected (0.6571 g, 63.9% yield).

## 5.3 Results and Discussion

While Dr. Rorabacher already confirmed the Nernstian relationship between copper(II) stability constants and potential, the relationship was only investigated in aqueous solutions, whereas

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most DSSC electrolytes use acetonitrile as the solvent. To discern the relationship between the redox potential and stability constants of copper complexes in acetonitrile, data from previous studies was analyzed, specifically concentrating on the stability constants of these complexes in acetonitrile.<sup>98,99</sup> After all the collated data was plotted, Figure 5.2A, a linear regression, with a fixed slope of -0.059, was applied, resulting in the equation y = -0.059x + 0.9002. This equation was then used to simulate the stability constants of redox shuttled utilized in DSSC by using their previous determined redox potentials, Figure 5.2B.<sup>38,39,41,94,95</sup>





The simulated plots reveal a pattern: copper complexes that undergo ligand substitution display more positive potentials and subsequently exhibit lower stability constants compared to the  $[Cu(TBP)_4]^{2+/+}$  redox shuttle, while those complexes that do not undergo ligand substitution have more negative potentials and thus higher stability constants. This correlation underscores the role of redox potential as a potential tool for predicting the susceptibility of copper complexes to ligand substitution.

The validation of the simulated data was pursued by examining four copper complexes utilized in DSSCs, based on their relevance to the study's goals and their distinctive redox potentials. The selected complexes were  $[Cu(TBP)_4]^{2+/+}$ ,  $[Cu(dmbpy)_2]^{2+/+}$ ,  $[Cu(dbmed)]^{2+/+}$ , and  $[Cu(bpyPY4)]^{2+/+}$ . The  $[Cu(TBP)_4]^{2+/+}$  was chosen as a reference point for comparative evaluation, forming the baseline against which other complexes were assessed. The selection of  $[Cu(dmbpy)_2]^{2+/+}$  was motivated by its positive redox potential, placing it as one of the copper redox shuttles with the highest predicted stability constant among those commonly employed in DSSCs. Conversely,  $[Cu(bpyPY4)]^{2+/+}$  was singled out for its negative redox potential, reflecting its status among copper redox shuttles with the lowest potentials integrated into DSSCs. The selection of  $[Cu(dbmed)]^{2+/+}$  was due to its redox potential closely resembling that of  $[Cu(TBP)_4]^{2+/+}$ , which enabled a targeted exploration of ligand substitution behavior while upholding a uniform potential.

For [Cu(dmbpy)<sub>2</sub>]<sup>2+/+</sup>, [Cu(dbmed)]<sup>2+/+</sup>, and [Cu(bpyPY4)]<sup>2+/+</sup> the stability constants were determined via the application of square wave voltammetry. Due to the high stability of copper(II) complexes in acetonitrile, making them difficult to measure, the stability constants of the copper(I) form were experimentally determined. Copper(I) complexes have been shown to have a significantly lower stability constant in acetonitrile than in water. This has been attributed to the significantly higher binding energy of copper(I) to acetonitrile than that of water, causing about a 10<sup>6</sup> decrease in stability constants in acetonitrile relative to their aqueous values.<sup>99,100</sup> Square wave voltammetry was utilized to determine the stability constant of the copper(I) form of the complexes. When using square wave voltammetry, assuming the sweep rate is held constant, the copper(I) oxidation peak can be directly related to the [Cu<sup>I</sup>L] following the equation

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$$i = nFAC(\pi D\sigma)^{\frac{1}{2}}X(\sigma t)$$
(5.1)

where i is the peak current, n is the number of electrons transferred, F is the Faraday constant, C is the bulk concentration of Cu<sup>I</sup>L, D is the diffusion coefficient,  $\sigma = (nFv/RT)$ , v is the sweep rate, R is the gas constant, T is the absolute temperature, and X( $\sigma$ t) is the normalized current. The concentration at each measurement was determined using the proportionality of the peak current, i, for the measurement compared to the peak current when all copper is bound to ligand, i<sub> $\infty$ </sub>, usually at 120% ligand added, following the equation [CuL] = C<sub>Cu</sub>(i/i<sub> $\infty$ </sub>).

From the combination of definition of equilibrium constant between copper and a ligand

$$K_{CuL} = \frac{[CuL]}{[Cu][L]} \tag{5.2}$$

and the known concentrations of copper, C<sub>Cu</sub>, and ligand, C<sub>L</sub>,

$$C_{Cu} = [Cu] + [CuL]$$
 (5.3)  
 $C_L = [L] + [CuL]$  (5.4)

a new equation can be derived

$$[CuL] = \frac{K_{CuL}C_L(C_{Cu} - [CuL])}{1 + K_{CuL}(C_{Cu} - [CuL])}$$
(5.5)

then substituting equation 5.5 into equation 5.1 yields the equation

$$\frac{C_{Cu}}{i} = \frac{1}{Y} + \frac{1}{YK_{CuL}(C_L - [CuL])}$$
 (5.6)

where  $C_{Cu}$  is the total concentration of copper in solution,  $C_L$  is the total concentration of ligand in solution, i is the peak current,  $K_{CuL}$  is the stability constant of the copper(I) form of the complex, and Y is the product of several electrochemical constants. By plotting  $C_{Cu}$ /i by 1/( $C_L$  – [CuL]) and taking a linear regression of the plot, you obtain a slope of 1/YK<sub>CuL</sub> and an intercept of 1/Y. By dividing the intercept by the slope, one is left with K<sub>CuL</sub>. To get the stability constant of the copper(II) form, the Nerst equation was used

$$E_{Cu^{II}L}{}^{f} = E_{Cu(I/II)solv}{}^{f} - \frac{2.303RT}{F}\log\frac{K_{Cu^{II}L}}{K_{Cu^{I}L}}$$
(5.7)

where  $E_{Cu(I/II)solv}^{f}$  is the formal potential of the solvated copper(I/II),  $[Cu(ACN)_{4}]^{2+/+}$ , redox couple, which was found to be 0.601 V vs ferrocene<sup>99</sup>.

The log of stability constants of the copper(II) for of the complexes were found to be 9.05, 15.02, and 21.53 respectively for the  $[Cu(dmbpy)_2]^{2+/+}$ ,  $[Cu(dbmed)]^{2+/+}$ , and  $[Cu(bpyPY4)]^{2+/+}$  complexes. These results match well with the log of the predicted stability constants found previously, 9.49, 15.34, and 22.55 respectively. However, when the  $[Cu(TBP)_4]^{2+/+}$  complex was attempted to be measured via square wave voltammetry it was found that the electron kinetics of the complex were too slow at the sweep rate used for a redox wave to show, so a different technique was used to determine the copper(II) stability constant.



Figure 5.13: The square wave voltammetry plots for 2.0 mM of A) [Cu(dmbpy)<sub>2</sub>]OTf<sub>2</sub>, blue, B) [Cu(dbmed)]OTf<sub>2</sub>, orange, C) [Cu(bpyPY4)]OTf<sub>2</sub>, green, and [Cu(ACN)<sub>4</sub>]OTf<sub>2</sub>, in anhydrous acetonitrile containing 0.1 M LiOTf. D) The UV-Vis spectra of 2.0 mM [Cu(dbmed)]OTf<sub>2</sub> titrated increasing equivalents of TBP. For all spectra as the concentration of ligand increases the darker the spectra.

