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The Electro- and Photocatalytic Activity of a Ni-NNSS Schiff-Base Complex for Hydrogen Generation

Catherine F. Wise

College of William and Mary

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The Electro- and Photocatalytic Activity of a Ni-NNSS Schiff-Base Complex for Hydrogen Generation

A thesis submitted in partial fulfillment of the requirement
for the degree of Bachelors of Science in Department of Chemistry from
The College of William and Mary

By
Catherine F. Wise

Accepted for Honors

William R. McNamara

Leslie M. Waters

Robert D. Pike

Kristin Wustholz

Williamsburg, VA
April 27, 2015
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Abstract
Developing an efficient and cost-effective method of harvesting solar energy will greatly help to solve the global energy crisis, as the sun provides more energy in an hour than the world uses in an entire year. One of the most promising solutions to this problem is artificial photosynthesis, a process that mimics photosynthesis in plants to store energy in the chemical bonds of hydrogen gas. In order to develop systems for artificial photosynthesis, stable and active catalysts that can reduce protons must be identified. The new complexes, [Ni^{II} (Httfasbz)] and [Ni^{II} (L2)] (where $L2 = (2E, 2'E)$-dibenzyl 2,2'- (1,2-diphenylethane-1,2-diylidene)bis(hydrazinecarbodithioate)), were characterized and then analyzed as electrocatalysts for hydrogen generation. Both were found to be active catalysts for electrochemical proton reduction, with [Ni^{II} (Httfasbz)] giving an $i_c/i_p$ of 6.4 and [Ni^{II} (L2)] giving an $i_c/i_p$ of 42.9 in solutions of CH$_3$CN. [Ni^{II} (Httfasbz)] was further studied in a system for photochemical hydrogen generation. As a photocatalyst, [Ni^{II} (Httfasbz)] is both active and stable, producing TONs over 1100 after 18 hours and continuing to generate hydrogen for over 70 hours.
Introduction

Global Energy Crisis

One of the most pressing environmental problems facing our world today is the global energy crisis. As a result of rapid industrialization and a growing world population, annual global primary energy consumption has increased drastically in recent years and is predicted to reach 27 TW by 2050 and 43 TW by 2100.\(^1\) Currently, the majority of that energy is derived from fossil fuels, but Earth’s supply of fossil fuels is steadily dwindling. The 2014 BP Statistical Review of World Energy estimated that the world oil reserves will last 53 years, coal reserves will last 113 years, and natural gas reserves will last 55 years.\(^2\) Although it is possible to continue supplying our energy needs with fossil fuels for the next few decades, use of these natural resources contributes to major environmental problems, particularly the increase in atmospheric carbon dioxide (CO\(_2\)) levels.

Atmospheric CO\(_2\) levels have fluctuated drastically for hundreds of thousands of years but began to increase steadily in the 1700s, coinciding with the beginning of the Industrial Revolution.\(^3\) At this time, humans started burning coal to power factories, causing copious amounts CO\(_2\) to be released into the air as a byproduct. In the past 60 years, the increase in atmospheric CO\(_2\) has become more rapid, and current levels hover around 400 parts per million (ppm).\(^3\) Atmospheric CO\(_2\) absorbs infrared radiation, trapping heat in the atmosphere instead of allowing it to escape into space. Other common atmospheric gases, such as water vapor, nitrous oxide, and methane, also contribute to this process, which is known as the greenhouse effect.\(^4\) While the natural greenhouse effect is required for maintaining above-freezing temperatures on Earth,
anthropogenic CO₂ emission from burning fossil fuels amplifies this effect, causing global surface temperatures to increase to levels that are harmful to the environment. Additionally, because atmospheric CO₂ has no natural destruction mechanism, continued CO₂ accumulation will exacerbate the problems associated with global warming and negatively impact the environment for thousands of years.

**Solar Energy and Artificial Photosynthesis**

To solve the global energy crisis and mitigate the effects of global warming, researchers must develop a carbon-neutral power source. Renewable energy sources like hydropower, geothermal, and wind energy are all carbon-neutral, but there are several limitations to these methods. Solar energy is the most promising form of renewable energy because of its incredible potential. Every hour, 430 exajoules of energy from the sun hits the Earth, which is more than the world consumes in an entire year.

Nonetheless, solar energy is one of the least widely used renewable energy sources, and it only accounted for 0.18% of total primary energy consumption in the U.S. in 2011 (Figure 1). The large discrepancy between solar energy potential and solar energy usage exists because scientists have yet to develop efficient

![Figure 1. U.S. Total Primary Energy Consumption, 2011.](image)
and cost-effective methods for capturing and storing solar energy to use at night when the sun is not shining. However, finding a solution to this problem would almost immediately solve the global energy crisis.

Currently, researchers are exploring several potential options, including photovoltaics, solar thermal technology, and artificial photosynthesis. Photovoltaics (PVs) convert sunlight directly into electricity by using a semiconductor to create charge separation across a junction. Connecting PVs to electric circuits results in current generation and can generate power of several hundred watts. However, PVs are limited due to low efficiencies and high costs. The highest recorded solar cell efficiency is 46%, but efforts are being made to develop new materials to improve efficiency, such as semiconductor quantum dots, hybrid inorganic/organic systems, and multiple band-gap absorbers. Additionally, although the price of PVs has decreased significantly in recent years, from $0.21 kWh$ in 2010 to $0.11 kWh$ in 2013, the cost remains about twice as high as that of fossil fuel-derived electricity sources.

Another option to harness solar energy is solar thermal technology, which converts light energy into heat and then uses that heat to run a mechanical generator. As a result, it is possible to store the heat energy produced during the day and convert it to electricity at night. Additionally, solar thermal technology is a cost-effective way of capturing, converting, and storing solar energy, with lower production costs for electricity generation than some fossil fuels. However, solar thermal technology cannot be implemented everywhere, as it requires 0.25 to 1.0 square miles of land receiving direct sunlight in order to work efficiently.
The most promising option for solar energy capture and storage is artificial photosynthesis (AP), which mimics photosynthesis in plants by storing energy in the chemical bonds of hydrogen gas. AP relies on the concept of water splitting, which occurs by two half reactions, one oxidizing water into oxygen gas and the other reducing protons to hydrogen gas, as shown in equations (1) and (2).

\[
\begin{align*}
(1) & \quad 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \\
(2) & \quad 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2
\end{align*}
\]

These two half reactions can be optimized separately to attain maximum efficiency. A system for proton reduction consisting of a chromophore, semiconductor, sacrificial donor, and proton reduction catalyst is depicted in Figure 2.

**Figure 2.** Photocatalytic Proton Reduction

In the system, light strikes the chromophore, causing a charge-transfer excitation of an electron from the valence band into the conduction band of a semiconductor. This creates an electron-accepting hole, and once charge accumulates, the electron is transferred to a catalyst that reduces protons to hydrogen gas. The hydrogen gas produced can be burned as a clean fuel with only water as a byproduct. However, before such a system can be developed, new proton reduction catalysts that are derived from Earth-abundant metals must be identified.
Proton Reduction Catalysts

In nature, the metalloenzyme hydrogenase reduces protons to hydrogen, but it cannot be used for AP because it can only be obtained in limited quantities and is unstable outside its natural environment. Thus, in order for an AP system to be successful, synthetic catalysts that perform the same function must be developed. Noble metals like platinum can effectively reduce protons but are too expensive to be used on a large scale. To be viable for widespread use in solar fuel technologies, the active site of the proton reduction catalyst must contain an Earth-abundant metal such as nickel, cobalt, or iron. Ideally, proton reduction catalysts will also be able to operate in an aqueous environment at high turnover frequencies and a low overpotential. Overpotential refers to the difference between catalytic potential and thermodynamic potential of proton reduction and is related to catalyst efficiency. A lower overpotential reflects a more efficient catalyst because less energy is required for catalysis to occur. Another indicator of catalyst efficiency is a high Faradaic yield, which is measured by applying a constant potential to an electrochemical system over time and determining the amount of hydrogen produced. The calculated Faradaic yield is a ratio of hydrogen produced to the expected amount of hydrogen generation based on the charge consumed by the system.

