

## Research paper

## Tridentate bis(2-pyridylmethyl)amine iron catalyst for electrocatalytic proton reduction



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## ABSTRACT

For widespread applicability, successful complexes for catalytic hydrogen generation should be inexpensive and easy to synthesize. To this end, a series of tetradentate Fe(III) polypyridyl monophenolate complexes was recently reported that are stable and active electrocatalysts for reducing protons into hydrogen gas. While these complexes were active for hydrogen generation, the ligands were synthesized in moderate to good yield after multiple synthetic steps. Herein we report a tridentate iron dipyrindyl amine analogue for hydrogen generation that is synthesized in a single synthetic step from commercially available materials. The resulting complex is an active electrocatalyst operating at  $-0.95$  V vs SHE ( $-1.57$  V vs  $\text{Fc}^+/\text{Fc}$ ) with a TOF =  $16\text{ s}^{-1}$ . The complex is also a precatalyst for photocatalytic hydrogen evolution when paired with fluorescein (chromophore) and triethylamine (sacrificial electron source) in a 1:1 ethanol:water mixture.

## 1. Introduction

With industrial growth of less developed nations, overall global energy demands are projected to expand by approximately 2.3% per year [1]. Globally, fossil fuels are the most widely utilized source of fuel. Owing to rising atmospheric carbon dioxide, a primary reliance on oil, coal, and natural gas threatens the global ecosystem. Therefore, it is critical to develop new methods to harvest renewable energy in order to diversify the global energy portfolio. Solar energy is a widely abundant and promising source for renewable energy [1]. Through Artificial Photosynthesis (AP), solar energy is harvested and used to split water into  $\text{H}_2$  and  $\text{O}_2$ , representing a promising avenue to access solar fuel. The reductive side of AP focuses on the conversion of protons to hydrogen gas through electrocatalysis or photocatalysis. Therefore, it is important to develop inexpensive catalysts made from earth-abundant materials that can act as robust catalysts for hydrogen generation [2].

Recently, many complexes containing first-row transition metals, such as Ni and Co, have been identified as hydrogen-generation electrocatalysts [3]. These complexes are often hamstrung by limited stability in the presence of water or low photocatalytic activity. To circumvent this limitation, multidentate polypyridyl ligands have been found to generate hydrogen from aqueous solutions [4]. While there have been many noteworthy examples of successful Co or Ni catalysts, there are also several examples of active catalysts containing the most earth-abundant transition metal, Fe [5]. Similarly to the Co and Ni

examples, many Fe electrocatalysts either decompose or are inactive in the presence of water. Recently, however, there have been several complexes reported that are stable in water and generate hydrogen in aqueous conditions [6,7].

In recent advances, we have reported a series of tetradentate Fe(III) polypyridyl monophenolate catalysts (Fig. 1, 1, 3, 4) and a polypyridyl sulfinate complex (Fig. 1, 2) that are active electrocatalysts for proton reduction [8]. Complexes 1–3 operate with overpotentials ranging from 300 to 800 mV and are stable and active in the presence of water. Complex 1 is a highly active electrocatalyst ( $i_c/i_p = 7.8$ ) that operates with an 800 mV overpotential, while complex 2 is more active ( $i_c/i_p = 13$ ) but exhibits lower stability [8]. Adding electron withdrawing nitro groups to complex (3) resulted in a less active catalyst ( $i_c/i_p = 5$ ) with a much lower overpotential (300 mV) [8]. Gratifyingly, complex 1–3 were also found to be active photocatalysts for hydrogen generation when paired with fluorescein as the chromophore and triethylamine as the sacrificial source of electrons [9]. The photocatalytic systems were stable and active ( $> 2100$  TONs) over the course of 24 h. In order to overcome diffusion, a ligand was developed to immobilize these complexes on metal oxide semiconductors. The resulting complexes were significantly more active than the homogeneous systems and were also able to be recycled after use [10].

