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## A Nickel Complex of a Conjugated Bisdithiocarbazate Schiff Base for the Photocatalytic Production of Hydrogen

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**ABSTRACT.** We report a nickel complex containing a conjugated bis-dithiocarbazate ligand that is an active catalyst for the reduction of protons into hydrogen gas. Light-driven hydrogen generation is observed from a system containing this molecular nickel catalyst coupled with a fluorescein photosensitizer and triethylamine sacrificial donor. The photocatalytic system is stable for over 70 hours, achieving 3300 turnovers with respect to catalyst. The complex is also an active electrocatalyst for proton reduction with catalysis occurring at -1.7 V vs. Fc<sup>+</sup>/Fc. The nickel bis-dithiocarbazate complex represents a highly active and stable catalyst for hydrogen generation.

### Introduction

Converting solar energy into stored chemical potential in the form of fuel is a promising solution to increasing energy demands.<sup>1-3</sup> The process of artificial photosynthesis (AP) utilizes photons to split water into  $O_2$  and  $H_2$ .<sup>1</sup> The reductive side of this process involves the conversion of protons into H<sub>2</sub> upon irradiation with visible light. Early work in this area relied on the use of noble metals that are able to reduce protons at low overpotential.<sup>2</sup> More recently, the focus has shifted towards developing systems that utilize catalysts containing earth-abundant metals such as iron,<sup>3</sup> cobalt,<sup>4</sup> nickel,<sup>5</sup> and molybdenum.<sup>6</sup> Typically, photocatalytic systems for hydrogen generation contain a catalyst, photosensitizer (PS), and a sacrificial source of electrons.<sup>7</sup> A significant problem with many homogeneous noble-metal-free systems is that hydrogen generation often ceases after 10-16 hours of irradiation.<sup>4,5</sup> In systems containing organic chromophores, this instability is often due to the generation of PS radical anions that undergo decomposition when the system operates through a reductive quenching pathway.<sup>8</sup> Therefore, it is of great interest to develop robust photocatalytic systems containing earth abundant metals that generate hydrogen in aqueous solutions. Herein we report a homogeneous nickel complex containing a bisdithiocarbazate Schiff base ligand for the photocatalytic generation of hydrogen from aqueous solutions.

Recently, the use of redox-active ligands in catalysts for hydrogen generation has been explored.<sup>9</sup> Furthermore, synergy between metaland ligand- based redox activity can improve the performance of proton reduction catalysts.<sup>10</sup> A particularly interesting class of redox active ligands involves conjugated bis-dithiocarbazate Schiff base compounds bearing N<sub>2</sub>S<sub>2</sub> donor atoms (Figure 1).<sup>11</sup> Ligand **1** displays an irreversible reduction at -1.9 V vs. Fc<sup>+</sup>/Fc (see supporting information) and tetradentate analogues containing only N-donor atoms have been found to be redox active.<sup>12</sup> Copper complexes containing **1** were reported, and Cu<sup>III</sup>, Cu<sup>II</sup>, and Cu<sup>I</sup> redox states were observed using electrochemical and computational techniques.<sup>11</sup> Interestingly, it was determined that the ligand did not undergo any redox reactions when coordinated to Cu.<sup>11</sup> The remarkable ability of the ligand to stabilize Cu in three different oxidation states, coupled with the potential redox activity of the ligand made it of interest to examine the implementation in the multielectron chemistry of H<sub>2</sub> production.



Figure 1. Left: Bis-dithiocarbazate ligand (1). Right: Nickel catalyst (2).

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To this end, we have synthesized a nickel complex containing a bisdthiocarbazate ligand (2). The complex acts as an electrocatalyst for proton reduction, with catalysis occurring at -1.7 V vs.  $Fc^+/Fc$ . When 2 is combined with fluorescein (FI) as the PS and triethylamine (TEA) as the sacrificial electron donor, the system generates hydrogen upon irradiation with visible light. The system is remarkably stable, producing hydrogen for 3 days. Herein we describe the structure and catalytic activity of this unique nickel catalyst.