Nickel Catalysts for Proton Reduction

Due to their high activity and stability, nickel catalysts for proton reduction have received much attention in recent years. Most extensively studied are the \([\text{Ni}(\text{P}_2\text{N}_2)_2]\) catalyst systems designed by DuBois et al. (Figure 3) that mimic the active site of hydrogenase by containing pendant amines that function as a proton relay. Such catalysts have shown
proton reduction activity both photocatalytically and electrocatalytically. For instance, photocatalytic experiments on the \([\text{Ni}(\text{P}^{R'}_2\text{N}^{R''}_2)\text{2}^+\text{]}\) catalyst (where \((\text{P}^{R'}_2\text{N}^{R''}_2)\) is bis(1,5-\(R'\)-diphospho-3,7-\(R''\)-diazocyclooctane) resulted in \(\text{H}_2\) generation with a turnover frequency of \(460 \pm 60 \text{ hr}^{-1}\) and a turnover number (TON) of \(723 \pm 171\). Examined electrochemically, the same complex showed quasi-reversible waves for \(\text{Ni}^{II}/I\) and \(\text{Ni}^{I/0}\) redox couples and catalytic current enhancement both in aqueous buffer and with the addition of triflic acid to a water/acetonitrile solution for a Faradaic yield of \(85 \pm 4\%\). Other nickel catalyst systems for proton reduction include macrocyclic and pincer complexes (Figure 3), which operate at fairly low overpotentials and show catalytic current enhancements in electrochemical experiments with added acid. The macrocyclic complexes are highly active, while the pincer complexes are very stable and efficient, achieving Faradaic yields of 90-95%. Nickel catalysts for photocatalytic proton reduction are also widely studied. A series of nickel thiolate complexes (Figure 3) reported by Eisenberg et al. produced TONs ranging between 1500 and 7500 after 30 hours of irradiation by green-emitting LED light. Under oxidative quenching conditions, these photocatalytic systems are very stable, with catalytic activity occurring for more than 60 hours. Nickel thio-carbazate complexes have also shown high activity for photocatalytic hydrogen generation, with TONs around 8000 after 24 hours. Both of these systems are noble metal free, as they use the organic dye fluorescein as a photosensitizer, making them fairly inexpensive and viable for more widespread use. Nonetheless, further research can be conducted to develop new nickel catalysts that can increase the activity and stability of these photocatalytic systems.
Redox Active Ligands

There has been great interest in developing catalysts using noninnocent, or redox active, ligands for proton reduction. Noble metals can catalyze multi-electron processes like proton reduction quite efficiently, but as previously mentioned, current research is focused on developing catalysts using Earth-abundant metals to reduce the cost of proton reduction systems. Changes in oxidation state for Earth-abundant metals often occur one electron at a time, and two consecutive one-electron transfers at a metal can cause side reactions not conducive to efficient catalytic processes. However, in complexes with redox active ligands, the ligands can possess several electronic structures, so the metal oxidation state is often ambiguous. Because both the metal center and the ligand can undergo redox reactions, multi-electron processes are viable for complexes containing Earth-abundant metals. As a result, the use of redox-active ligands allows transition metal
catalysts to achieve reactivity otherwise seen only for noble metals. Additionally, previous research has indicated that complexes containing transition metals and noninnocent ligands are highly active catalysts that operate at low overpotentials.

Therefore, the redox active ligand \( \text{H}_3\text{ttfasbz} \) (Scheme 1), reported by Wieghardt et al., was of particular interest for the development of proton reduction catalysts. \( \text{H}_3\text{ttfasbz} \), synthesized by refluxing S-benzyldithiocarbazate and 4-thenoyl-2,2,2-trifluoroacetone in ethanol, is a bis-dithiocarbazate Schiff base with \( \text{N}_2\text{S}_2 \) donor atoms. A tetradeionate, soft ligand, \( \text{H}_3\text{ttfasbz} \) can make strong bonds to lower oxidation state metals. The copper complex of \( \text{H}_3\text{ttfasbz} \) has been previously described. Although the neutral complex contains trivalent copper, electrochemical processes allow copper to achieve its +2 and +1 oxidation states as well. Additionally, the complex exhibits redox activity at -0.126 V vs. \( \text{Fc}^{+/0} \) for \( \text{Cu}^{III/II} \) and -1.67 V vs. \( \text{Fc}^{+/0} \) for \( \text{Cu}^{II/I} \). This result indicated that the ligand could be complexed with other first row transition metals, such as iron, nickel, or cobalt, to be tested as a proton reduction catalyst.

Scheme 1. \( \text{H}_3\text{ttfasbz} \) tautomerism
Experimental

Materials and Methods
4-thenoyl-2,2,2-trifluoroacetone was purchased from Alfa Aesar. Benzyl chloride and carbon disulfide were purchased from Aldrich. Nickel (II) acetate tetrahydrate and potassium hydroxide were purchased from Fisher Scientific. Hydrazine hydrate, benzil (99%), triethylamine (99.7%), tetra-n-butylammoniumhexafluorophosphate (98%), and fluorescein were purchased from Acros Organics. All reagents were used without further purification.

Syntheses

S-Benzyldithiocarbazate (5). This procedure was modified from the literature method.27 Potassium hydroxide (11.45 g, 0.20 mol) was dissolved in 70 mL of ethanol (EtOH). Hydrazine hydrate (9.72 mL, 0.20 mol) was added to the solution, which was then was cooled to 0°C. The solution remained in an ice bath while carbon disulfide (12.05 mL, 0.20 mol) was added drop-wise over 2 hours. Benzyl chloride (23.0 mL, 0.20 mol) was also added drop-wise over 2 hours, and a white precipitate formed. The precipitate was collected via vacuum filtration, washed with water, and dried overnight. A yield of 33.4% was obtained. The 1H NMR spectrum matched the literature values.27

(2Z, 2'Z)-dibenzy1 2,2'-(4,4,4-trifluoro-1-(thiophen-2-yl)butane-1,3-diylidene)bis(hydradinecarbobithioate) (H3ttfbszb, 6). The ligand was synthesized according to literature methods, as depicted in Scheme 2.26 In a roundbottom flask, 5 (567.2 mg, 2.86 mmol) was dissolved in 12.5 mL of EtOH. The solution was stirred and heated to 78°C, turning clear and colorless in the process. To this solution, 4-thenolo-
2,2,2-trifluoroacetone (317.9 mg, 1.43 mmol) was added. The solution, which turned yellow upon addition of the 4-thenoyl-2,2,2-trifluoroacetone, was allowed to reflux for 24 hours. An off-white precipitate formed and was collected via vacuum filtration for a yield of 19.3%. The $^1$H and $^{13}$C NMR spectra matched literature values.\textsuperscript{26} $^1$H NMR (DMSO) $\delta$: 11.6 (1H, s); 8.1 (1H, s); 7.9 (1H, d); 7.8 (1H, d); 7.2-7.5 (11 H, m); 4.4 (4H, m); 4.2 (1H, d); 3.5 (1H, d). $^{13}$C NMR (CDCl$_3$) $\delta$: 39.0, 39.8, 40.5, 88.7 (q, CF$_3$), 127.6, 128.0, 128.69, 128.71, 129.3, 129.6, 131.2, 131.5, 132.0, 134.7, 135.6, 149.5, 196.3, 206.7.