In order to design a system with widespread applicability for hydrogen generation, it is critical to develop a cost-effective catalyst that is stable and active. While the use of inexpensive first-row metals is

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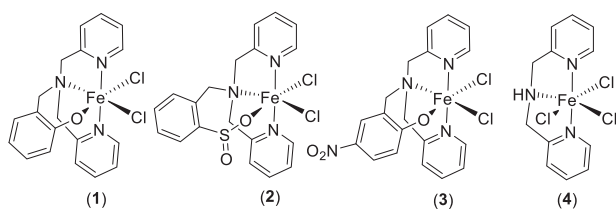


Fig. 1. Iron polypyridyl complexes.<sup>8</sup>

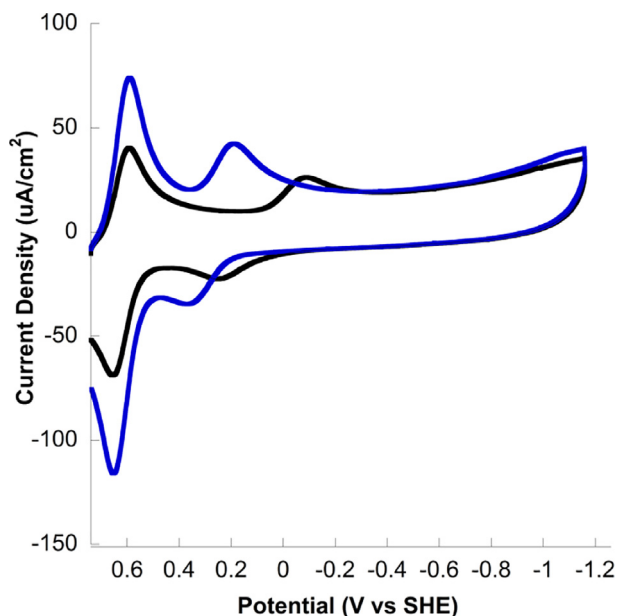


Fig. 2. CVs of **1** (0.23 mM) in CH<sub>3</sub>CN with and **4** (0.20 mM, black) 0.1 M TBAPF<sub>6</sub> (blue). Ferrocene was added as an internal reference (reversible redox couple at 0.624 V). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

essential, the ligand set must also be readily synthesized in high yields. To this end, we seek to simplify our catalyst precursors to produce a readily synthesized complex that can be obtained at low cost and in high yields. Herein we report a bis(2-pyridylmethyl)amine Fe(III) complex that is synthesized from commercially available materials in high yield (**4**) and is an active electrocatalyst for hydrogen generation. In addition to being an active electrocatalyst, the complex is an active pre-catalyst for photocatalytic hydrogen generation in aqueous solutions.

## 2. Materials and methods

All experiments were performed under Ar unless otherwise indicated. Triethylamine (99.7%), tetra-*n*-butyl-ammoniumhexafluorophosphate (98%), and fluorescein (extra pure grade) were purchased from Acros Organics. Acetonitrile for electrochemical and photochemical experiments was dried using an LC Technology Solutions Bench Top Solvent Purification System. All other reagents were purchased from Fischer Scientific and were used without further purification.

## 3. Instrumentation

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on an Agilent 400MR DD2 spectrometer operating in the pulse Fourier transform mode and chemical shifts are referenced to residual solvent. UV–Vis spectra were recorded using an Agilent Cary 60 UV–Vis Spectrophotometer using sealed quartz cuvettes degassed under Ar prior to scans. GC analysis

was recorded on a Bruker Scion 436 gas chromatograph.

## 3.1. Synthesis

**Bis(pyridin-2-ylmethyl)amine Fe(III) Chloride (**4**).** This catalyst was synthesized using a modified literature procedure [11]. FeCl<sub>3</sub>·6H<sub>2</sub>O (289 mg, 1.07 mmol) was dissolved in 10 mL of methanol. This mixture was added to a solution of bis(2-pyridylmethyl)amine (0.203 mL, 1.12 mmol) in 5 mL of methanol. The reaction was stirred at room temperature for 30 min before cooling in an ice bath for 45 min. The yellow solid was filtered off, washed with cold methanol and diethyl ether, and dried on vacuum to afford 312 mg of the complex (0.86 mmol, 80.9% yield). M/Z<sup>+</sup> for [C<sub>12</sub>H<sub>12</sub>N<sub>3</sub>FeCl<sub>3</sub> + Na + H] = 382.94178 expected, 382.941955 observed. Anal calc'd for FeC<sub>12</sub>H<sub>12</sub>N<sub>3</sub>Cl<sub>3</sub>·H<sub>2</sub>O: C, 37.98%; H, 3.98%; N, 11.07%. Found: C, 38.02%; H, 4.02%; N, 11.04%.