#### 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 (3).** This procedure was modified from a literature method.<sup>13</sup> 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 and cooled to 0°C. Carbon disulfide (12.05 mL, 0.20 mol) was added drop-wise to the cooled solution over 2 hours. Benzyl chloride (23.0 mL, 0.20 mol) was also added drop-wise over 2 hours. A white precipitate formed upon addition of benzyl chloride. The precipitate was collected via vacuum filtration, washed with water, and dried overnight to give a white powder (33.4% yield). The <sup>1</sup>H and <sup>13</sup>C NMR spectra matched what was reported in the literature.<sup>13</sup>

(2*Z*, 2'*Z*)-dibenzyl 2,2'-(4,4,4-trifluoro-1-(thiophen-2-yl)butane-1,3-diylidene)bis(hydrazinecarbodithioate) (1). The ligand was synthesized according to literature procedure.<sup>11</sup> A solution of **3** (567.2 mg, 2.86 mmol) in 12.5 mL of EtOH was stirred and heated to reflux. Upon heating, the solution turned clear and colorless. To this solution, 4-thenoly-2,2,2-trifluoroacetone (317.9 mg, 1.43 mmol) was added. The resulting yellow solution was refluxed for 24 hours. An off-white precipitate formed and was collected via vacuum filtration to yield 19.3% of the white product. The <sup>1</sup>H and <sup>13</sup>C NMR spectra matched literature values.<sup>11</sup> <sup>1</sup>H NMR (DMSO-d6)  $\delta$ : 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 39.0, 39.8, 40.5, 88.7 (q, CF<sub>3</sub>), 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.

[**Ni<sup>II</sup>(Httfasbz)**] (2). This procedure was adapted from the previously reported [Cu<sup>III</sup>(ttfasbz)] synthesis.<sup>11</sup> In a Schlenk flask, 1 (75.0 mg, 0.128 mmol) was dissolved in 53.0 mL of methanol (MeOH) under Ar. The solution was stirred and heated at 65°C. A solution of nickel (II) acetate tetrahydrate (32.0 mg, 0.128 mmol) in 15 mL MeOH was added to the ligand solution via cannula. The

resulting solution was heated for 1 hour and then stirred an additional 2 hours at room temperature. A brown precipitate formed and was collected using 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 **2** in dicholormethane. MS: m/z expected = 638.96; m/z found = 638.96. Anal. Calcd. for NiC<sub>24</sub>H<sub>19</sub>F<sub>3</sub>N<sub>4</sub>S<sub>5</sub>: C, 45.08%; H, 2.99%; N, 8.76%. Found: C, 45.20%; H, 3.17%; N, 8.81%. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 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.

#### Instrumentation

<sup>1</sup>H and <sup>13</sup>C NMRs were performed on an Agilent 400MR DD2 instrument operating in pulse Fourier transform mode. Chemical shifts were referenced to residual solvent. Mass spectrometry was carried out 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 K $\alpha$  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 (diameter = 0.30 cm), a Pt auxiliary electrode, and an SCE reference electrode. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, 0.1 M) was used as the electrolyte. Ferrocene was added and used as an internal reference. All electrochemical experiments were performed under an Ar atmosphere. The working and auxiliary electrodes were polished with alumina powder paste (0.05  $\mu$ m) on a cloth-covered polishing pad and then rinsed with water and acetonitrile before each scan (unless otherwise noted). For the acid addition experiments, trifluoroacetic acid (TFA) was added under argon.

Acid Addition Study. In an electrochemical cell, 0.5 mg of crystals of **2** were dissolved in 5.0 mL of 0.1 M TBAPF<sub>6</sub> in  $CH_3CN$ . Cyclic voltammograms (CVs) were obtained at different concentrations of [TFA].