For  $[Cu(TBP)_4]^{2+/+}$  the redox couple was electrochemically irreversible at the sweep rates used for the square wave measurement, so instead UV-Vis was used to determine the relative stability constant between  $[Cu(TBP)_4]^{2+/+}$  and  $[Cu(dbmed)]^{2+/+}$ . Since the difference of the predicted stability constants for the  $[Cu(dbmed)]OTf_2$  and the  $[Cu(TBP)_4]OTf_2$  complexes is small, only 10.6, UV-Vis spectroscopy can be used to determine the equillibrium constant for the reaction

$$[Cu(dbmed)](OTf)_2 + 4 TBP \qquad [Cu(TBP)_4](OTf)_2 + dbmed$$
(Scheme 5.1)

The wavelength of 1100 nm was used due to the minimal contribution from the [Cu(TBP)<sub>4</sub>] complex, free TBP, and free dbmed to the absorbance at this wavelength. Due to this we can use the Beer-Lambert law

$$A = \varepsilon_{CuL} b[CuL] \tag{5.8}$$

where  $\varepsilon_{CuL}$  is the extinction coefficient of the [Cu(dbmed)]OTf<sub>2</sub> complex, b is the path length in cm, and [CuL] is the concentration of the [Cu(dbmed)]OTf<sub>2</sub> complex in solution. By using the definition of an equilibrium constant

$$K_{CuL} = \frac{[Cu(TBP)_4][dbmed]}{[Cu(dbmed)][TBP]^4}$$
(5.9)

and the definitions of the analytical concentrations of copper(II),  $C_{Cu}$ , and dbmed,  $C_{dbmed}$ , and TBP,  $C_{TBP}$ , in solution

$$C_{Cu} = [Cu(TBP)_{4}] + [Cu(dbmed)] (5.10)$$

$$C_{dbmed} = [dbmed] + [Cu(dbmed)] (5.11)$$

$$C_{TBP} = [TBP]^{4} + [Cu(TBP)_{4}] (5.12)$$

under the assumption that all the copper(II) is complexed with a ligand, the equilibrium coefficient calculation can be rearranged to be

$$K_{eq} = \frac{(C_{Cu} - [Cu(dbmed)])(C_{dbmed} - [Cu(dbmed)])}{[Cu(dbmed)](C_{TBP} - C_{Cu} - [Cu(dbmed)])}$$
(5.13)

Using this relationship the equilibrium constant for the relationship between [Cu(dbmed)]OTf<sub>2</sub> and [Cu(TBP)<sub>4</sub>]OTf<sub>2</sub> was determined to be 1.02 ( $\pm$  0.27) which, when referenced against the stability constant for [Cu(dbmed)]OTf<sub>2</sub>, gave a stability constant of 16.74 for [Cu(TBP)<sub>4</sub>]OTf<sub>2</sub>, which is close to the predicted stability constant of 16.21.

	Experimental Cu(II) stability constant	Simulated Cu(II) stability constant	Percent Error (%)
Cu(dmpby)2	9.05	9.49	4.92
Cu(dbmed)	15.02	15.34	2.01
Cu(bpyPY4)	21.53	22.55	4.73
Cu(TBP)4	16.68	16.21	2.80

Table 5.8: Simulated and experimental copper(II) stability constants and the percent error in between the measurements.

The stability constants determined for all the copper complexes are listed in Table 5.1 along with the predicted stability constant and the percent error for each copper complex. The comparison between these experimental results and the simulated data revealed that all the complexes displaying deviations of less than 5% from the simulated outcomes. This agreement to the predictive model denotes the potential of the redox potential-stability constant relationship to be used as a predictive tool for anticipating ligand substitution behavior.



Figure 5.4: A plot of copper redox potentials versus the log of the simulated, orange, and experimental, blue, stability constant of the copper(II) form of the redox complex found in acetonitrile. The linear fit equation for the experimental results was found to be y = -0.060x + 0.900.

Additionally, to deepen insights, the potential of each redox shuttle was plotted against the measured stability constant, enabling a subsequent linear regression analysis. This analysis yielded a slope of -0.060, closely mirroring the anticipated fundamental value of -0.059. Although it is important to note that this relationship should only hold true as long as the stability constants of the copper(I) form of the redox couple have similar values. This adherence to theoretical expectations further underscores the legitimacy of the correlation, offering a compelling avenue for leveraging redox potential to predict ligand substitution behavior in copper complexes.

### **5.4 Conclusions**

This study capitalizes on Dr. Rorabacher's work, revealing a compelling connection between redox potential and stability constants in copper complexes. This correlation enables a predictive model of potential-stability constant relationships. Assuming the stability constants of the copper(I) form are consistent, this model facilitates the accurate prediction of copper complexes. Specifically, it helps distinguish between those that undergo ligand substitution and those that do not. Validation with four relevant copper complexes shows the predictive model's accuracy. Given the knowledge that ligand substitution can be beneficial for DSSCs, enhancing efficiencies could be achieved by enabling ligand substitution with a base that induces a smaller negative shift in the solution potential.<sup>38</sup> This predictive method could allow for the selection of targeted redox shuttle/base combinations, aiming to maximize the efficiency of DSSC devices. This work paves the way for informed design and optimization of copper-based redox shuttles in dye-sensitized solar cells, offering new dimensions for enhancing their performance.

## WORKS CITED

- (1) Friedlingstein, P.; O'Sullivan, M.; Jones, M. W.; Andrew, R. M.; Gregor, L.; Hauck, J.; Le Quéré, C.; Luijkx, I. T.; Olsen, A.; Peters, G. P.; Peters, W.; Pongratz, J.; Schwingshackl, C.; Sitch, S.; Canadell, J. G.; Ciais, P.; Jackson, R. B.; Alin, S. R.; Alkama, R.; Arneth, A.; Arora, V. K.; Bates, N. R.; Becker, M.; Bellouin, N.; Bittig, H. C.; Bopp, L.; Chevallier, F.; Chini, L. P.; Cronin, M.; Evans, W.; Falk, S.; Feely, R. A.; Gasser, T.; Gehlen, M.; Gkritzalis, T.; Gloege, L.; Grassi, G.; Gruber, N.; Gürses, Ö.; Harris, I.; Hefner, M.; Houghton, R. A.; Hurtt, G. C.; Iida, Y.; Ilyina, T.; Jain, A. K.; Jersild, A.; Kadono, K.; Kato, E.; Kennedy, D.; Klein Goldewijk, K.; Knauer, J.; Korsbakken, J. I.; Landschützer, P.; Lefèvre, N.; Lindsay, K.; Liu, J.; Liu, Z.; Marland, G.; Mayot, N.; McGrath, M. J.; Metzl, N.; Monacci, N. M.; Munro, D. R.; Nakaoka, S.-I.; Niwa, Y.; O'Brien, K.; Ono, T.; Palmer, P. I.; Pan, N.; Pierrot, D.; Pocock, K.; Poulter, B.; Resplandy, L.; Robertson, E.; Rödenbeck, C.; Rodriguez, C.; Rosan, T. M.; Schwinger, J.; Séférian, R.; Shutler, J. D.; Skjelvan, I.; Steinhoff, T.; Sun, Q.; Sutton, A. J.; Sweeney, C.; Takao, S.; Tanhua, T.; Tans, P. P.; Tian, X.; Tian, H.; Tilbrook, B.; Tsujino, H.; Tubiello, F.; van der Werf, G. R.; Walker, A. P.; Wanninkhof, R.; Whitehead, C.; Willstrand Wranne, A.; Wright, R.; Yuan, W.; Yue, C.; Yue, X.; Zaehle, S.; Zeng, J.; Zheng, B. Global Carbon Budget 2022. Earth Syst Sci Data 2022, 14 (11), 4811–4900. https://doi.org/10.5194/essd-14-4811-2022.
- (2) International Energy Agency. CO2 Emissions in 2022; 2023. www.iea.org.
- (3) Hausfather, Z.; Peters, G. P. Emissions the 'Business as Usual' Story Is Misleading. *Nature* **2020**, *577* (7792), 618–620. https://doi.org/10.1038/d41586-020-00177-3.
- (4) Center for Sustainable Systems, U. of M. Photovoltaic Energy Factsheet; 2023.
- (5) International Energy Agency. *Solar PV*; 2023.
- Gueymard, C. A.; Myers, D.; Emery, K. Proposed Reference Irradiance Spectra for Solar Energy Systems Testing. *Solar Energy* 2002, *73* (6), 443–467. https://doi.org/10.1016/S0038-092X(03)00005-7.
- (7) U.S. DOE. The SunShot Initiative.
- Jung, H. S.; Lee, J.-K. Dye Sensitized Solar Cells for Economically Viable Photovoltaic
   Systems. J Phys Chem Lett 2013, 4 (10), 1682–1693. https://doi.org/10.1021/jz400112n.
- (9) Becquerel, E. Mémoire Sur Les Effets Électriques Produits Sous l'influence Des Rayons Solaires. *Comptes Rendus* **1839**, *9*, 561–567.
- (10) Moser, J. Notiz ber Verst rkung Photoelektrischer Strome Durch Optische Sensibilisirung. *Monatshefte f or Chemie* **1887**, 8 (1), 373–373. https://doi.org/10.1007/BF01510059.