## 4. Cyclic voltammetry

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>) was used as the electrolyte. Ferrocene was added and used as an internal reference. All electrochemical experiments were performed under Ar. The working and auxiliary electrodes were polished with alumina powder (0.05 μm) on a cloth-covered polishing pad and rinsed with water and acetonitrile before each scan. For the acid addition experiments, approximately 0.5 mg of the catalyst was dissolved in 5.0 mL of 0.1 M TBAPF<sub>6</sub> in CH<sub>3</sub>CN. Cyclic voltammograms (CVs) were obtained upon addition of trifluoroacetic acid (TFA) under a blanket of Ar.

**Catalyst Concentration Dependence.** A 5.2 mM stock solution of **4** was prepared by dissolving 0.0125 g **4** crystals with 0.1 M TBAPF<sub>6</sub> in CH<sub>3</sub>CN in a 5 mL volumetric flask. A 5 mL solution of 0.1 M TBAPF<sub>6</sub> CH<sub>3</sub>CN was prepared in an electrochemical cell. 200 μL 1.1 M TFA (44 mM) was added to the cell, which was degassed with Ar. CVs were taken at 200 mV/s without any catalyst, then in the presence of 0.2 mM, 0.3 mM, 0.4 mM, and 0.5 mM catalyst from the **4** stock solution. CVs were obtained using a glassy carbon working electrode, a Pt auxiliary, and an SCE reference electrode. The working and auxiliary electrodes were polished with 0.05 μm alumina powder paste prior to each acquisition. All *i*<sub>c</sub> values were obtained using a previously published method.<sup>8</sup>

**Determination of Overpotential.** Due to tendencies towards homoconjugation of trifluoroacetic acid in acetonitrile, it is difficult to accurately calculate overpotential [12,13]. TFA was chosen as the proton source for the previously reported systems owing to its low background reduction at negative potentials [8]. TFA was used in this study in order to directly compare **4** with the previously reported catalysts. To account for homoconjugation, overpotentials were calculated by taking the difference between the half-wave potential of the catalytic reduction event (*E*<sub>1/2</sub>) and the reference potential (*E*<sub>ref</sub>) of 10 mM trifluoroacetic acid in CH<sub>3</sub>CN.<sup>12</sup>

## 5. Controlled potential coulometry

Controlled potential coulometry (CPC) experiments were conducted in a closed 500 mL four-neck round-bottom flask. The catalyst (3.3 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 of which were submerged in solution and separated by VYCOR frits. The solution was purged with argon, and TFA was added, resulting in a 65 mM solution. A CPC was run at −0.57 V vs SHE (−1.2 V versus Fc<sup>+</sup>/Fc) for 1800 s. Hydrogen generation was measured

using GC analysis after 1800 s by removing a sample of 100  $\mu\text{L}$  of gas from the headspace of each test tube. The hydrogen gas in the headspace was compared with a methane internal reference to give a faradaic yield of 98%.

## 6. Photocatalytic hydrogen evolution studies

Hydrogen evolution studies were conducted by preparing 1:1 EtOH:H<sub>2</sub>O solutions with catalyst ( $0.4 \times 10^{-3}$  M), fluorescein ( $4.0 \times 10^{-3}$  M), and 10% v/v TEA/H<sub>2</sub>O solution. The solutions were placed in test tubes and sealed with septa and wrapped in foil to exclude light. The samples were degassed for 15 min under Ar. 1.0 mL of gas from the headspace of each test tube was then removed using a 10.0 mL Hamilton gastight syringe, and 1.0 mL of CH<sub>4</sub> gas was added to each cell as an internal standard. The test tubes were inserted into a custom-built holder attached to a small motor that spins samples at 3 revolutions/min above a stir plate, and irradiated in a green LED apparatus ( $\lambda = 520\text{nm}$ ,  $P = 0.12\text{W}$ ). LEDs of this wavelength were selected because of the compatibility with a broad range of chromophores. A fan cooled the assembly to maintain room temperature in the apparatus during the experiment. Hydrogen generation was measured using GC analysis at specified time points from the beginning of irradiation by removing a sample of 100  $\mu\text{L}$  of gas from the headspace of each test tube.