**Bulk Electrolysis.** Controlled-potential coulometry (CPC) experiments were conducted in a closed 500 mL four-neck roundbottom flask. Complex **2** (0.5 mg) was added to 50 mL of 0.1 M TBAPF<sub>6</sub> in CH<sub>3</sub>CN. The flask was capped with two vitreous carbon electrodes and a silver wire reference electrode, all submerged in solution and separated by VYCOR frits. A CPC was run at -1.8 V vs. Fc<sup>+</sup>/Fc for 1800s, resulting in a faradaic yield of 98%. No hydrogen was observed when the experiment was performed without catalyst.

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Scan Rate Dependence. In an electrochemical cell, 0.5 mg of 2 was dissolved in 5.0 mL of 0.1 M TBAPF<sub>6</sub> in CH<sub>3</sub>CN. Cyclic voltammograms were taken at scan rates ranging from 150 mV/s to 900 mV/s.

**Rinse Test.** This procedure was modified from an experiment reported by Dempsey et al.<sup>17</sup> A CV of 0.5 mg of **8** was taken in the presence of 0.66 mM TFA. The electrodes were then rinsed with CH<sub>3</sub>CN only (about 50 mL total). Without polishing, the electrodes were placed in a solution of 0.66 mM TFA in CH<sub>3</sub>CN and another CV was obtained.

Hydrogen Evolution Studies. Stock solutions were prepared of 2 (1  $x 10^{-4}$  M in CH<sub>3</sub>CN) and Fl (4.0 x 10<sup>-3</sup> 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. 2.0 mL of 10% V/V triethylamine (TEA)/H<sub>2</sub>O was added to each. The resulting solutions had a total volume of 4.0 mL with a 5% TEA concentration by volume. For each sample, 1.0 mL of Ar was removed from the headspace, and 1.0 mL of CH<sub>4</sub> was injected for use as an internal standard. The samples were then irradiated with light from green light-emitting diodes ( $\lambda$ =520 nm, 0.12 W). An LED ribbon was attached to the outside of a jacketed beaker. The beaker was cooled to 20 °C and the test tubes containing the samples were rotated inside the beaker (see supporting information). 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. The reported pH values were obtained using a Thermo Scientific Orion STAR A111 pH meter on the mixed solvent solutions. pH values were obtained before and after photolysis.

**Catalyst Concentration Studies.** Four test tubes were prepared, each with 1.60 mL of the 4.0 x  $10^{-3}$  M Fl stock solution. To the four test tubes, 30 µL, 40 µL, 70 µL, and 100 µL of a  $1.0 \times 10^{-4}$  M stock solution of **2** were added, respectively. Ethanol was added to each test tube to give a total volume of 2.0 mL. All of the test tubes were sealed with airtight septa, wrapped in aluminum foil, and degassed with Ar. To each sample, 2.0 mL of 10% V/V TEA/H<sub>2</sub>O was added, and the solution was degassed for an additional 15 minutes. The resulting solutions had a total volume of 4.0 mL with a 5% TEA (0.36 M) concentration by volume. CH<sub>4</sub> was used as an internal standard and the test tubes were irradiated with green LEDs overnight.

**Fluorescein Concentration Studies.** Six test tubes were prepared, each with 50  $\mu$ L of the 1.0 x 10<sup>-4</sup> M stock solution of **2**. To the test tubes, 4.0 x 10<sup>-3</sup> M Fl was added in amounts ranging from 1.0 mL to 1.8 mL. Ethanol was also added to give a total volume of 2.0 mL. The test tubes were sealed and degassed with Ar. While the solutions degassed, 2.0 mL of 10% V/V TEA/H<sub>2</sub>O was added to give a concentration 0.36 M TEA in each test tube. Methane was used as an internal standard and the test tubes were irradiated with green LEDs overnight.