- (11) Gerischer, H.; Tributsch, H. Elektrochemische Untersuchungen Zur Spektralen Sensibilisierung von ZnO-Einkristallen. *Berichte der Bunsengesellschaft für physikalische Chemie* **1968**, *72* (3), 437–445. https://doi.org/10.1002/bbpc.196800013.
- ANDERSON, S.; CONSTABLE, E. C.; DARE-EDWARDS, M. P.; GOODENOUGH, J. B.;
   HAMNETT, A.; SEDDON, K. R.; WRIGHT, R. D. Chemical Modification of a Titanium (IV)
   Oxide Electrode to Give Stable Dye Sensitisation without a Supersensitiser. *Nature* 1979, 280 (5723), 571–573. https://doi.org/10.1038/280571a0.
- (13) Matsumura, M.; Matsudaira, S.; Tsubomura, H.; Takata, M.; Yanagida, H. Dye Sensitization and Surface Structures of Semiconductor Electrodes. *Industrial & Engineering Chemistry Product Research and Development* **1980**, *19* (3), 415–421. https://doi.org/10.1021/i360075a025.
- (14) Vlachopoulos, Nick.; Liska, Paul.; Augustynski, Jan.; Graetzel, Michael. Very Efficient Visible Light Energy Harvesting and Conversion by Spectral Sensitization of High Surface Area Polycrystalline Titanium Dioxide Films. J Am Chem Soc 1988, 110 (4), 1216–1220. https://doi.org/10.1021/ja00212a033.
- (15) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Graetzel, M. Conversion of Light to Electricity by Cis-X2bis(2,2'-Bipyridyl-4,4'-Dicarboxylate)Ruthenium(II) Charge-Transfer Sensitizers (X = Cl-, Br-, I-, CN-, and SCN-) on Nanocrystalline Titanium Dioxide Electrodes. *J Am Chem Soc* 1993, 115 (14), 6382–6390. https://doi.org/10.1021/ja00067a063.
- (16) Feldt, S. M.; Gibson, E. A.; Gabrielsson, E.; Sun, L.; Boschloo, G.; Hagfeldt, A. Design of Organic Dyes and Cobalt Polypyridine Redox Mediators for High-Efficiency Dye-Sensitized Solar Cells. J Am Chem Soc 2010, 132 (46), 16714–16724. https://doi.org/10.1021/ja1088869.
- (17) Daeneke, T.; Kwon, T.-H.; Holmes, A. B.; Duffy, N. W.; Bach, U.; Spiccia, L. High-Efficiency Dye-Sensitized Solar Cells with Ferrocene-Based Electrolytes. *Nat Chem* 2011, 3 (3), 211– 215. https://doi.org/10.1038/nchem.966.
- (18) Bai, Y.; Yu, Q.; Cai, N.; Wang, Y.; Zhang, M.; Wang, P. High-Efficiency Organic Dye-Sensitized Mesoscopic Solar Cells with a Copper Redox Shuttle. *Chemical Communications* **2011**, 47 (15), 4376. https://doi.org/10.1039/c1cc10454c.
- (19) Cao, Y.; Liu, Y.; Zakeeruddin, S. M.; Hagfeldt, A.; Grätzel, M. Direct Contact of Selective Charge Extraction Layers Enables High-Efficiency Molecular Photovoltaics. *Joule* 2018, 2 (6), 1108–1117. https://doi.org/10.1016/j.joule.2018.03.017.
- (20) Ren, Y.; Zhang, D.; Suo, J.; Cao, Y.; Eickemeyer, F. T.; Vlachopoulos, N.; Zakeeruddin, S. M.; Hagfeldt, A.; Grätzel, M. Hydroxamic Acid Pre-Adsorption Raises the Efficiency of

Cosensitized Solar Cells. *Nature* **2023**, *613* (7942), 60–65. https://doi.org/10.1038/s41586-022-05460-z.

- (21) Ondersma, J. W.; Hamann, T. W. Conduction Band Energy Determination by Variable Temperature Spectroelectrochemistry. *Energy Environ Sci* **2012**, *5* (11), 9476. https://doi.org/10.1039/c2ee22926a.
- (22) Boschloo, G.; Hagfeldt, A. Characteristics of the Iodide/Triiodide Redox Mediator in Dye-Sensitized Solar Cells. *Acc Chem Res* **2009**, *42* (11), 1819–1826. https://doi.org/10.1021/ar900138m.
- (23) Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; Curchod, B. F. E.; Ashari-Astani, N.; Tavernelli, I.; Rothlisberger, U.; Nazeeruddin, Md. K.; Grätzel, M. Dye-Sensitized Solar Cells with 13% Efficiency Achieved through the Molecular Engineering of Porphyrin Sensitizers. *Nat Chem* 2014, 6 (3), 242–247. https://doi.org/10.1038/nchem.1861.
- (24) Shi, J.; Zhang, Y.; Luo, B.; Chen, L. Synthesis and Structural Characterization of the Copper(II) Complex with N, N'-Bis-(1-Benzimidazolylethyl)Ethylenediamine. *Inorganica Chim Acta* **1989**, *162* (1), 29–31. https://doi.org/10.1016/S0020-1693(00)83115-1.
- (25) Randall, D. W.; Gamelin, D. R.; LaCroix, L. B.; Solomon, E. I. Electronic Structure Contributions to Electron Transfer in Blue Cu and CuA. *JBIC Journal of Biological Inorganic Chemistry* 2000, 5 (1), 16–29. https://doi.org/10.1007/s007750050003.
- (26) Hattori, S.; Wada, Y.; Yanagida, S.; Fukuzumi, S. Blue Copper Model Complexes with Distorted Tetragonal Geometry Acting as Effective Electron-Transfer Mediators in Dye-Sensitized Solar Cells. J Am Chem Soc 2005, 127 (26), 9648–9654. https://doi.org/10.1021/ja0506814.
- (27) Bai, Y.; Yu, Q.; Cai, N.; Wang, Y.; Zhang, M.; Wang, P. High-Efficiency Organic Dye-Sensitized Mesoscopic Solar Cells with a Copper Redox Shuttle. *Chemical Communications* **2011**, *47* (15), 4376. https://doi.org/10.1039/c1cc10454c.
- (28) Colombo, A.; Dragonetti, C.; Magni, M.; Roberto, D.; Demartin, F.; Caramori, S.; Bignozzi, C. A. Efficient Copper Mediators Based on Bulky Asymmetric Phenanthrolines for DSSCs. ACS Appl Mater Interfaces 2014, 6 (16), 13945–13955. https://doi.org/10.1021/am503306f.
- (29) Cong, J.; Kinschel, D.; Daniel, Q.; Safdari, M.; Gabrielsson, E.; Chen, H.; Svensson, P. H.; Sun, L.; Kloo, L. Bis(1,1-Bis(2-Pyridyl)Ethane)Copper( <scp>i</Scp> / <scp>ii</Scp> ) as an Efficient Redox Couple for Liquid Dye-Sensitized Solar Cells. J Mater Chem A Mater 2016, 4 (38), 14550–14554. https://doi.org/10.1039/C6TA06782D.