## 7. Results and discussion

Complex **4** was originally synthesized and examined for catalytic catechol dioxygenase activity [11]. We synthesized this complex using a modified procedure where bis(2-pyridylmethyl)amine was added directly to a methanolic solution of FeCl<sub>3</sub>·6H<sub>2</sub>O. The resulting complex (**4**) precipitates out of methanol in excellent yield (> 80%) after 30 min of stirring at room temperature. Both precursors are commercially available and the total cost of catalyst assembly is estimated to be roughly \$25 (USD) per gram of catalyst when precursors, solvents, and yield are taken into account. Complex **4** exhibits a quasi-reversible Fe(III)/Fe(II) redox couple at 0.07 V vs SHE (-0.55 V vs Fc<sup>+</sup>/Fc), compared to the reversible redox couple of **1** at 0.22 V vs SHE (-0.4 V vs Fc<sup>+</sup>/Fc) (Fig. 2). The quasi-reversible nature of this redox couple is likely due to the labile nature of the chloride ligands. The Fe(III)/Fe(II) redox couple for **4** is ~150 mV more cathodic than what is observed for the phenolate complexes (Table 1). From these CVs of the complexes, we estimate that the complex would operate with an overpotential that is 150 mV greater than what is observed for the phenolate complexes.

Upon addition of trifluoroacetic acid, a shift in the redox couple for Fe(III)/Fe(II) is observed for complex **1** from 0.22 V to 0.32 V vs SHE (Fig. 3, left) [8]. This shift is attributed to the protonation of the phenol group, resulting in either a CECE or CEEC mechanism. Similarly, upon addition of TFA, the redox couple for Fe(III)/Fe(II) shifts from 0.07 V to 0.32 V vs SHE for complex **4** (Fig. 3, right), indicating that this catalyst operates under a similar mechanism where protonation of the complex is the first step (C) followed by subsequent reduction (E) and chemical (C) steps.

**Table 1**  
Summary of electrocatalytic proton reduction of 2 mM catalysts upon addition of 8.8 mM TFA in CH<sub>3</sub>CN [8].

| Catalyst | $i_c/i_p$ | $E_{1/2}$ (Fe <sup>III</sup> /Fe <sup>II</sup> ) (V vs. SHE) | $E_{cat}$ (H <sup>+</sup> /H <sub>2</sub> ) (V vs. SHE) | Overpotential (mV) |
|----------|-----------|--------------------------------------------------------------|---------------------------------------------------------|--------------------|
| 1        | 7.8       | 0.22                                                         | -0.95                                                   | 800                |
| 2        | 13        | 0.34                                                         | -0.95                                                   | 800                |
| 3        | 5.3       | 0.17                                                         | -0.56                                                   | 300                |
| 4        | 6.8       | 0.07                                                         | -0.98                                                   | 800                |

$$\frac{i_c}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RTk_{obs}[H^+]^2}{Fv}}$$

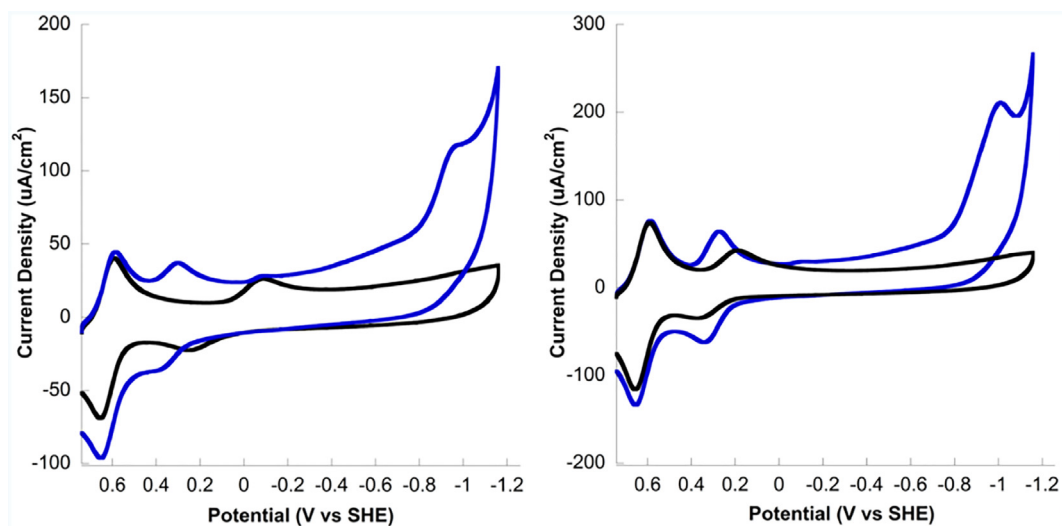
Complex **4** was found to be an active catalyst for proton reduction (Fig. 4). Upon the addition of trifluoroacetic acid (TFA) in CH<sub>3</sub>CN, a catalytic wave was observed at -0.98 V vs SHE (-1.6 V vs. Fc<sup>+</sup>/Fc) compared to the catalytic wave observed for **1** at -0.95 V vs SHE (-1.57 V vs Fc<sup>+</sup>/Fc), resulting in an  $i_c/i_p = 6.8$ . Although the Fe(III)/Fe(II) redox couple in the absence of acid is 100 mV different for complexes **1** and **4**, the catalytic wave is observed at nearly the same potential (-0.98 V vs SHE). TFA was chosen as the proton source due to low background reduction at potentials lower than -1.18 V vs SHE [8,14]. Calculations using the half-wave potential of this reduction indicate that the catalysis occurs with an 800 mV overpotential (see supporting information). When more acid is added, a larger current enhancement is observed (Fig. 4). A linear relationship between  $i_c$  and [TFA] is observed when varying [TFA], suggesting a second order dependence on proton concentration (Fig. 4). The catalyst is highly active for proton reduction with an  $i_c/i_p = 6.8$ . According to the above equation, plotting  $i_c/i_p$  vs. [TFA] should be linear at different scan rates [15].  $k$  can be calculated from the slope of a plot of  $i_c/i_p$  at various  $v$  vs.  $v^{-1/2}$  (see supporting information) [4b]. This corresponds to a  $k_{obs} = 8400 \text{ M}^{-1}\text{s}^{-1}$  and a turnover frequency (TOF) of  $16 \text{ s}^{-1}$ . In this respect, complex **4** is similar to the phenolate complexes in terms of activity and overpotential.