\begin{center}
\textbf{Scheme 2. Synthesis of 6.}
\end{center}

\begin{center}
\textbf{(2E, 2'E)-dibenzyl 2,2'-}(1,2-diphenylethane-1,2-diylidene)bis(hydrazinecarbodithioate) (L$_2$, 7). The ligand was synthesized according to a procedure modified from the literature method for the synthesis of 6.\textsuperscript{26} This synthesis is depicted in Scheme 3. S-benzyldithiocarbazate (49.9 mg, 2.52 mmol) was dissolved in 11 mL of EtOH in a roundbottom flask. The white, cloudy solution was stirred and heated to 78°C, and it turned clear and colorless. To this solution, benzil (26.5 mg, 1.26 mmol) was added. The solution turned yellow and was allowed to reflux for 21 hours. The yellow precipitate that formed was collected via vacuum filtration for a 45.5% yield. $^1$H NMR (CDCl$_3$) $\delta$: 4.43 (4H, s); 7.29 (10H, m); 7.37 (4H, d); 7.50 (6H, q); 9.90 (2H, s).
\end{center}

\begin{center}
\textbf{Scheme 3. Synthesis of 7.}
\end{center}
[Ni\textsuperscript{II}(Httfasbz)] (8). This procedure was adapted from the previously reported [Cu\textsuperscript{III}(ttfasbz)] synthesis\textsuperscript{26} and is depicted in Scheme 4. In a Schlenk flask, 6 (75.0 mg, 0.128 mmol) was dissolved in 53.0 mL of methanol (MeOH) under an Ar atmosphere. The solution was stirred and heated to 65°C. In a pear-shaped flask, nickel (II) acetate tetrahydrate (32.0 mg, 0.128 mmol) was dissolved in 16.0 mL MeOH and degassed with Ar for 15 minutes. The nickel solution was added to the Schlenk flask under Ar via cannula, causing an immediate color change from cloudy white to dark reddish-brown. The solution was heated for 1 hour and then was left to stir for 2 hours at room temperature. A brown precipitate formed and was collected via vacuum filtration to give a yield of 52.0%. Crystals suitable for X-ray diffraction were obtained by diffusion of hexanes into a concentrated solution of 8 in dichloromethane. MS: m/z expected = 638.96; m/z found = 638.96. Anal. Calcd. for NiC\textsubscript{24}H\textsubscript{19}F\textsubscript{3}N\textsubscript{4}S\textsubscript{5}: C, 45.08%; H, 2.99%; N, 8.76%. Found: C, 45.20%; H, 3.17%; N, 8.81%. \textsuperscript{1}H NMR (CDCl\textsubscript{3}) δ: 7.43 (3 H, m); 7.35 (4H, m); 7.30 (6H, m); 7.05 (1H, m); 4.34 (2H, d); 4.20 (2H, d); 4.15 (2H, m). \textsuperscript{13}C NMR (CDCl\textsubscript{3}) δ: 29.5, 29.7, 36.0, 40.0, 127.5, 127.9, 128.8, 129.2, 129.4, 131.2, 134.7, 136.2, 148.2, 198.0.

\[ \text{Scheme 4. Synthesis of 8.} \]

[Ni(L2)] (9). This procedure was adapted from the synthesis of 8 and is depicted in Scheme 5. In a Schlenk flask, 7 (50.6 mg, 0.089 mmol) was dissolved in 37 mL of MeOH under an Ar atmosphere, and the resulting yellow solution was heated to 65°C. In a pear-
shaped flask, nickel (II) acetate tetrahydrate (22.1 mg, 0.089 mmol) was dissolved in 11 mL of MeOH and degassed with Ar for 15 minutes. The nickel solution was added to the Schlenk flask via cannula, and an immediate color change from yellow to dark brown was observed. The solution was heated for 30 minutes and then was allowed to stir overnight at room temperature. A dark green precipitate formed and was collected via vacuum filtration. The precipitate was dried on the vacuum line and then weighed to give a yield of 74.6%. Crystals were obtained by slow diffusion of hexanes into a concentrated solution of 9 in dichloromethane. Diffraction was too weak to obtain a reliable structure.

MS: m/z expected = 627.03; m/z found = 627.03. Anal. Calcd. for NiC$_{30}$H$_{24}$N$_{4}$S$_{4}$: C, 57.42%; H, 3.86%; N, 8.93%. $^1$H NMR (CDCl$_3$) $\delta$: 7.34 (4H, d); 7.15 (7H, m); 7.05 (3H, t); 6.95 (4H, m); 6.83 (2H, d); 4.25 (2H, s); 3.88 (2H, s).

Scheme 5. Synthesis of 9

Instrumentation

$^1$H and $^{13}$C NMRs were performed on an Agilent 400MR DD2 instrument operating in pulse Fourier transform mode. Chemical shifts were referenced to residual solvent. Elemental analysis was obtained at the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE 0650456. Mass spectrometry was carried out at the Cosmic Facility at Old Dominion University in Norfolk, VA, using positive electrospray ionization on a Bruker 12 Tesla APEX-Qe FTICR-MS with an Apollo II ion source.
X-Ray Diffractometry

A single crystal was mounted on a glass fiber and data was collected with graphite-monochromated Cu Kα radiation ($\lambda = 1.54187$ nm) on a Bruker-AXS three-circle diffractometer using a SMART Apex II CCD detector. The crystal structure was solved and refined using SIR2014 and SHELXL-2014/7.

Cyclic Voltammetry (CV)

A CH Instruments 620D potentiostat with a CH Instruments 680 amp booster was used for all experiments. Each experiment was performed in a standard three-electrode cell with a glassy carbon working electrode, a Pt auxiliary electrode, and an SCE reference electrode. Tetra-n-butylammoniumhexafluorophosphate (TBAPF$_6$, 0.1 M) was used as the electrolyte. Because the complexes are air sensitive, all electrochemical experiments were performed under an Ar atmosphere. Parafilm was wrapped around the cap of the electrochemical cell so that the cap had a tighter fit and exposure to air was reduced. The working and auxiliary electrodes were polished with alumina powder paste (0.05 µm) on a cloth-covered polishing pad and then rinsed with water and acetonitrile. For the acid addition experiments, trifluoroacetic acid (TFA) was added via Hamilton syringe to eliminate the potential for air exposure.

Acid Addition Study

In an electrochemical cell, 0.5 mg of crystals of 8 was dissolved in 5.0 mL of acetonitrile (CH$_3$CN), and TBAPF$_6$ (0.1 M) was added as the electrolyte. The electrochemical cell was degassed with Ar for 15 minutes. Cyclic voltammograms (CVs) were taken with no
acid added and after additions of 10 µL, 15 µL, 20 µL, 25 µL, and 30 µL of TFA (0.11 M). The CV was scanned from 0.00 to -1.40 V at a rate of 200 mV/s. A similar procedure was followed for 9 but a higher concentration of TFA (1.1 M) was used. CVs were taken with no acid added and after additions of 10 µL, 20 µL, and 30 µL of TFA. The CV was scanned from 0.00 to -1.60 V at a rate of 200 mV/s. The CVs of both complexes were performed in a standard three-electrode cell with a glassy carbon working electrode, a Pt auxiliary electrode, and an SCE reference electrode. Prior to each scan, the working and auxiliary electrodes were polished on a cloth-covered polish pad with a paste of 0.05 µm alumina powder.

**Catalyst Concentration Dependence Study**

A stock solution was prepared of 8 (1.0 x 10⁻³ M) by dissolving 3.2 mg of crystals of 8 in CH₃CN in a 5.0 mL volumetric flask. In an electrochemical cell, 195 mg of TBAPF₆ was dissolved in 5 mL of CH₃CN. 30 µL of TFA (0.11 M) was also added to the cell, which was then degassed with Ar for 15 minutes. CVs were taken without catalyst and in the presence of 0.05 mM, 0.06 mM, 0.07 mM, and 0.08 mM catalyst. All CVs were scanned from 0.00 to -1.40 V at a rate of 200 mV/s. The experiment was performed in a standard three-electrode cell with a glassy carbon working electrode, a Pt auxiliary electrode, and an SCE reference electrode. Prior to each scan, the working and auxiliary electrodes were polished on a cloth-covered polish pad with a paste of 0.05 µm alumina powder.
Scan Rate Dependence Study

In an electrochemical cell, 0.5 mg of 8 was dissolved in 5.0 mL CH₃CN and TBAPF₆ (0.1 M) was added as the electrolyte. Cyclic voltammograms were taken at scan rates ranging from 150 mV/s to 900 mV/s. The same experiment was performed using 0.5 mg of 9. The CVs were performed in a standard three-electrode cell with a glassy carbon working electrode, a Pt auxiliary electrode, and an SCE reference electrode. Prior to each scan, the working and auxiliary electrodes were polished on a cloth-covered polish pad with a paste of 0.05 µm alumina powder.

Rinse Test

This procedure was modified from the experiment reported by Dempsey et al.²⁸ A CV of 0.5 mg of 8 was taken in the presence of 30 µL of TFA. The electrodes were then rinsed copiously with CH₃CN (about 200 mL total). Without polishing, the electrodes were placed in a solution of just CH₃CN and another CV was taken. The CVs were performed in a standard three-electrode cell with a glassy carbon working electrode, a Pt auxiliary electrode, and an SCE reference electrode. Prior to the first scan, the working and auxiliary electrodes were polished on a cloth-covered polish pad with a paste of 0.05 µm alumina powder.