- (30) Freitag, M.; Giordano, F.; Yang, W.; Pazoki, M.; Hao, Y.; Zietz, B.; Grätzel, M.; Hagfeldt, A.; Boschloo, G. Copper Phenanthroline as a Fast and High-Performance Redox Mediator for Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry C* 2016, 120 (18), 9595–9603. https://doi.org/10.1021/acs.jpcc.6b01658.
- (31) Saygili, Y.; Söderberg, M.; Pellet, N.; Giordano, F.; Cao, Y.; Muñoz-García, A. B.; Zakeeruddin, S. M.; Vlachopoulos, N.; Pavone, M.; Boschloo, G.; Kavan, L.; Moser, J.-E.; Grätzel, M.; Hagfeldt, A.; Freitag, M. Copper Bipyridyl Redox Mediators for Dye-Sensitized Solar Cells with High Photovoltage. J Am Chem Soc 2016, 138 (45), 15087–15096. https://doi.org/10.1021/jacs.6b10721.
- Hu, M.; Shen, J.; Yu, Z.; Liao, R.-Z.; Gurzadyan, G. G.; Yang, X.; Hagfeldt, A.; Wang, M.; Sun, L. Efficient and Stable Dye-Sensitized Solar Cells Based on a Tetradentate Copper(II/I) Redox Mediator. ACS Appl Mater Interfaces 2018, 10 (36), 30409–30416. https://doi.org/10.1021/acsami.8b10182.
- (33) Long, H.; Zhou, D.; Zhang, M.; Peng, C.; Uchida, S.; Wang, P. Probing Dye-Correlated Interplay of Energetics and Kinetics in Mesoscopic Titania Solar Cells with 4- *Tert* -Butylpyridine. *The Journal of Physical Chemistry C* 2011, *115* (29), 14408–14414. https://doi.org/10.1021/jp202826m.
- (34) XIONG, B.; ZHOU, B.; ZHU, Z.; GAO, T.; LI, L.; CAI, J.; CAI, W. Adsorption of 4 -tert-Butylpyridine on TiO 2 Surface in Dye-Sensitized Solar Cells. Chin J Chem 2008, 26 (1), 70– 76. https://doi.org/10.1002/cjoc.200890040.
- (35) Kashif, M. K.; Axelson, J. C.; Duffy, N. W.; Forsyth, C. M.; Chang, C. J.; Long, J. R.; Spiccia, L.; Bach, U. A New Direction in Dye-Sensitized Solar Cells Redox Mediator Development: In Situ Fine-Tuning of the Cobalt(II)/(III) Redox Potential through Lewis Base Interactions. J Am Chem Soc 2012, 134 (40), 16646–16653. https://doi.org/10.1021/ja305897k.
- (36) Nakade, S.; Kanzaki, T.; Kubo, W.; Kitamura, T.; Wada, Y.; Yanagida, S. Role of Electrolytes on Charge Recombination in Dye-Sensitized TiO 2 Solar Cell (1): The Case of Solar Cells Using the I<sup>-</sup>/I<sub>3</sub> Redox Couple. *J Phys Chem B* **2005**, *109* (8), 3480–3487. https://doi.org/10.1021/jp0460036.
- (37) Kusama, H.; Konishi, Y.; Sugihara, H.; Arakawa, H. Influence of Alkylpyridine Additives in Electrolyte Solution on the Performance of Dye-Sensitized Solar Cell. *Solar Energy Materials and Solar Cells* **2003**, *80* (2), 167–179. https://doi.org/10.1016/j.solmat.2003.08.001.
- (38) Wang, Y.; Hamann, T. W. Improved Performance Induced by *in Situ* Ligand Exchange Reactions of Copper Bipyridyl Redox Couples in Dye-Sensitized Solar Cells. *Chemical Communications* **2018**, *54* (87), 12361–12364. https://doi.org/10.1039/C8CC07191H.

- (39) Fürer, S. O.; Milhuisen, R. A.; Kashif, M. K.; Raga, S. R.; Acharya, S. S.; Forsyth, C.; Liu, M.; Frazer, L.; Duffy, N. W.; Ohlin, C. A.; Funston, A. M.; Tachibana, Y.; Bach, U. The Performance-Determining Role of Lewis Bases in Dye-Sensitized Solar Cells Employing Copper-Bisphenanthroline Redox Mediators. *Adv Energy Mater* **2020**, *10* (37). https://doi.org/10.1002/aenm.202002067.
- Hu, M.; Shen, J.; Yu, Z.; Liao, R.-Z.; Gurzadyan, G. G.; Yang, X.; Hagfeldt, A.; Wang, M.; Sun, L. Efficient and Stable Dye-Sensitized Solar Cells Based on a Tetradentate Copper(II/I) Redox Mediator. ACS Appl Mater Interfaces 2018, 10 (36), 30409–30416. https://doi.org/10.1021/acsami.8b10182.
- (41) Rui, H.; Shen, J.; Yu, Z.; Li, L.; Han, H.; Sun, L. Stable Dye-Sensitized Solar Cells Based on Copper(II/I) Redox Mediators Bearing a Pentadentate Ligand. Angewandte Chemie International Edition 2021, 60 (29), 16156–16163. https://doi.org/10.1002/anie.202104563.
- (42) Michaels, H.; Benesperi, I.; Edvinsson, T.; Muñoz-Garcia, A.; Pavone, M.; Boschloo, G.; Freitag, M. Copper Complexes with Tetradentate Ligands for Enhanced Charge Transport in Dye-Sensitized Solar Cells. *Inorganics (Basel)* **2018**, *6* (2), 53. https://doi.org/10.3390/inorganics6020053.
- (43) Jeffrey D. Sachs. The Road to Clean Energy Starts Here. *Sci Am* **2007**.
- (44) Bierbaum, R. M.; Matson, P. A. Energy in the Context of Sustainability. *Daedalus* **2013**, 142 (1), 146–161. https://doi.org/10.1162/DAED\_a\_00191.
- El Chaar, L.; lamont, L. A.; El Zein, N. Review of Photovoltaic Technologies. *Renewable and Sustainable Energy Reviews* 2011, 15 (5), 2165–2175. https://doi.org/10.1016/j.rser.2011.01.004.
- Parida, B.; Iniyan, S.; Goic, R. A Review of Solar Photovoltaic Technologies. *Renewable and Sustainable Energy Reviews* 2011, 15 (3), 1625–1636. https://doi.org/10.1016/j.rser.2010.11.032.
- (47) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. *Chem Rev* **2010**, *110* (11), 6595–6663. https://doi.org/10.1021/cr900356p.
- Liu, Q.; Jiang, Y.; Jin, K.; Qin, J.; Xu, J.; Li, W.; Xiong, J.; Liu, J.; Xiao, Z.; Sun, K.; Yang, S.;
   Zhang, X.; Ding, L. 18% Efficiency Organic Solar Cells. *Sci Bull (Beijing)* 2020, *65* (4), 272–275. https://doi.org/10.1016/j.scib.2020.01.001.
- (49) Lu, M. N.; Su, T.; Pylnev, M.; Long, Y.; Wu, T.; Tsai, M.; Wei, T. Stepwise Optimizing Photovoltaic Performance of Dye-sensitized Cells Made under 50-lux Dim Light. *Progress*
*in Photovoltaics: Research and Applications* **2021**, *29* (5), 533–545. https://doi.org/10.1002/pip.3406.