When [TFA] is held constant and catalyst is introduced, a catalytic wave is also observed at -1.57 V. When more catalyst is added, a larger current enhancement is observed (Fig. 5). After several additions of **4** there is a linear relationship between [4] and  $i_c/i_p$ . This suggests that there is a first order dependence on [4], resulting in an overall rate expression of  $\text{rate} = k[4][H^+]^2$  similar to what is observed for the phenolate catalysts.<sup>8</sup>

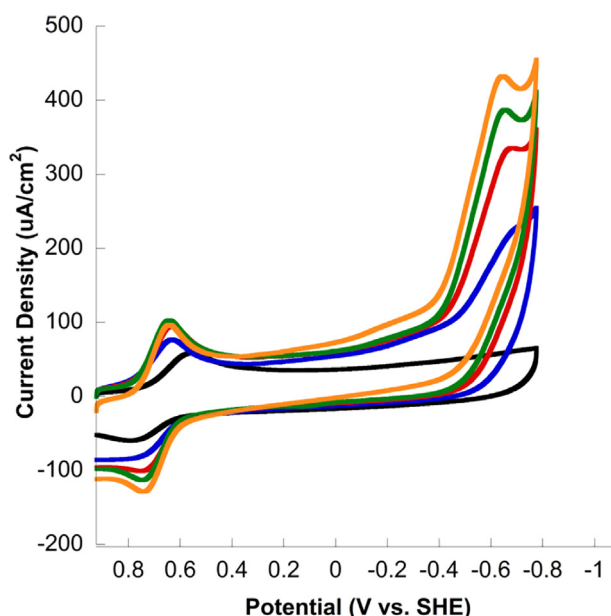
With complex **4** operating as an electrocatalyst for proton reduction, it was also of interest to determine if **4** would operate as an active photocatalyst for hydrogen generation. In order to test photocatalytic activity with **4**, it was important to incorporate a chromophore that was capable of reducing these complexes. Several common chromophore and sacrificial donor pairings that operate with catalysts of similar reduction potentials were examined including: fluorescein (Fl) with TEA, eosin Y (EY) with triethanolamine (TEOA), and tris(2,2'-bipyridyl)ruthenium(II) chloride [Ru(bpy)<sub>3</sub>]<sup>2+</sup> with ascorbic acid (AA). Hydrogen evolution was only observed when using Fl as a chromophore and triethylamine as a sacrificial donor. It must be noted that EY bleached rapidly and is not able to reduce the catalyst. With respect to the [Ru(bpy)<sub>3</sub>]<sup>2+</sup>/AA pairing, it is possible that ascorbic acid is reacting with the complex and shutting down activity. This is similar to what was observed for the phenolate complexes, **1**–**3**. Triethylamine (TEA) was chosen as the sacrificial electron donor due to its ability to quench fluorescein under photocatalytic conditions [2,15]. Based on the electrochemical data (Table 1), both Fl\* (-1.48 V vs SHE) or Fl<sup>-</sup> (-1.08 V vs SHE) are capable of reducing complex **4** ( $E_{1/2}$  for Fe<sup>III/II</sup> = 0.32 V to 0.02 V vs SHE).