Hydrogen Evolution Studies

Stock solutions were prepared of 8 (1 x 10⁻⁴ M in CH₃CN) and fluorescein (4.0 x 10⁻³ M in EtOH). In test tubes, solutions of 2.0 mL were prepared with varying amounts of catalyst, fluorescein, and EtOH. The samples were sealed with airtight septa and
degassed with Ar. While the samples degassed, 2.0 mL of 10% V/V triethylamine (TEA)/H₂O was added to each, making the total solution 5% TEA by volume. For each sample, 1.0 mL of Ar was removed from the headspace and 1.0 mL of CH₄ was injected for use as an internal standard. The samples were then irradiated with light from an arc lamp. A Newport 66902 Arc Lamp Housing with a Newport 69911 Mercury Arc Lamp Power Supply was used for all experiments. After irradiation, 100 µL gas samples were taken from the headspace of each test tube and injected into a Bruker Scion 436 gas chromatograph to measure H₂ evolution.

**GC Calibration**

One 500 mL round bottom flask was filled with CH₄ gas and one with H₂ gas via balloons. In a test tube, a solution of 2 mL of CH₃CN and 2 mL of H₂O was prepared. The sample was sealed with an airtight septa and degassed with Ar. Using a gas syringe, 1.0 mL of gas was removed from the test tube and 1.0 mL of CH₄ was added as an internal standard. Variable amounts of H₂ gas, ranging from 10 µL to 500 µL, were then added to the test tube. Gas samples of 100 µL were injected into a Bruker Scion 436 gas chromatograph to determine the ratio of H₂ to CH₄ peak heights. The peak height ratios were plotted versus the volume of H₂ added (Figure A9). The linear trendline of this data was used to calculate volume of H₂ generated for the hydrogen evolution studies.

**Catalyst Concentration Studies**

Four test tubes were prepared, each with 1.15 mL of the 4.0 x 10⁻³ M fluorescein stock solution. To the four test tubes, 30 µL, 40 µL, 50 µL, and 60 µL of a 1.0 x 10⁻⁴ M stock
solution of 8 were added, respectively. Then, ethanol was added to each test tube so that the total volume equaled 2.0 mL. All of the test tubes were sealed with airtight septa, wrapped in aluminum foil, and degassed with Ar. To each, 2.0 mL of 10% V/V TEA/H₂O was added, and the solution was degassed for an additional 15 minutes. Using a gas syringe, 1.0 mL of Ar was removed from the headspace of each test tube and 1.0 mL of CH₄ was injected as an internal standard. The test tubes were irradiated by the arc lamp for about 19 hours. Then, 100 µL of gas from the headspace of each test tube was injected into the GC for analysis.

Fluorescein Concentration Studies

Six test tubes were prepared, each with 50 µL of the 1.0 x 10⁻⁴ M stock solution of 8. To the test tubes, 4.0 x 10⁻³ M fluorescein was added in amounts ranging from 0.80 mL to 1.80 mL. Ethanol was also added so that each test tube contained 2.0 mL of solution. The test tubes were sealed with airtight septa, wrapped in aluminum foil to prevent light exposure, and degassed with Ar. While the solutions degassed, 2.0 mL of 10% V/V TEA/H₂O was added, bringing the TEA concentration in each test tube to 0.36 M. Using a gas syringe, 1.0 mL of Ar was removed from the headspace of the test tube, and 1.0 mL of CH₄ was injected as an internal standard. The test tubes were irradiated with light from the arc lamp overnight. 100 µL of gas from the headspace of each test tube was injected into the GC for analysis.
**Measuring H₂ Evolution over Time**

Six test tubes were prepared, each with 200 µL of the 1.0 x 10⁻³ M stock solution of 8, 1.70 mL of the 4.0x10⁻³ M stock solution of fluorescein, and 0.10 mL of ethanol. The test tubes were sealed with airtight septa, wrapped in aluminum foil to prevent light exposure, and degassed with Ar. While the solutions degassed, 2.0 mL of 10% V/V TEA/H₂O was added to each sample. After 15 minutes of degassing, 1.0 mL of Ar from the headspace was removed using a gas syringe, and 1.0 mL of CH₄ was injected into each test tube to be used as an internal standard. The test tubes were irradiated with 455 nm light from the arc lamp. H₂ evolution was determined by GC analysis at various time points after the start of irradiation by sampling 100 µL of gas from the headspace of the test tubes.

A similar experiment was performed with different concentrations of TEA and fluorescein. Test tubes were prepared with 200 µL of the 1.0 x 10⁻³ M stock solution of 8, 0.50 mL of the 4.0 x 10⁻³ M fluorescein stock solution, 1.30 mL of ethanol, and 2.0 mL of 1.96% V/V TEA/H₂O. H₂ evolution was measured over a period of 70 hours at various times after the start of irradiation. Additional TEA (4 µL, 0.1% V/V) was added to each test tube after 31 and 48 hours of irradiation in order to replenish sacrificial donor and lengthen the lifetime of the system.

**Quenching Studies**

For the catalyst quenching experiment, stock solutions of fluorescein (4.0 x 10⁻³ M) in EtOH and 8 (8.0 x 10⁻⁴ M) in CH₃CN were prepared. In an air-free cuvette, 7.5 µL of the fluorescein stock solution was diluted with 3.0 mL of a solution of 1:1 EtOH:H₂O at pH = 13. Both the catalyst and fluorescein solutions were degassed with Ar for 20 minutes,
and a positive pressure of Ar was maintained in the sample vials throughout the experiment using an Ar balloon. Catalyst solution was added to the cuvette in 5 µL increments, and the fluorescence intensity was monitored by exciting the sample at 430 nm with a PerkinElmer LS 55 Luminescence Spectrometer. A total of 100 µL of catalyst solution was added, and a Stern-Volmer plot was used to calculate the catalyst’s quenching coefficient.

The TEA quenching experiment followed a similar procedure. The fluorescein solution was prepared in the same manner. Pure TEA was degassed with Ar for 20 minutes. To observe fluorescence quenching by TEA, the degassed TEA was added to the air-free cuvette in 30 µL increments. A total of 300 µL of TEA was added, and a Stern-Volmer plot was used to calculate the quenching coefficient for TEA.

**UV-Vis Absorption**

To compare the absorbance peaks of 8 and 9, two quartz cuvettes were filled with dilute solutions of each catalyst in dichloromethane (DCM). UV-Vis absorption scans were taken from 200 nm to 800 nm at medium speed. To examine the conditions of photocatalytic proton reduction, 5 µL of fluorescein (4.0 x 10^{-3} M), 400 µL of 8, and 1.095 mL of EtOH were added to an airfree cuvette. While degassing this solution with Ar, 1.5 mL of 10% V/V TEA/H_{2}O was added, and the degassing was continued for 15 minutes. The cuvette was placed 25 cm from the arc lamp and was irradiated with 455 nm light. UV-Vis absorbance scans were taken after 1, 4, 5, 7, 8, and 22 hours of irradiation. All UV-Vis absorption measurements were performed using an Agilent Cary 60 UV-Vis.
Results and Discussion

Once complex 8 was synthesized, it was of interest to determine its molecular structure using X-ray crystallography. Suitable crystals were obtained via slow diffusion of hexanes into a solution of 8 in dichloromethane. Single crystal X-ray diffraction was performed on a brown block crystal. The resulting crystal structure shows that, as predicted, the complex is tetradentate with bonds from the central Ni atom to two sulfur atoms and two nitrogen atoms (Figure 4). A tetradentate structure is desirable for proton reduction catalysts because it stabilizes the transition metal center while still allowing for the binding of H atoms to the metal. However, it is interesting to note that the binding to nitrogen is not symmetrical as it was in the crystal structure for [Cu$^{III}$(ttfasbz)] reported by Wieghardt et al.$^{26}$ To keep the Ni center in its +2 oxidation state and maintain a neutral complex, the ligand assumes a dianionic form when binding to Ni, which causes the unusual binding pattern between the metal center and the nitrogens. Table 1 depicts the bond lengths (Å) and angles (°) for 8 and Table 2 provides selected X-ray crystallography data.