- (50) Cao, Y.; Liu, Y.; Zakeeruddin, S. M.; Hagfeldt, A.; Grätzel, M. Direct Contact of Selective Charge Extraction Layers Enables High-Efficiency Molecular Photovoltaics. *Joule* 2018, 2 (6), 1108–1117. https://doi.org/10.1016/j.joule.2018.03.017.
- (51) Freitag, M.; Teuscher, J.; Saygili, Y.; Zhang, X.; Giordano, F.; Liska, P.; Hua, J.; Zakeeruddin, S. M.; Moser, J.-E.; Grätzel, M.; Hagfeldt, A. Dye-Sensitized Solar Cells for Efficient Power Generation under Ambient Lighting. *Nat Photonics* **2017**, *11* (6), 372–378. https://doi.org/10.1038/nphoton.2017.60.
- (52) Kakiage, K.; Aoyama, Y.; Yano, T.; Oya, K.; Fujisawa, J.; Hanaya, M. Highly-Efficient Dye-Sensitized Solar Cells with Collaborative Sensitization by Silyl-Anchor and Carboxy-Anchor Dyes. *Chemical Communications* **2015**, *51* (88), 15894–15897. https://doi.org/10.1039/C5CC06759F.
- (53) Grätzel, M. Dye-Sensitized Solar Cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2003**, *4* (2), 145–153. https://doi.org/10.1016/S1389-5567(03)00026-1.
- (54) Sapp, S. A.; Elliott, C. M.; Contado, C.; Caramori, S.; Bignozzi, C. A. Substituted Polypyridine Complexes of Cobalt(II/III) as Efficient Electron-Transfer Mediators in Dye-Sensitized Solar Cells. *J Am Chem Soc* 2002, *124* (37), 11215–11222. https://doi.org/10.1021/ja027355y.
- (55) Nusbaumer, H.; Zakeeruddin, S. M.; Moser, J.; Grätzel, M. An Alternative Efficient Redox Couple for the Dye-Sensitized Solar Cell System. *Chemistry – A European Journal* 2003, 9 (16), 3756–3763. https://doi.org/10.1002/chem.200204577.
- (56) Yum, J.-H.; Baranoff, E.; Kessler, F.; Moehl, T.; Ahmad, S.; Bessho, T.; Marchioro, A.; Ghadiri, E.; Moser, J.-E.; Yi, C.; Nazeeruddin, Md. K.; Grätzel, M. A Cobalt Complex Redox Shuttle for Dye-Sensitized Solar Cells with High Open-Circuit Potentials. *Nat Commun* 2012, 3 (1), 631. https://doi.org/10.1038/ncomms1655.
- (57) Boschloo, G.; Hagfeldt, A. Characteristics of the Iodide/Triiodide Redox Mediator in Dye-Sensitized Solar Cells. Acc Chem Res 2009, 42 (11), 1819–1826. https://doi.org/10.1021/ar900138m.
- (58) Saygili, Y.; Söderberg, M.; Pellet, N.; Giordano, F.; Cao, Y.; Muñoz-García, A. B.;
  Zakeeruddin, S. M.; Vlachopoulos, N.; Pavone, M.; Boschloo, G.; Kavan, L.; Moser, J.-E.;
  Grätzel, M.; Hagfeldt, A.; Freitag, M. Copper Bipyridyl Redox Mediators for Dye-Sensitized
  Solar Cells with High Photovoltage. J Am Chem Soc 2016, 138 (45), 15087–15096.
  https://doi.org/10.1021/jacs.6b10721.

- (59) Feldt, S. M.; Wang, G.; Boschloo, G.; Hagfeldt, A. Effects of Driving Forces for Recombination and Regeneration on the Photovoltaic Performance of Dye-Sensitized Solar Cells Using Cobalt Polypyridine Redox Couples. *The Journal of Physical Chemistry C* 2011, *115* (43), 21500–21507. https://doi.org/10.1021/jp2061392.
- (60) Mosconi, E.; Yum, J.-H.; Kessler, F.; Gómez García, C. J.; Zuccaccia, C.; Cinti, A.; Nazeeruddin, M. K.; Grätzel, M.; De Angelis, F. Cobalt Electrolyte/Dye Interactions in Dye-Sensitized Solar Cells: A Combined Computational and Experimental Study. J Am Chem Soc 2012, 134 (47), 19438–19453. https://doi.org/10.1021/ja3079016.
- (61) Rorabacher, D. B. Electron Transfer by Copper Centers. *Chem Rev* **2004**, *104* (2), 651–698. https://doi.org/10.1021/cr020630e.
- (62) Kaim, W.; Rall, J. Copper—A"Modern" Bioelement. *Angewandte Chemie International Edition in English* **1996**, *35* (1), 43–60. https://doi.org/10.1002/anie.199600431.
- Birker, P. J. M. W. L.; Helder, J.; Henkel, G.; Krebs, B.; Reedijk, J. Synthesis and Spectroscopic Characterization of Copper(I) and Copper(II) Complexes with 1,6-Bis(2-BenzimidazolyI)-2,5-Dithiahexane (BBDH). X-Ray Structure of Trigonal-Bipyramidal Coordinated [Cu(BBDH)CI]CI.2C2H5OH. *Inorg Chem* 1982, 21 (1), 357–363. https://doi.org/10.1021/ic00131a064.
- (64) Freitag, M.; Daniel, Q.; Pazoki, M.; Sveinbjörnsson, K.; Zhang, J.; Sun, L.; Hagfeldt, A.; Boschloo, G. High-Efficiency Dye-Sensitized Solar Cells with Molecular Copper Phenanthroline as Solid Hole Conductor. *Energy Environ Sci* 2015, 8 (9), 2634–2637. https://doi.org/10.1039/C5EE01204J.
- (65) Rodrigues, R. R.; Lee, J. M.; Taylor, N. S.; Cheema, H.; Chen, L.; Fortenberry, R. C.; Delcamp, J. H.; Jurss, J. W. Copper-Based Redox Shuttles Supported by Preorganized Tetradentate Ligands for Dye-Sensitized Solar Cells. *Dalton Transactions* **2020**, *49* (2), 343–355. https://doi.org/10.1039/C9DT04030G.
- (66) Boschloo, G.; Häggman, L.; Hagfeldt, A. Quantification of the Effect of 4- Tert -Butylpyridine Addition to I<sup>-</sup>/I<sub>3</sub> Redox Electrolytes in Dye-Sensitized Nanostructured TiO <sup>2</sup> Solar Cells. J Phys Chem B 2006, 110 (26), 13144–13150. https://doi.org/10.1021/jp0619641.
- (67) Koops, S. E.; O'Regan, B. C.; Barnes, P. R. F.; Durrant, J. R. Parameters Influencing the Efficiency of Electron Injection in Dye-Sensitized Solar Cells. *J Am Chem Soc* 2009, 131 (13), 4808–4818. https://doi.org/10.1021/ja8091278.
- (68) Long, H.; Zhou, D.; Zhang, M.; Peng, C.; Uchida, S.; Wang, P. Probing Dye-Correlated Interplay of Energetics and Kinetics in Mesoscopic Titania Solar Cells with 4- *Tert* -