Quenching Experiments. Stock solutions of fluorescein  $(4.0 \times 10^{-3} \text{ M in EtOH})$  and 2  $(8.0 \times 10^{-4} \text{ M in CH}_3\text{CN})$  were prepared. In an air-

free cuvette, 7.5  $\mu$ L of the fluorescein stock solution was diluted with 3.0 mL of a solution of 1:1 EtOH:H<sub>2</sub>O. 0.1 M KOH was added drop-wise to the aqueous ethanol solution to give a solution pH of 13.0. Both the catalyst and fluorescein solutions were purged with Ar for 20 minutes, and a positive pressure of Ar was maintained in the sample vials throughout the experiment using a balloon. Catalyst solution was added to the cuvette in 5  $\mu$ L increments, and the fluorescence intensity was monitored by exciting the sample at 430 nm with a PerkinElmer LS 55 Luminescence Spectrometer. Quenching of Fl with TEA followed a similar procedure.

**UV-Vis Absorption.** To examine the conditions of photocatalytic proton reduction,  $6.7 \times 10^{-6}$  M fluorescein and  $1.3 \times 10^{-4}$  M **2**, in ethanol were added to an airfree cuvette. While purging the solution with Ar, 1.5 mL of 10% V/V TEA/H<sub>2</sub>O was added to give a final TEA concentration of 5%. The cuvette was placed 25 cm from a Hg/Xe arc lamp and was irradiated with > 420 nm light. All UV-Vis absorption measurements were performed using an Agilent Cary 60 UV-Vis Spectrophotometer.

#### **Results and Discussion**

The ligand was synthesized according to literature procedure.<sup>11</sup> The reaction of ligand **1** with  $[Ni(OAc)_2]$  in methanol gave the neutral Ni<sup>II</sup> complex (**2**) in moderate yield (52%). Interestingly, the previously reported reaction of ligand **1** with  $[Cu(OAc)_2]$  gave a neutral complex with trivalent copper.<sup>11</sup> In the copper complexation reaction, the ligand acts as a tribasic acid; upon chelation, a methylene proton is abstracted by base to give a  $\beta$ -diketiminate backbone. However, when reacted with  $[Ni(OAc)_2]$ , the ligand acts as a dibasic acid, to give the neutral Ni<sup>II</sup> complex. Attempts to further deprotonate the ligand using additional equivalents of base were unsuccessful. X-ray quality crystals of **2** were obtained by slow diffusion of hexanes into a dichloromethane solution of **2**.



**Figure 2.** ORTEP diagram of **2**. Ellipsoids are at the 50% probability level with hydrogen omitted for clarity.

The structure confirms that the dibasic form of the ligand is coordinated to Ni to give a distorted square planar complex. The ligand forms 4, 5, and 7 membered chelate rings with S2-Ni-N1 and S3-Ni-N3 bond angles of 73.61° and 88.30°, respectively. Bond lengths of 1.293 Å and 1.314 Å are consistent with C-N double bonds. C-C bond lengths of ~1.5 Å for C9-C14 and C14-C15 are within the accepted range for C-C single bonds. This is in contrast Published on 13 July 2015. Downloaded by Yale University Library on 18/07/2015 13:36:03.

to what was observed for copper coordination. When coordinated to copper, the ligand is trianionic, forming a neutral Cu<sup>III</sup> complex.<sup>11</sup> The Cu complex is square planar forming only 5-membered chelate rings.<sup>11</sup> When coordinated to Ni, the ligand is dianionic, forming a neutral Ni<sup>II</sup> complex with less favorable 4- and 7-membered chelate rings.

Table 1. Selected	l bond	lengths	[Å]	and	angles	[°]	for <b>2</b> .
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Bond Length (Å)				
N(1)-N(2)	)	1.381(3)		
N(1)-C(8)	)	1.314(4)		
N(2)-C(9)	)	1.293(3)		
N(3)-N(4)	)	1.401(3)		
N(3)-C(15	5)	1.293(4)		
N(4)-C(17	7)	1.307(3)		
C(9)-C(14	4)	1.510(4)		
C(14)-C(1	5)	1.512(4)		
Bond Angle (°)				
S(2)-Ni(1)	)-N(1)	73.61(8)		
S(3)-Ni(1)	)-N(3)	88.30(7)		
Ni(1)-S(2	)-C(8)	76.16(9)		
Ni(1)-S(3	)-C(17)	94.75(9)		