![Figure 4. ORTEP diagram of 8. Ni (teal), N (blue), S (yellow), C (gray), and F (green). Hydrogen atoms have been omitted for clarity.](image)
Table 1. Selected bond lengths [Å] and angles [°] for 8.

<table>
<thead>
<tr>
<th>Bond Lengths/Angles</th>
<th>Value</th>
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<tr>
<td>Ni(1)-S(2)</td>
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</tr>
<tr>
<td>Ni(1)-S(3)</td>
<td>2.1358(9)</td>
</tr>
<tr>
<td>Ni(1)-N(1)</td>
<td>1.907(2)</td>
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<tr>
<td>Ni(1)-N(3)</td>
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<tr>
<td>N(1)-N(2)</td>
<td>1.381(3)</td>
</tr>
<tr>
<td>N(1)-C(8)</td>
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<tr>
<td>N(2)-C(9)</td>
<td>1.293(3)</td>
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<tr>
<td>N(3)-N(4)</td>
<td>1.401(3)</td>
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<tr>
<td>N(3)-C(15)</td>
<td>1.293(4)</td>
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<td>N(4)-C(17)</td>
<td>1.307(3)</td>
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<tr>
<td>C(9)-C(14)</td>
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<td>C(14)-C(15)</td>
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Table 2. Selected X-ray crystallography data for 8.

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<th>Property</th>
<th>Value</th>
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<td>Empirical formula</td>
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<td>T (K)</td>
<td>100(2) K</td>
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<td>Space group</td>
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<td>a (Å)</td>
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</tr>
<tr>
<td>b (Å)</td>
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</tr>
<tr>
<td>c (Å)</td>
<td>27.7375(8)</td>
</tr>
<tr>
<td>( \alpha ) (deg)</td>
<td>90</td>
</tr>
<tr>
<td>( \beta ) (deg)</td>
<td>90</td>
</tr>
<tr>
<td>( \gamma ) (deg)</td>
<td>90</td>
</tr>
<tr>
<td>( V ) (Å(^3))</td>
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<tr>
<td>Final R indices (all data)</td>
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<tr>
<td>No. of independent reflections</td>
<td>13604</td>
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<tr>
<td>( R_{\text{int}} )</td>
<td>0.0524</td>
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</table>

A crystal structure of 9 was also desired after the complex was synthesized. However, dark green crystals of 9 grown by slow diffusion of hexanes into dichloromethane were too thin to be solved definitively by single crystal X-ray diffraction. Attempts to grow larger crystals more suitable for X-ray diffraction by vapor diffusion of hexanes into dichloromethane were unsuccessful. However, preliminary X-ray results indicated the same nitrogen binding pattern to the Ni center as was seen with 8. Again, like 8, the structure is tetradeinate, with bonds from the central Ni atom to two nitrogen atoms and two sulfur atoms.

Analysis and comparison of the UV-Vis absorbance spectra of 8 and 9 provides additional structural information about the two complexes. A solution of crystals of 8 in DCM showed absorption peaks at 275, 325, 405, 470, and 515 nm. Similarly, a solution
of crystals of 9 in DCM showed absorption peaks at 265, 310, 375, and 465 nm. The 275 nm peak of 8 and the 265 nm peak of 9 can be attributed to the $\pi \rightarrow \pi^*$ transitions in the aromatic regions of these complexes. Absorbance peaks in the 300 nm region of Schiff base complexes are typical of intramolecular charge transfer (ICT) transitions. In the case of both 8 and 9, these transitions are due to $\pi$ electron delocalization between lone pairs on the nitrogen atoms and the $\pi$ bonds of the aromatic rings. The peak at 325 nm in the UV-Vis spectrum of 8 (Figure 5) and those at 310 nm and 375 nm in the spectrum of 9 (Figure 6) correspond to these transitions. Finally, the peaks in the visible region of the UV-Vis spectra can be attributed to the metal to ligand charge transfer (MLCT) between the Ni $d\pi$ and ligand $\pi^*$ orbitals. In 8, these transitions occur at 405, 470, and 515 nm, while in 9, the transitions occur at 465 and 700 nm. These absorbances in the visible region match with the observed color of the complexes.

![Figure 5. UV-Vis absorbance spectrum of 8 in dichloromethane](image)
Once characterized, the two complexes were tested for their ability to electrocatalytically generate hydrogen. Cyclic voltammograms (CVs) of crystals of 8 in CH$_3$CN reveal a reversible redox couple for Ni(II/I) at -0.85 V vs. SCE (Figure 7). An irreversible reduction event at -1.35 V vs. SCE occurred upon addition of a proton source, trifluoroacetic acid (TFA). Subsequent additions of TFA caused larger current enhancements at this potential, and an $i_c/i_p$ of 6.4 was observed in the presence of 0.66 mM TFA (Figure 8). This current enhancement signifies the presence of catalytic proton reduction at -1.35 V. A plot of peak current density of the catalytic reduction peak vs. TFA concentration demonstrates a linear relationship between catalytic activity and proton concentration, which corresponds to a second order reaction with respect to [H$^+$]. (Figure 9)
Figure 7. CVs of 0.5 mg 8 in 5 mL CH₃CN with 0.1 M TBAPF₆ scanned from -0.40 to -1.20 V with no acid added at 150 mV/s (black), 300 mV/s (red), 450 mV/s (orange), 600 mV/s (green), 750 mV/s (blue), and 900 mV/s (purple).

Figure 8. CVs of 0.5 mg 8 in 5 mL CH₃CN with 0.1 M TBAPF₆ from 0.00 to -1.40 V at a scan rate of 200 mV/s without acid added (black) and in the presence of 0.22 mM (red), 0.33 mM (yellow), 0.44 mM (green), 0.55 mM (blue), and 0.66 mM (purple) TFA. A catalytic reduction is observed at -1.35 V with an $i_c/i_p$ of 6.4.
To obtain the overall rate equation for 8, the dependence of current density on catalyst concentration was determined (Figure 10). The linear correlation between peak current density and [TFA] ($R^2 = 0.98$) indicates a second order reaction with regards to acid concentration.

Figure 9. Peak current density vs. [TFA] corresponding to Figure 8. The linear relationship between peak current density and [TFA] ($R^2 = 0.98$) indicates a second order reaction with regards to acid concentration.

To obtain the overall rate equation for 8, the dependence of current density on catalyst concentration was determined (Figure 10). The linear correlation between peak current density and catalyst concentration (Figure 11) indicates a first order reaction in catalyst. Thus, the overall rate expression for proton reduction by 8 is $R = k[8][H^+]^2$. 
Figure 10. CVs of 5 mL CH$_2$CN containing 30 µL of 0.11 M TFA from 0.00 to -1.40 V at 200 mV/s with 0.02 mM (black), 0.03 mM (red), 0.04 mM (green), and 0.05 mM (blue) 8 added in the presence of 0.1M TBAPF$_6$.

Figure 11. Peak current density vs. [8] corresponding to Figure 10. The linear relationship between peak current density and [8] ($R^2 = 0.98$) indicates a first order reaction with regards to [8].
The acid addition study provides some insight into the mechanism of proton reduction. The redox couple for Ni(II/I) remains at -0.85 V upon addition of TFA, indicating that an electrochemical reduction occurs before the chemical step in the mechanism. After reduction from Ni(II) to Ni(I), the complex gets protonated and an increase in current density with subsequent TFA additions is observed at -1.35 V vs. SCE. To determine whether this increased current density corresponds to catalytic activity of the complex, the \(i_c/i_p\) had to be calculated. Catalytic activity is defined by having a ratio peak current density in the presence of acid \((i_c)\) to peak current density with no acid present \((i_p)\) greater than four. The acid addition study demonstrates that the \(i_c/i_p\) for 8 equals 6.4, which indicates that the complex is indeed catalytic.