Butylpyridine. *The Journal of Physical Chemistry C* **2011**, *115* (29), 14408–14414. https://doi.org/10.1021/jp202826m.

- (69) Giordano, M.; Volpi, G.; Bonomo, M.; Mariani, P.; Garino, C.; Viscardi, G. Methoxy-Substituted Copper Complexes as Possible Redox Mediators in Dye-Sensitized Solar Cells. *New Journal of Chemistry* 2021, 45 (34), 15303–15311. https://doi.org/10.1039/D1NJ02577E.
- (70) Deng, Z.; Yang, X.; Yang, K.; Zhang, L.; Wang, H.; Wang, X.; Sun, L. Helical Copper Redox Mediator with Low Electron Recombination for Dye-Sensitized Solar Cells. ACS Sustain Chem Eng 2021, 9 (15), 5252–5259. https://doi.org/10.1021/acssuschemeng.0c08195.
- Kavan, L.; Saygili, Y.; Freitag, M.; Zakeeruddin, S. M.; Hagfeldt, A.; Grätzel, M.
   Electrochemical Properties of Cu(II/I)-Based Redox Mediators for Dye-Sensitized Solar
   Cells. *Electrochim Acta* 2017, 227, 194–202.
   https://doi.org/10.1016/j.electacta.2016.12.185.
- (72) Kannankutty, K.; Chen, C.-C.; Nguyen, V. S.; Lin, Y.-C.; Chou, H.-H.; Yeh, C.-Y.; Wei, T.-C. Tert -Butylpyridine Coordination with [Cu(Dmp) 2]<sup>2+/+</sup> Redox Couple and Its Connection to the Stability of the Dye-Sensitized Solar Cell. ACS Appl Mater Interfaces 2020, 12 (5), 5812– 5819. https://doi.org/10.1021/acsami.9b19119.
- (73) Addison, A. W.; Burke, P. J.; Henrick, K.; Rao, T. N.; Sinn, E. Pentacoordinate Copper Complexes of Nitrogen-Sulfur Donors: Structural Chemistry of Two Complexes of Bis(2-(2-Benzimidazolyl)Ethyl) Sulfide with the Sulfur Alternatively in Equatorial and Axial Coordination Modes. *Inorg Chem* **1983**, *22* (24), 3645–3653. https://doi.org/10.1021/ic00166a030.
- (74) Yang, L.; Powell, D. R.; Houser, R. P. Structural Variation in Copper( <scp>i</Scp>) Complexes with Pyridylmethylamide Ligands: Structural Analysis with a New Four-Coordinate Geometry Index, τ<sub>4</sub>. *Dalton Trans.* **2007**, No. 9, 955–964. https://doi.org/10.1039/B617136B.
- (75) Niu, J.; Zhou, H.; Li, Z.; Xu, J.; Hu, S. An Efficient Ullmann-Type C–O Bond Formation Catalyzed by an Air-Stable Copper(I)–Bipyridyl Complex. J Org Chem 2008, 73 (19), 7814– 7817. https://doi.org/10.1021/jo801002c.
- (76) Linfoot, C. L.; Richardson, P.; Hewat, T. E.; Moudam, O.; Forde, M. M.; Collins, A.; White, F.; Robertson, N. Substituted [Cu(i)(POP)(Bipyridyl)] and Related Complexes: Synthesis, Structure, Properties and Applications to Dye-Sensitised Solar Cells. *Dalton Transactions* 2010, *39* (38), 8945. https://doi.org/10.1039/c0dt00190b.
- (77) Zimmer, K. D.; Shoemaker, R.; Ruminski, R. R. Synthesis and Characterization of a Fluxional Re(I) Carbonyl Complex Fac-[Re(CO)3(Dpop')Cl] with the Nominally Tri-Dentate

Ligand Dipyrido(2,3-a:3',2'-j)Phenazine (Dpop'). *Inorganica Chim Acta* **2006**, *359* (5), 1478–1484. https://doi.org/10.1016/j.ica.2005.11.042.

- (78) Zhang, J.; Siu, K.; Lin, C. H.; Canary, J. W. Conformational Dynamics of Cu(i) Complexes of Tripodal Ligands: Steric Control of Molecular Motion. *New Journal of Chemistry* 2005, 29 (9), 1147. https://doi.org/10.1039/b509050d.
- (79) Colombo, A.; Dragonetti, C.; Magni, M.; Roberto, D.; Demartin, F.; Caramori, S.; Bignozzi, C. A. Efficient Copper Mediators Based on Bulky Asymmetric Phenanthrolines for DSSCs. *ACS Appl Mater Interfaces* 2014, 6 (16), 13945–13955. https://doi.org/10.1021/am503306f.
- (80) Hattori, S.; Wada, Y.; Yanagida, S.; Fukuzumi, S. Blue Copper Model Complexes with Distorted Tetragonal Geometry Acting as Effective Electron-Transfer Mediators in Dye-Sensitized Solar Cells. J Am Chem Soc 2005, 127 (26), 9648–9654. https://doi.org/10.1021/ja0506814.
- (81) Saygili, Y.; Söderberg, M.; Pellet, N.; Giordano, F.; Cao, Y.; Muñoz-García, A. B.;
  Zakeeruddin, S. M.; Vlachopoulos, N.; Pavone, M.; Boschloo, G.; Kavan, L.; Moser, J.-E.;
  Grätzel, M.; Hagfeldt, A.; Freitag, M. Copper Bipyridyl Redox Mediators for Dye-Sensitized
  Solar Cells with High Photovoltage. *J Am Chem Soc* 2016, *138* (45), 15087–15096.
  https://doi.org/10.1021/jacs.6b10721.
- (82) Le Fur, M.; Beyler, M.; Le Poul, N.; Lima, L. M. P.; Le Mest, Y.; Delgado, R.; Platas-Iglesias, C.; Patinec, V.; Tripier, R. Improving the Stability and Inertness of Cu( <scp>ii</Scp> ) and Cu( <scp>i</Scp> ) Complexes with Methylthiazolyl Ligands by Tuning the Macrocyclic Structure. *Dalton Transactions* **2016**, *45* (17), 7406–7420. https://doi.org/10.1039/C6DT00385K.
- (83) Cong, J.; Kinschel, D.; Daniel, Q.; Safdari, M.; Gabrielsson, E.; Chen, H.; Svensson, P. H.; Sun, L.; Kloo, L. Bis(1,1-Bis(2-Pyridyl)Ethane)Copper( <scp>i</Scp> / <scp>ii</Scp> ) as an Efficient Redox Couple for Liquid Dye-Sensitized Solar Cells. J Mater Chem A Mater 2016, 4 (38), 14550–14554. https://doi.org/10.1039/C6TA06782D.
- (84) Yang, K.; Yang, X.; Deng, Z.; Jiang, M. High Stability Tetradentate Ligand Copper Complexes and Organic Small Molecule Hybrid Electrolyte for Dye-Sensitized Solar Cells. *Electrochim Acta* 2022, 432, 141108. https://doi.org/10.1016/j.electacta.2022.141108.
- (85) Noviandri, I.; Brown, K. N.; Fleming, D. S.; Gulyas, P. T.; Lay, P. A.; Masters, A. F.; Phillips, L. The Decamethylferrocenium/Decamethylferrocene Redox Couple: A Superior Redox Standard to the Ferrocenium/Ferrocene Redox Couple for Studying Solvent Effects on the Thermodynamics of Electron Transfer. *Journal of Physical Chemistry B* 1999, *103* (32), 6713–6722. https://doi.org/10.1021/jp991381+.