A UV-Vis spectrum of the complex (see supporting information) shows absorption peaks at 380 nm, 470 nm, and 515 nm. The absorption band centered at 380 nm corresponds to MLCT, while the bands centered at 470 nm and 515 nm are characteristic of d-d transitions present in low-spin square planar Ni<sup>II</sup> complexes.<sup>14</sup>

Cyclic Voltammograms (CVs) of the complex in acetonitrile reveal a reversible redox couple for Ni(II/I) at -1.25 V vs. Fc<sup>+</sup>/Fc.



**Figure 3.** CVs of 0.16 mM **2** in  $CH_3CN$  with 0.1M TBAPF<sub>6</sub> 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 peak separation of 70 mV is observed under these conditions, which is consistent with what is observed for the Fc<sup>+</sup>/Fc redox couple under the same conditions. With the addition of known concentrations of trifluoroacetic acid (TFA), an irreversible reduction event is observed at -1.7 V vs. Fc<sup>+</sup>/Fc. When additional TFA is added, the current enhancement increases (Figure 3). TFA was chosen as the proton source due to the relatively small amount of background reduction that is observed at the catalytic potential of 2 (see supporting information). The current enhancement is linear with increasing [TFA], suggesting that catalysis is second order with respect to [TFA] (see supporting information). The catalyst is unstable at high acid concentrations and decomposes when [TFA] > 1 mM. The catalytic wave grows out of the Ni(II/I) redox couple at a more cathodic potential. Therefore, the first step is proposed to involve an electrochemical reduction, which is followed by protonation and reduction events (ECEC or ECCE). Similar to the previously reported cobalt dithiolene catalysts, protonation of can take place at either the metal or the coordinated sulfur atom.<sup>4,15</sup>

To confirm that this current enhancement corresponds to catalytic hydrogen generation, bulk electrolysis was performed at -1.8 V vs. Fc<sup>+</sup>/Fc. Hydrogen was observed in the bulk electrolysis, corresponding to a Faradaic yield of 98%.

With the recent discovery that oxime-containing catalysts suffer from ligand hydrogenation resulting in the deposition of a catalytically active film on the electrode surface, it was of interest to probe whether such a film was depositing on our electrode surface.<sup>16</sup> Additionally, a Ni precatalyst was recently reported that formed catalytically active films on the electrode surface.<sup>17</sup> In order to determine if a surface adsorbed species was being formed from their complex, the authors performed a rinse test.<sup>17</sup> They found that after catalysis, the complex left a catalytically active film on the glassy carbon electrode. This electrode was then used to generate hydrogen in a solution that contained only an acid, supporting electrolyte, and solvent. In contrast to this study, complex 2 has not been found to deposit a stable catalytically active film. In order to demonstrate this, a CV was taken with 2 in the presence of TFA to show the catalytic reduction event (Figure 4, black). This electrode was then rinsed with CH<sub>3</sub>CN rather than polishing and was placed in a cell containing only CH<sub>3</sub>CN, TFA, and supporting electrolyte. The resulting CV (Figure 4, purple) did not show a catalytic reduction event. Furthermore, when an electrode is used for bulk electrolysis with 2 at -1.8 V vs.  $Fc^+/Fc$ , no stable catalytically active film is observed on the electrode surface. Although these experiments do not definitively rule out the possibility of heterogeneous catalysis or ligand hydrogenation, they suggest that a stable catalytically active film is not being deposited on the electrode surface under these conditions.

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**Figure 4.** CV of 0.16 mM 2 with 0.66 mM TFA in CH<sub>3</sub>CN (black). CV using the same unpolished electrode in 5 mL of 0.66 mM TFA in CH<sub>3</sub>CN with no catalyst (purple). No catalytic wave is observed as a result of surface absorption.