The electrocatalytic activity of 9 was also examined. Cyclic voltammograms of 9 in CH\(_3\)CN reveal a reversible redox couple for Ni(II/I) at -0.85 V vs. SCE (Figure 12). An irreversible redox event at -1.10 V vs. SCE occurred upon addition of TFA. Subsequent additions of TFA caused larger current enhancements at this potential, and an \(i_c/i_p\) of 42.9 was observed with 30 µL of TFA added (Figure 13). This significant current enhancement indicates catalytic proton reduction occurring at -1.10 V.
Figure 12. CVs of 0.5 mg 9 in 5 mL CH₃CN with 0.1 M TBAPF₆ scanned from -0.40 to -1.20 V with no acid added at 150 mV/s (black), 300 mV/s (red), 450 mV/s (orange), 600 mV/s (green), 750 mV/s (blue), and 900 mV/s (purple).

Figure 13. CVs of 0.5 mg of 9 in 5 mL of CH₃CN with 0.1 M TBAPF₆ from 0.00 to -1.60 V at a scan rate of 200 mV/s without acid added (black) in the presence of 2.2 mM (red), 4.4 mM (green), and 6.6 mM (blue) of 1.1 M TFA.
Often, complexes that function in systems for electrocatalytic proton reduction also have the ability to generate hydrogen photocatalytically. Therefore, once complex 8 was determined to be an active electrocatalyst, it was of interest to incorporate it into a system for photocatalytic hydrogen evolution. In such a system, a solution of photosensitizer, catalyst, and sacrificial donor is irradiated by light, and electron transfer occurs via collisions between these species. There are several options for compounds that can be used as photosensitizers, including ruthenium (II) tris-bipyridine ([Ru(bpy)_3]^{2+}), fluorescein, and eosin Y. While [Ru(bpy)_3]^{2+} is the most stable of the three photosensitizers, it contains a noble metal, making it very expensive. On the other hand, fluorescein and eosin Y are both organic dyes that are relatively inexpensive and thus would be more viable for integration into a large-scale system for photocatalytic proton reduction. Due to the cathodic electrochemical redox potential of 8, it was hypothesized that 8 would be a good candidate for photocatalytic proton reduction using fluorescein as the photosensitizer. In its excited state, fluorescein has a reduction potential of -1.70 V vs. SCE.\(^{30}\)

To maximize the amount of hydrogen generated, the conditions and experimental set-up of the photochemical system were optimized. Experiments were performed that varied the concentration of either fluorescein or catalyst while keeping the other constant. It was expected that a higher fluorescein concentration would be favorable because it would reduce the likelihood of the chromophore being destroyed by light, which is known as photobleaching. Similarly, increasing catalyst concentration should increase H\(_2\) generation. However, too high a catalyst concentration will result in low TONs because H\(_2\) production does not increase linearly with catalyst concentration. Other parameters
that were optimized included the distance of the sample test tubes from the light source and the light filter wavelength used when irradiating the solutions. Samples too close to the arc lamp overheat, which promotes fluorescein decomposition and photobleaching. On the other hand, samples too far from the lamp do not receive high enough intensity light to efficiently excite fluorescein. It was found that setting the test tube ring stand 41.5 cm from the arc lamp produced the best results. Additionally, the optimal light wavelength filter was found to be 455 nm. This filter prevents wavelengths below 455 nm from reaching the samples, which prolongs the lifetime of the system, since exposure to short wavelengths might induce fluorescein decomposition.

First, an experiment was performed to determine the optimal catalyst concentration. When catalyst concentration was increased from \(7.50 \times 10^{-7}\) M to \(1.25 \times 10^{-6}\) M, the turnovers of \(H_2\) also increased. However, catalyst concentrations above \(1.25 \times 10^{-6}\) M in solution of \(0.36\) M TEA and \(1.15 \times 10^{-3}\) M fluorescein had slightly lower \(H_2\) turnover numbers. The low TON at these high concentrations can be attributed to bleaching of the fluorescein or to self-quenching, which limits the lifetime of the system. With a catalyst concentration of \(1.25 \times 10^{-6}\) M, a TON of 1100 was observed, indicating that the system is active for photocatalytic hydrogen generation. The results of the experiment are depicted in Table 3.

<table>
<thead>
<tr>
<th>[Fluorescein] (M)</th>
<th>[Catalyst] (M)</th>
<th>(H_2) (µL)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.15 \times 10^{-3})</td>
<td>(7.50 \times 10^{-7})</td>
<td>24.8</td>
<td>370</td>
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<tr>
<td>(1.15 \times 10^{-3})</td>
<td>(1.00 \times 10^{-6})</td>
<td>85.4</td>
<td>950</td>
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<tr>
<td>(1.15 \times 10^{-3})</td>
<td>(1.25 \times 10^{-6})</td>
<td>123</td>
<td>1100</td>
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<tr>
<td>(1.15 \times 10^{-3})</td>
<td>(1.50 \times 10^{-6})</td>
<td>6.67</td>
<td>49</td>
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</table>

Table 3. Photocatalytic \(H_2\) generation with \(1.15 \times 10^{-3}\) M fluorescein, \(0.36\) M TEA, and varying concentrations of 8. The optimal catalyst concentration was found to be \(1.25 \times 10^{-6}\) M, yielding a TON of 1100.
At the ideal catalyst concentration, an experiment was performed varying the fluorescein concentration to further optimize the system. In general, TONs increased with increasing fluorescein concentration, but there was some variation. The TONs ranged from 170 to 470, with the highest TON occurring at a $1.8 \times 10^{-3}$ M fluorescein concentration. The results of the experiment are depicted in Table 4.

<table>
<thead>
<tr>
<th>[Fluorescein] (M)</th>
<th>[Catalyst] (M)</th>
<th>$H_2$ ($\mu$L)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8.0 \times 10^{-4}$</td>
<td>$1.25 \times 10^{-6}$</td>
<td>19.6</td>
<td>170</td>
</tr>
<tr>
<td>$1.0 \times 10^{-3}$</td>
<td>$1.25 \times 10^{-6}$</td>
<td>27.1</td>
<td>240</td>
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<td>$1.6 \times 10^{-3}$</td>
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<td>26.4</td>
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<tr>
<td>$1.8 \times 10^{-3}$</td>
<td>$1.25 \times 10^{-6}$</td>
<td>53.2</td>
<td>470</td>
</tr>
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</table>

Table 4. Photocatalytic $H_2$ generation with $1.25 \times 10^{-6}$ M 8, 0.36 M TEA, and varying concentrations of fluorescein. The optimal fluorescein concentration was found to be $1.8 \times 10^{-3}$ M, yielding a TON of 470.

As previously mentioned, the turnover number for hydrogen generation by 8 can be determined using a calibration curve comparing the peak areas of $H_2$ and $CH_4$ in a gas chromatogram. Based on the calibration curve, the amount of $H_2$ produced ($\mu$L) is linearly related to the area ratio of $H_2$ to $CH_4$ with a slope of 201.16, as shown in equation (3).

$$\mu L H_2 = 201.16 \left( \frac{Area H_2}{Area CH_4} \right)$$

Equation (3)

TON is defined as moles of $H_2$ per mole of catalyst. Moles of catalyst are determined during the experimental set-up and moles of $H_2$ can be calculated from $\mu$L.
Thus, TONs for the [Ni^{II}(Httfasbz)] system can be calculated in the following manner:

\[
\mu L H_2 = 201.16 \frac{18266.6}{29758.5} = 123.5 \\
123.5 \mu L H_2 \times \frac{1 L}{1 \times 10^6 \mu L} \times \frac{1 mol}{22.4 L} = 5.51 \times 10^{-6} mol H_2 \\
50 \mu L catalyst \times \frac{1 L}{1 \times 10^6 \mu L} \times \frac{0.1 mmol}{1 L} \times \frac{1 mol}{1000 mmol} = 5 \times 10^{-9} mol \\

TON = \frac{5.51 \times 10^{-6} mol H_2}{5 \times 10^{-9} mol catalyst} = 1100
\]

In order to determine a turnover frequency (TOF) for hydrogen generation, the production of hydrogen was analyzed over time by GC analysis. Hydrogen production was observed after one hour of irradiation but in amounts too small to be accurately integrated and measured by the calibration curve. Once hydrogen generation could be detected, it was seen to increase linearly for over 28 hours \((R^2 = 0.9995)\) (Figure 14). The slope of the linear trendline gives a TOF of 26.5 \(\mu L \ H_2 \ hr^{-1}\) for 8.