- Yang, E. S.; Chan, M.-S.; Wahl, A. C. Electron Exchange between Ferrocene and Ferrocenium Ion. Effects of Solvent and of Ring Substitution on the Rate. *J Phys Chem* **1980**, *84* (23), 3094–3099. https://doi.org/10.1021/j100460a025.
- (87) Michaels, H.; Rinderle, M.; Freitag, R.; Benesperi, I.; Edvinsson, T.; Socher, R.; Gagliardi, A.; Freitag, M. Dye-Sensitized Solar Cells under Ambient Light Powering Machine Learning: Towards Autonomous Smart Sensors for the Internet of Things. *Chem Sci* 2020, *11* (11), 2895–2906. https://doi.org/10.1039/C9SC06145B.
- (88) Bechlars, B.; D'Alessandro, D. M.; Jenkins, D. M.; Iavarone, A. T.; Glover, S. D.; Kubiak, C. P.; Long, J. R. High-Spin Ground States via Electron Delocalization in Mixed-Valence Imidazolate-Bridged Divanadium Complexes. *Nat Chem* **2010**, *2* (5), 362–368. https://doi.org/10.1038/nchem.585.
- (89) Bechlars, B.; D'Alessandro, D. M.; Jenkins, D. M.; Iavarone, A. T.; Glover, S. D.; Kubiak, C. P.; Long, J. R. High-Spin Ground States via Electron Delocalization in Mixed-Valence Imidazolate-Bridged Divanadium Complexes. *Nat Chem* **2010**, *2* (5), 362–368. https://doi.org/10.1038/nchem.585.
- (90) Raithel, A. L.; Kim, T.-Y.; Nielsen, K. C.; Staples, R. J.; Hamann, T. W. Low-Spin Cobalt(
   <scp>ii</Scp> ) Redox Shuttle by Isocyanide Coordination. *Sustain Energy Fuels* 2020, 4
   (5), 2497–2507. https://doi.org/10.1039/D0SE00314J.
- (91) Swarts, P. J.; Conradie, J. Redox Data of Ferrocenylcarboxylic Acids in Dichloromethane and Acetonitrile. *Data Brief* **2020**, *30*, 105650. https://doi.org/10.1016/j.dib.2020.105650.
- (92) Baillargeon, J.; Xie, Y.; Hamann, T. W. Bifurcation of Regeneration and Recombination in Dye-Sensitized Solar Cells via Electronic Manipulation of Tandem Cobalt Redox Shuttles. ACS Appl Mater Interfaces 2017, 9 (39), 33544–33548. https://doi.org/10.1021/acsami.7b01626.
- (93) Kannankutty, K.; Chen, C.-C.; Nguyen, V. S.; Lin, Y.-C.; Chou, H.-H.; Yeh, C.-Y.; Wei, T.-C. Tert -Butylpyridine Coordination with [Cu(Dmp) 2] 2+/+ Redox Couple and Its Connection to the Stability of the Dye-Sensitized Solar Cell. ACS Appl Mater Interfaces 2020, 12 (5), 5812–5819. https://doi.org/10.1021/acsami.9b19119.
- Yang, K.; Yang, X.; Deng, Z.; Jiang, M. High Stability Tetradentate Ligand Copper Complexes and Organic Small Molecule Hybrid Electrolyte for Dye-Sensitized Solar Cells. *Electrochim Acta* 2022, 432, 141108. https://doi.org/10.1016/j.electacta.2022.141108.
- (95) Devdass, A.; Watson, J.; Firestone, E.; Hamann, T. W.; Delcamp, J. H.; Jurss, J. W. An Efficient Copper-Based Redox Shuttle Bearing a Hexadentate Polypyridyl Ligand for DSCs

under Low-Light Conditions. *ACS Appl Energy Mater* **2022**, *5* (5), 5964–5973. https://doi.org/10.1021/acsaem.2c00344.

- (96) Bernardo, M. M.; Heeg, M. J.; Schroeder, R. R.; Ochrymowycz, L. A.; Rorabacher, D. B. Comparison of the Influence of Saturated Nitrogen and Sulfur Donor Atoms on the Properties of Copper(II/I)-Macrocyclic Polyamino Polythiaether Ligand Complexes: Redox Potentials and Protonation and Stability Constants of CuIL Species and New Structural Data. *Inorg Chem* **1992**, *31* (2), 191–198. https://doi.org/10.1021/ic00028a013.
- (97) Rorabacher, D. B. Electron Transfer by Copper Centers. *Chem Rev* **2004**, *104* (2), 651–698. https://doi.org/10.1021/cr020630e.
- (98) Chaka, G.; Kandegedara, A.; Heeg, M. J.; Rorabacher, D. B. Comparative Study of Donor Atom Effects on the Thermodynamic and Electron-Transfer Kinetic Properties of Copper( <scp>ii</Scp> / <scp>i</Scp> ) Complexes with Sexadentate Macrocyclic Ligands. [Cu<sup>II/I</sup> ([18]AneS 4 N 2)] and [Cu<sup>II/I</sup> ([18]AneS 4 O 2)]. Dalton Trans. 2007, No. 4, 449–458. https://doi.org/10.1039/B612252C.
- (99) Aronne, L.; Yu, Q.; Ochrymowycz, L. A.; Rorabacher, D. B. Effect of Macrocyclic Ligand Constraints upon the Kinetics of Complex Formation and Dissociation and Metal Ion Exchange. Copper(II) Complexes with Cyclohexanediyl Derivatives of the Cyclic Tetrathiaether [14]AneS4 in 80% Methanol. *Inorg Chem* 1995, 34 (7), 1844–1851. https://doi.org/10.1021/ic00111a036.
- (100) Deng, H.; Kebarle, P. Bond Energies of Copper Ion–Ligand L Complexes CuL 2 <sup>+</sup> Determined in the Gas Phase by Ion–Ligand Exchange Equilibria Measurements. J Am Chem Soc 1998, 120 (12), 2925–2931. https://doi.org/10.1021/ja973814x.

**APPENDIX A: CHAPTER 2 SUPPLEMENTARY DATA** 



Figure 2.1A: <sup>1</sup>H-NMR spectrum (500 MHz, CDCl<sub>3</sub>) of dbmed.