When designing the photocatalytic system, it was of interest to incorporate a chromophore that was noble-metal-free and capable of reducing the complex. Fluorescein (Fl) was chosen for its ability to reduce catalysts with similarly cathodic reduction potentials.<sup>8</sup> Complex **2** is able to accept an electron from either 1Fl<sup>\*</sup> (-2.1 V vs. Fc<sup>+</sup>/Fc) or Fl<sup>-</sup> (-1.7 V vs. Fc<sup>+</sup>/Fc).<sup>8</sup> Photolysis of a solution of fluorescein, triethylamine, and **2** in 1:1 EtOH:H<sub>2</sub>O using green-light-emitting diodes ( $\lambda$ =520 nm, 0.12 W) at 20 °C resulted in H<sub>2</sub> generation. The evolution of hydrogen gas was measured by GC analysis of the headspace gases. Experiments without catalyst did not yield any observable hydrogen gas. Furthermore, the addition of 0.5 mL of Hg to the reaction vessel did not alter the hydrogen generation of the system, suggesting that colloidal Ni does not play a role in the observed hydrogen generation.

The system is most active between pH = 12.5-13, which is consistent with what has been previously reported for photocatalytic systems using Fl/TEA.<sup>8</sup> Hydrogen generation decreases at lower pH due to the photolytic decomposition of Fl at  $pH < 12.^{8,18}$ Additionally, TEA has been found to perform better as an electron donor at higher pH.<sup>8,19</sup> Owing to the proposed ECEC or ECCE mechanism for electrocatalysis with **2**, the first step in the photocatalytic system is likely the reduction of **2** to give **2**<sup>-</sup>. This is followed by protonation at either the metal center or on the ligand to give **2**-H. Reduction of **2**-H could give a [**2**-H]<sup>-</sup> intermediate that is protonated prior to the formation of H<sub>2</sub>.

The optimal catalyst and chromophore concentrations were found to be 1.25  $\mu$ M and 1.6 mM, respectively (see supporting information). Under these conditions, hydrogen generation increases linearly with time. Interestingly, hydrogen is evolved at a consistent rate for over

70 hours, corresponding to a turnover number (TON) of 3300 (Figure 5). Related homogeneous systems combing Ni catalysts with TEA and Fl have achieved up to 8000 TONs after 24 hours of irradiation with decomposition being observed after just 15 hours.<sup>5,8</sup> Although complex **2** exhibits lower activity, the system is remarkably stable compared to related systems.



**Figure 5.** Hydrogen production from systems containing **2** (1.25  $\mu$ M), Fl (1.6 mM), and TEA (5%) in 1:1 EtOH/H<sub>2</sub>O. The system was irradiated with  $\lambda$  = 520 nm LEDs.

Owing to the unprecedented stability of this system, it was of great interest to determine whether hydrogen generation proceeds through a reductive or oxidative quenching pathway. Reductive quenching has been observed in related systems in which TEA quenches the excited <sup>1</sup>FI\* to form FI<sup>-</sup> which ultimately reduces the catalyst.<sup>5,8</sup> Consistent with previously reported systems, we find that TEA quenches <sup>1</sup>FI\* under our experimental conditions (1:1 EtOH: H<sub>2</sub>O, pH = 13) following good Stern-Volmer behaviour with a quenching rate constant of 3.00 x 10<sup>8</sup> M<sup>-1</sup>s<sup>-1</sup> ± 0.045 x 10<sup>8</sup> M<sup>-1</sup>s<sup>-1</sup> (Figure 6).



**Figure 6.** *Left:* Emission spectra of Fl as a function of [TEA]; *Right:* Stern-Volmer plot for photoluminescence quenching of Fl by TEA.