**Figure 14.** Amount of \(H_2\) produced (\(\mu L\)) by a solution of fluorescein (1.70 \(x\) \(10^{-4}\) M), 8 (5 \(x\) \(10^{-5}\) M), and 5% V/V TEA over time. \(H_2\) generation shows a linear correlation to time \((R^2 = 0.9995)\) and is produced at a rate of 26.5 \(\mu L \ H_2 \ hr^{-1}\).
Systems for photocatalytic proton reduction can proceed through two pathways, reductive quenching and oxidative quenching (Figure 15). In the reductive quenching pathway, light excites the fluorescein, which then gets reduced by the sacrificial donor, TEA. The reduced fluorescein ($\text{Fl}^-$) donates an electron to the catalyst, which can then reduce protons to hydrogen. In oxidative quenching, the excited fluorescein transfers an electron to the catalyst prior to being reduced by TEA. This pathway proceeds through an oxidized fluorescein intermediate, which is significantly more stable than $\text{Fl}^-$. In fact, production of $\text{Fl}^-$ can lead to photobleaching, and the catalytic system will no longer function. Thus, in theory, proceeding through oxidative quenching would result in a system with a longer lifetime and increased TON. The expected mechanistic pathway of a given photocatalytic system can be determined based on the rate of quenching of the fluorescein excited state by TEA and catalyst. A faster rate of quenching by TEA favors the reductive quenching pathway, while a faster rate of quenching by the catalyst favors the oxidative quenching pathway.

**Figure 15.** Reductive and Oxidative Quenching Pathways
To better understand the photocatalytic mechanism of our system, quenching studies were performed to monitor fluorescence quenching by both 8 and TEA. The fluorescence quenching of Fl* by 8 was performed in a solution of 1:1 H₂O:EtOH at pH 13 to mimic the conditions of the photochemical experiments. The Stern-Volmer plot of fluorescein quenching by 8 showed positive curvature at higher quencher concentrations, which indicates that the system is undergoing both static quenching and dynamic quenching31 (Figure 16). Static quenching could result from either fluorescein pi-stacking or bonding between fluorescein and nickel. Using a linear Stern-Volmer relationship, a quenching coefficient of 5.01 x 10¹² M⁻¹ s⁻¹ was obtained for 8, which represents the combined contributions of both static and dynamic quenching. The occurrence of both static and dynamic quenching explains the observation of a quenching coefficient beyond the diffusion limit of 1 x 10¹⁰ M⁻¹ s⁻¹. On the other hand, only dynamic quenching was seen for the fluorescence quenching of Fl* by TEA. The quenching followed a linear Stern-Volmer relationship with a quenching coefficient of 3.00 x 10⁸ M⁻¹ s⁻¹ (Figure 17).

**Figure 16.** Fluorescence Quenching of Fl* (4.0 x 10⁻³ M) by 8 in 1:1 EtOH:H₂O at pH = 13. Emission spectra (left) and Stern-Volmer plot (right).
Knowing the quenching coefficients and concentrations of 8 and TEA used in each experiment allows for the determination of the favored photochemical pathway. For both the fluorescein concentration and catalyst concentration experiments, the concentration of TEA in each sample was 0.36 M. With a quenching coefficient of $3.00 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ for TEA, the quenching rate is calculated to be $1.1 \times 10^8 \text{ s}^{-1}$. In the same experiments, the catalyst concentration ranged from $7.50 \times 10^{-7}$ M to $1.50 \times 10^{-6}$ M. With a quenching coefficient of $5.01 \times 10^{12} \text{ M}^{-1}\text{s}^{-1}$ for 8, the quenching rates are between $3.56 \times 10^6 \text{ s}^{-1}$ and $7.52 \times 10^6 \text{ s}^{-1}$. In all cases, the TEA quenching rate exceeds that of the catalyst, and thus reductive quenching is favored. However, decreasing the TEA concentration and increasing the concentration of 8 can produce the desired oxidative quenching pathway. With a catalyst concentration of $5.0 \times 10^{-5}$ M and a TEA concentration of $7.0 \times 10^{-2}$ M, the quenching rates of 8 and TEA are $2.5 \times 10^8 \text{ s}^{-1}$ and
2.1 \times 10^7 \text{s}^{-1}, \text{respectively. Thus, since the catalyst operates at a faster rate, the reaction is more likely to occur through the oxidative quenching pathway.}

Using the aforementioned conditions that favor oxidative quenching, an experiment was performed that measured the amount of H$_2$ (µL) generated over time (Figure 18). Hydrogen production increased linearly for 30 hours but began to plateau at 31 hours. The sacrificial donor was replenished by adding 4 µL of TEA, and H$_2$ production increased back to its former rate. Sacrificial donor had to be replenished again after 48 hours of irradiation, and the system lasted for 22 more hours until the rate of H$_2$ production began to decrease again. The observation of continued H$_2$ production after over 70 hours of irradiation indicates that the stability of this system for photocatalytic H$_2$ generation is greatly enhanced under oxidative quenching conditions and confirms the hypothesis that this pathway is more desirable.

**Figure 18.** H$_2$ generation (µL) over time from a solution of fluorescein (5 \times 10^{-4} M), 8 (5 \times 10^{-5} M), and 1.96% V/V TEA. 0.1% V/V TEA was added after 31 hours and 48 hours of irradiation.
To further examine the photocatalytic mechanism, UV-Vis absorption was performed on a solution of catalyst, fluorescein, and TEA in 1:1 EtOH:H₂O. Using substrate concentrations equivalent to those in the H₂ generation experiments results in too high a fluorescein absorbance and too low a catalyst absorbance to be effectively studied. Nonetheless, UV-Vis spectra of samples with low fluorescein and high catalyst concentration still provide insight into the mechanism of photochemical catalysis (Figure 19). A relatively linear decrease in fluorescein absorbance ($\lambda = 490$ nm) was observed over time. An absorbance peak corresponding to 8 ($\lambda = 427$ nm) showed an increase in absorbance for the first 8 hours of irradiation, but decreased significantly by 22 hours of irradiation. Additionally, beginning at 5 hours of irradiation, a new absorbance peak grew in around 470 nm, which may be attributed to the anion form of fluorescein ($\lambda = 472$ nm).³² This result would indicate that the fluorescein is getting protonated at some point during the catalytic cycle. However, a more likely explanation is that the new peak around 470 nm appears as a result of static quenching of the chromophore by the catalyst. Static quenching causes the formation of a new catalyst-fluorescein complex, which absorbs at its own unique wavelength, slightly different from that of just fluorescein.³³ The absorbance for the 470 nm peak increased from 5 to 8 hours of irradiation, indicating that more static quenching occurs as the reaction proceeds. However, as with the other absorption peaks, the absorbance around 470 nm decreased substantially after 22 hours of irradiation, which suggests that both fluorescein and catalyst decompose over time.
To ensure that complex 8 was indeed acting as a catalyst for electrocatalytic and photocatalytic proton reduction, several control experiments were performed. Direct reduction of TFA can occur at the working electrode, so CVs were taken of TFA in CH$_3$CN to demonstrate that the background current from TFA is negligible (Figure 20). Current density enhancement from direct reduction of TFA increased slightly with increasing concentrations of TFA, but the majority of the current is used by the catalyst for proton reduction.

**Figure 19.** UV-Vis Spectra of a solution of fluorescein (6.67x10$^{-6}$ M), 8 (1.3x10$^{-4}$ M) and 5% V/V TEA:H$_2$O after 4 (black), 5 (red), 7 (yellow), 8 (green), and 22 (blue) hours of irradiation with light from an arc lamp.
The stability of the catalyst in the solution was tested under both electrochemical and photochemical conditions by performing control experiments using NiCl₂ and 6.

CVs of NiCl₂ in CH₃CN demonstrated an irreversible redox couple at -0.99 V vs. SCE with no acid added. Upon addition of 10 µL of TFA as a proton source, the irreversible redox event shifted to -1.14 V vs. SCE and was accompanied by current enhancement (Figure 21). Subsequent acid additions shifted the redox event to more cathodic potentials and showed a greater current enhancement. However, with a 30 µL addition of TFA, the \( i_c/i_p \) is only 2.87, which indicates that NiCl₂ is not an active catalyst for proton reduction. Additionally, it is clear that the catalytic activity of 8 does not result from decomposition of the complex and a reduction event at the nickel alone, as the Ni(II/I) redox potential in the CVs of 8 does not match with that of NiCl₂.