Figure 2.3A: <sup>1</sup>H-NMR spectrum (500 MHz, CDCl<sub>3</sub>) of [Cu(dbmed)](OTf)<sub>2</sub>.



Figure 2.4A: Crystal structure of the [Cu(dbmed)]OTf species.

Table 2.1A: Selected bond lengths and angles for the [Cu(dbmed)]OTf complex. The bond lengths are reported in angstroms (Å) and bond angles are in degrees (°). The standard deviations of each value are shown in parenthesis.

Atom	Atom	Length/ Å	Atom	Atom	Atom	Angle/°
Cu1	N1	2.268(5)	N1	Cu1	N3	83.46(18 )
Cu1	N2	1.950(5)	N2	Cu1	N1	120.1(2)
Cu1	N3	2.302(5)	N2	Cu1	N3	82.8(2)
Cu1	N4	1.953(5)	N2	Cu1	N4	151.0(2)
			N4	Cul	N1	83.8(2)
			N4	Cul	N3	118.5(2)

## **APPENDIX B: CHAPTER 3 SUPPLEMENTARY DATA**

Atom	Atom	Length/Å	Atom	Atom	Atom	Angle/°
Cul	N1	2.019(2)	N1	Cul	N2	87.61(9)
Cu1	N2	2.086(2)	N1	Cul	N3	135.49(10)
Cu1	N3	2.078(2)	N3	Cul	N2	78.64(10)
Cu1	N4	2.011(2)	N4	Cul	N1	126.30(9)
			N4	Cu1	N2	137.50(9)
			N4	Cu1	N3	89.34(9)

Table 3.1A: Selected bond lengths and angles for the [Cu(bpyPY4)]OTf complex. The bond lengths are reported in angstroms (Å) and bond angles are in degrees (°). The standard deviations of each value are shown in parenthesis.

Table 3.2A: Selected bond lengths and angles for the [Cu(bpyPY4)]OTf<sub>2</sub> complex. The bond lengths are reported in angstroms (Å) and bond angles are in degrees (°). The standard deviations of each value are shown in parenthesis.

Atom	Atom	Length/Å	Atom	Atom	Atom	Angle/°
Cul	N1	1.969(3)	N1	Cu1	N2	81.88(11)
Cul	N2	2.208(3)	N1	Cu1	N3	88.16(12)
Cu1	N3	2.053(3)	N1	Cul	N4	81.95(12)
Cul	N4	1.993(3)	N1	Cul	N5	172.85(13)
Cul	N5	1.980(3)	N3	Cul	N2	86.34(11)
			N4	Cul	N2	133.89(12)
			N4	Cul	N3	135.76(12)
			N5	Cul	N2	96.68(11)
			N5	Cul	N3	98.76(12)
			N5	Cul	N4	94.20(12)



Figure 3.1A: : <sup>1</sup>H-NMR spectrum (500 MHz, CD<sub>3</sub>CN) of [Cu(bpyPY4)](TFSI)<sub>2</sub>.

**APPENDIX C: CHAPTER 4 SUPPLEMENTARY DATA** 



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Figure 4.5A: <sup>1</sup>H-NMR of [Cu(PY5)]TFSI<sub>2</sub> in deuterated acetonitrile.

Table 4.1A: Selected bond lengths and angles for the [Cu(PY5)]OTf complex. The bond lengths are reported in angstroms (Å) and bond angles are in degrees (°). The standard deviations of each value are shown in parenthesis.

Atom	Atom	Length/Å	Atom	Atom	Atom	Angle/°
Cu <sup>1</sup>	N <sup>15</sup>	2.057(3)	$N^{15}$	$Cu^1$	N <sup>31</sup>	90.20(14)
$Cu^1$	N <sup>31</sup>	2.100(4)	N <sup>37</sup>	$Cu^1$	$N^{15}$	88.69(15)
$Cu^1$	N <sup>37</sup>	1.980(4)	N <sup>37</sup>	$Cu^1$	$N^{31}$	90.51(15)
$Cu^1$	N <sup>44</sup>	1.938(4)	$N^{44}$	$Cu^1$	$N^{15}$	97.32(14)
			$N^{44}$	$Cu^1$	$N^{31}$	118.19(15)
			$N^{44}$	$Cu^1$	N <sup>37</sup>	150.50(16)

Atom	Atom	Length/Å	Atom	Atom	Atom	Angle/°
Cu1	N1	2.082(3)	N1	Cu1	N3	87.45(10)
Cu1	N2	2.035(3)	N1	Cu1	N5	175.41(11)
Cu1	N3	2.160(3)	N1	Cu1	N6	90.63(11)
Cu1	N4	2.038(3)	N2	Cu1	N1	82.47(11)
Cu1	N5	2.090(3)	N2	Cu1	N3	87.50(11)
Cu1	N6	2.369(3)	N2	Cu1	N4	176.29(11)
			N2	Cu1	N5	96.93(11)
			N2	Cu1	N6	91.25(12)
			N3	Cu1	N6	177.83(11)
			N4	Cu1	N1	99.16(11)
			N4	Cu1	N3	89.23(11)
			N4	Cu1	N5	81.17(11)
			N4	Cu1	N6	92.07(12)
			N5	Cu1	N3	87.98(11)
			N5	Cu1	N6	93.94(12)

Table 4.2A: Selected bond lengths and angles for the [Cu(PY5)]OTf<sub>2</sub> complex. The bond lengths are reported in angstroms (Å) and bond angles are in degrees (°). The standard deviations of each value are shown in parenthesis.

Table 4.3A: Selected bond lengths and angles for the [Cu(PY5)]TFSI<sub>2</sub> complex. The bond lengths are reported in angstroms (Å) and bond angles are in degrees (°). The standard deviations of each value are shown in parenthesis.

Atom	Atom	Length/Å	Atom	Atom	Atom	Angle/°
Cu <sup>(1)</sup>	N <sup>(2)</sup>	2.0224(14)	N <sup>(2)</sup>	Cu <sup>(1)</sup>	N <sup>(3)</sup>	82.00(6)
$Cu^{(1)}$	N <sup>(3)</sup>	2.0675(14)	N <sup>(2)</sup>	$Cu^{(1)}$	N <sup>(4)</sup>	92.78(6)
$Cu^{(1)}$	N <sup>(4)</sup>	2.1130(14)	N <sup>(2)</sup>	$Cu^{(1)}$	N <sup>(5)</sup>	98.97(6)
$Cu^{(1)}$	N <sup>(5)</sup>	2.0491(14)	N <sup>(2)</sup>	$Cu^{(1)}$	N <sup>(6)</sup>	175.34(6)
$Cu^{(1)}$	N <sup>(6)</sup>	2.0262(14)	N <sup>(3)</sup>	$Cu^{(1)}$	N <sup>(4)</sup>	87.35(6)
			N <sup>(5)</sup>	$Cu^{(1)}$	N <sup>(3)</sup>	175.30(6)
			N <sup>(5)</sup>	$Cu^{(1)}$	N <sup>(4)</sup>	88.00(6)
			N <sup>(6)</sup>	$Cu^{(1)}$	N <sup>(3)</sup>	97.08(6)
			N <sup>(6)</sup>	$Cu^{(1)}$	N <sup>(4)</sup>	91.74(6)
			N <sup>(6)</sup>	$Cu^{(1)}$	N <sup>(5)</sup>	82.32(6)