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Since reductive quenching is thought to lead to Fl decomposition,<sup>8</sup> it was of interest to probe whether the system can operate under an oxidative quenching pathway. Through oxidative quenching, the catalyst is reduced by <sup>1</sup>Fl\* to give Fl<sup>+</sup> and **2**<sup>-</sup>. The oxidized photosensitizer is then reduced by TEA. Figure 7 shows the emission spectra of Fl as a function of [**2**]. The catalyst quenches <sup>1</sup>Fl\* under our experimental hydrogen generation conditions (1:1 EtOH: H<sub>2</sub>O, pH = 13) following Stern-Volmer behaviour with a quenching rate constant of 5.0 x  $10^{12}$  M<sup>-1</sup>s<sup>-1</sup> ± 0.18 x  $10^{12}$  M<sup>-1</sup>s<sup>-1</sup>. A rate constant that is two orders of magnitude greater than the diffusion limit suggests the presence of both static and dynamic quenching of <sup>1</sup>Fl\* by **2**, with static quenching referring to quenching that occurs through non-diffusive interactions.



**Figure 7.** *Left*: Emission spectra of Fl as a function of [2]; *Right*: Stern-Volmer plot for photoluminescence quenching of Fl by **2**.

Static quenching in this system could result from a  $\pi$ -stacking or covalent interaction between Fl and 2. With fluorescein existing largely as a dianion at pH = 13, it is possible for it to coordinate to the Ni through an anionic oxygen atom. To further examine this possibility, UV-Vis spectroscopy was used to monitor the system over time. In this study, a cuvette containing  $6.7 \times 10^{-6}$  M Fl and 1.3x 10<sup>-4</sup> M catalyst and 5% TEA in 1:1 H<sub>2</sub>O:EtOH was irradiated. These experimental conditions represent the minimum amount of fluorescein and maximum amount of catalyst that still generate hydrogen. Although the absorbance for Fl is above 1.0, lower Fl concentrations do not evolve hydrogen. It is worth noting that as the absorbance peak for Fl ( $\lambda = 490$  nm) decreases, the absorbance associated with the catalyst increases ( $\lambda = 427$  nm). Additionally, the presence of an isosbestic point ( $\lambda = 485$  nm) and the growth of a new absorbance peak ( $\lambda = 427$  nm) reflects an interaction between Fl and 2. This interaction is reflected in the large oxidative quenching rate constant and could account for the high stability of the system.

Even though the rate of oxidative quenching is several orders of magnitude larger than rate of reductive quenching, the reductive quenching of <sup>1</sup>Fl\* dominates due to the higher concentration of TEA (0.36 M) relative to **2** (1.25  $\mu$ M). When the concentration of TEA is lowered to 1.96% TEA, oxidative quenching by **2** becomes more competitive. Under these conditions, Hydrogen generation is

observed and ceases once the TEA is consumed (see supporting information). However, when additional TEA is added, the system resumes generating hydrogen at the previous rate. This indicates that the photocatalytic system is robust and can operate through either a reductive or oxidative quenching pathways.



**Figure 8.** UV-Vis Spectra of a solution of Fl (6.7 x  $10^{-6}$  M), **2** (1.3 x  $10^{-4}$  M), and 5% TEA in 1:1 H<sub>2</sub>O:EtOH after 4 (black), 5 (blue), 7 (orange), and 8 (red) hours of irradiation with  $\lambda >$  420 nm light. *Inlay*: Zoomed in region showing isosbestic point.

#### Conclusions

In summary, we report a bis-dithiocarbazate nickel complex that is a robust catalyst for proton reduction in aqueous solvent mixtures. The catalyst is both highly active and stable, producing 3300 turnover after 70 hours of illumination when paired with a fluorescein photosensitizer and triethylamine sacrificial donor. The complex is also an active electrocatalyst in  $CH_3CN$ . Therefore, bis-dithiocarbazate nickel complexes are a promising new group of catalysts that are active for both photocatalytic and electrocatalytic proton reduction.

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#### Notes and references

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A nickel complex containing a conjugated bis-dithiocarbazate ligand is an active catalyst for the reduction of protons into hydrogen gas.