**Figure 20.** CVs scanned from 0.00 to -1.40 V in CH₃CN upon addition of 15 µL (black), 20 µL (purple), 25 µL (blue), and 30 µL (green) of TFA (0.11 M).
To demonstrate that the same distinction between 8 and NiCl₂ can be made for photochemical proton reduction, an experiment was performed at the optimized conditions for H₂ evolution by 8 except NiCl₂ replaced 8 in solution. After 18 hours of irradiation, the samples produced TONs around 200, which is significantly less than the TONs produced in the same amount of time by 8. Thus, it can be concluded that decomposition of 8 does not account for the photocatalytic proton reduction event.

To further support this conclusion, UV-Vis studies were performed using solutions of NiCl₂ and 6 in fluorescein with 5% V/V TEA:H₂O (Figures 22-23). In the experiment with NiCl₂, only absorbance by fluorescein (λ = 490 nm) was observed in the

**Figure 21.** CVs of 0.5 mg of NiCl₂ in 5mL of CH₃CN scanned from 0.00 to -1.40 V without acid and upon addition of 10 µL (blue), 20 µL (green), and 30 µL (black) of 0.11 M TFA.
visible region. After just two hours of irradiation, the solution had bleached and fluorescein absorbance was significantly reduced (Figure 22).

![UV-Vis spectra](image)

**Figure 22.** UV-Vis spectra of NiCl$_2$ (1.3 x 10$^{-4}$ M), fluorescein (1.3 x 10$^{-5}$ M), and 5% TEA/H$_2$O before (blue) and after 2 hours (orange) of irradiation with light from an arc lamp.

In the experiment with 6, the initial UV-Vis spectra showed fluorescein absorbance at 490 nm and absorbance by 6 in the UV region ($\lambda = 350$ nm). After one hour of irradiation, the ligand absorption remained unchanged, but the fluorescein peak had decreased dramatically (Figure 23). Since neither experiment showed additional peaks in the visible region upon irradiation, it can be concluded that the catalyst is not decomposing into ligand and nickel during the photochemistry experiments.
Even after confirming that 8 does not decompose during catalysis, it was necessary to demonstrate that it operates as a homogeneous catalyst and does not form nanoparticles. The formation of a heterogeneous species on the electrodes during electrocatalytic proton reduction can be evaluated with a rinse test. For this experiment, a CV was taken of the catalyst in CH$_3$CN with acid added to show the catalytic reduction event. Then, the electrodes were rinsed and moved into a cell containing only CH$_3$CN, and another CV was taken (Figure 24). If there are heterogeneous deposits on the electrodes, the second scan will also show a catalytic proton reduction event. However, in this case, no catalytic activity was observed after rinsing, which confirms that a heterogeneous substance did not form on the electrode surface during catalysis and

**Figure 23.** UV-Vis spectra of 6 (1.3 x 10$^{-4}$ M), fluorescein (1.3 x 10$^{-5}$ M), and 5% TEA/H$_2$O before (blue) and after 1 hour (orange) of irradiation with light from an arc lamp.
indicates that 8 operates as a homogeneous catalyst for electrocatalytic proton reduction. Additionally, it is important to note that no change in catalytic activity was observed when mercury was added to the catalytic system. This indicates that the complex does not form nanoparticles, but rather operates as a homogeneous catalyst for hydrogen generation.

Figure 24. CV of 0.5 mg of 8 with 30 µL of TFA (0.11 M) in 5 mL of CH₃CN scanned from 0.00 to -1.40 V (black). CV using the same unpolished electrodes in 5 mL of CH₃CN scanned from 0.00 to -1.40 V (purple).
Conclusion

Two new Ni-NNSS Schiff base complexes, 8 and 9, were synthesized and characterized. [NiII(Httfasbz)] was analyzed as both an electrocatalyst and photocatalyst for proton reduction, while [NiII(L2)] was examined only as an electrocatalyst. X-ray diffraction of slow-diffusion grown crystals demonstrated a square planar geometry for both complexes. Interestingly, in order to maintain the favorable $d^8$ square planar configuration, bonding between the ligand and metal occurs asymmetrically, since the ligand assumes its dianionic form. The complexes compromise steric stability for lower crystal field stabilization energy by forming a 7-membered ring and a 4-membered ring instead of the expected 5 and 6-membered rings. Both 8 and 9 were soluble in organic solvents and diamagnetic.

Cyclic voltammetry revealed 8 and 9 to be active electrocatalysts for proton reduction in acetonitrile, with $i_c/i_p$ values of 6.4 and 42.9, respectively. H$_2$ evolution from TFA by 8 was observed at a potential of -1.35 V vs. SCE, while 9 operated at a potential of -1.10 V vs. SCE. The tendency of 9 to decompose upon acid addition prevented further electrochemical studies, but 8 was characterized to determine its rate equation for electrocatalytic proton reduction. Linear relationships for both acid and catalyst concentration with respect to peak current density indicated that the rate of proton reduction by 8 is first order with respect to catalyst and second order with respect to acid. Thus, the rate expression is given by $R = k[8][H^+]^2$.

Complex 8 was further studied for its ability to function in a system for photochemical hydrogen generation. The catalyst and fluorescein concentrations were optimized at $1.25 \times 10^{-6}$ M and $1.80 \times 10^{-3}$ M, respectively. TONs of over 1100 were seen
after 18 hours of irradiation by an arc lamp, indicating that the system is active for photocatalytic H₂ production. Upon altering the concentrations of 8 and TEA to favor the oxidative quenching pathway, the system continued to generate H₂ for over 70 hours, which demonstrates that it is very stable. This system for photochemical hydrogen generation is desirable because it is noble metal free, making it inexpensive and viable for widespread use. Although the photocatalytic system is both active and stable when irradiated with light from an arc lamp, current efforts are being made to test the system with green-emitting LEDs. The green LEDs emit light at 520 nm,²⁰ which is close to the absorption maximum of fluorescein (490 nm). Therefore, the LEDs will excite fluorescein more readily, which in turn should increase the activity of the photocatalytic system.

Additionally, future work will include developing similar catalysts through modifications of 6 and studying 8 and 9 in other catalytic systems. Ligand 6 will be tuned to vary its electron-donating or electron-withdrawing properties and observe the effects on proton reduction capabilities in both electrochemical and photochemical systems. Furthermore, 9 will be studied for its activity as a photocatalyst for hydrogen generation. As an electrocatalyst, 9 was found to be more active than 8, so it is hypothesized that 9 will also be highly active in a system for photocatalytic proton reduction. Finally, the negative reduction potentials of both 8 and 9 make them attractive for integration into systems for electrocatalytic CO₂ reduction, which has been reported to occur at potentials between -1.30 and -1.60 V vs. SCE.³⁴
Appendix

Figure A1. $^1$H NMR of 6 in DMSO with integrations in blue.
Figure A2. $^{13}$C NMR of 6 in CDCl$_3$. 
Figure A3. $^1\text{H}$ NMR of 7 in CDCl$_3$. 
Figure A4. $^1$H NMR of 8 in CDCl$_3$ with integrations shown in blue.
Figure A5. $^{13}$C NMR of $8$ in CDCl$_3$. 
Figure A6. High-resolution mass spectrum of 8 in H₂O/MeOH. Analysis was completed through positive electrospray ionization on a Burker 12 Tesla APEX-Qe FTICR-MS with an Apollo II ion source. The expected molecular ions were observed with a difference of less than 1 ppm.
Figure A7. $^1$H NMR of 9 in CDCl$_3$ with integrations in blue.
Figure A8. High-resolution mass spectrum of 9 in H$_2$O/MeOH. Analysis was completed through positive electrospray ionization on a Burker 12 Tesla APEX-Qe FTICR-MS with an Apollo II ion source. The expected molecular ions were observed with a difference of less than 1 ppm.
Figure A9. Calibration curve of H$_2$ to CH$_4$ peak areas used for determination of photochemical hydrogen generation. The ratio of peak areas was plotted against the volume of H$_2$ injected into the GC. ($R^2 = 0.998$)
References
10 Eisenberg, R. Science, 2009, 324, 44-45.