Upon irradiation with green light-emitting diodes ( $\lambda = 520 \text{ nm}$ , 0.12 W), hydrogen evolution was observed for solutions containing complexes **4**, Fl, and 5% TEA in a 1:1 water:ethanol mixture (Fig. 6). The optimal catalyst and chromophore concentrations for photocatalysis were found to be 2  $\mu\text{M}$  and 1.9 mM, respectively. The system is also most active when pH = 12.5, which is consistent with other photocatalytic systems containing Fl and TEA [8]. The pH dependence can be attributed to the fact that TEA is a better electron donor at high pH while Fl is known to decompose at pH < 12.5 upon irradiation [16]. Experiments performed without catalyst did not yield any observable hydrogen gas by GC analysis. Furthermore, the addition of 0.5 mL of Hg to the reaction vessel did not alter the hydrogen generation of the system.

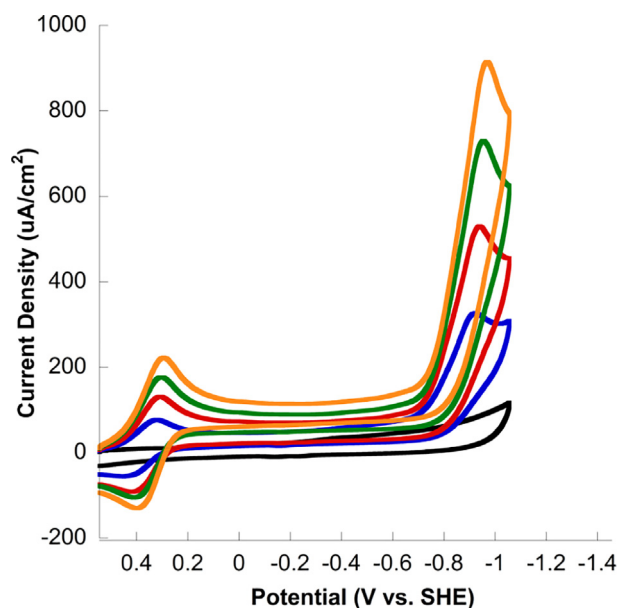
Under optimal photocatalytic conditions (1.9 mM Fl, 5% TEA, 2  $\mu\text{M}$



**Fig. 3.** Left: CVs of **1** without added TFA (black) and with 8.8 mM TFA (blue). Right: CVs of **4** without added TFA (black) and with 8.8 mM TFA (blue). Ferrocene was added as an internal reference. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** CVs of **4** (0.23 mM) in  $\text{CH}_3\text{CN}$  with 0.1 M  $\text{TBAPF}_6$  (blue) upon addition of 0 mM TFA (black), 2.2 mM TFA (blue), 4.4 mM TFA (red), 6.6 mM TFA (green) and 8.8 mM TFA (orange). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 5.** CVs in  $\text{CH}_3\text{CN}$  with 0.1 M  $\text{TBAPF}_6$  containing 44 mM TFA with 0.2 mM **4** (blue), 0.4 mM **4** (red), 0.6 mM **4** (green), and 0.8 mM **4** (orange) at  $\nu = 200 \text{ mV/s}$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

catalyst in 1:1  $\text{EtOH}:\text{H}_2\text{O}$ ), catalysis continues over 24 h, reaching a TON (with respect to **4**) of 3800. The presence of a short induction period ( $< 30 \text{ mins}$ ), suggests that complex **4** is likely acting as a pre-catalyst for photocatalytic hydrogen generation. Cessation of hydrogen generation after 24 h is accompanied by bleaching of the chromophore, suggesting that the system shuts down due to decomposition of chromophore, catalyst, or both. While photocatalytic experiments performed by adding a Hg drop to the reaction mixture did not alter hydrogen generation of the system, this does not rule out heterogeneous activity in the photocatalysis. Unlike Ni and Co which are well documented to form amalgams with Hg, Fe is not as likely to form amalgams with Hg. Additional control experiments using  $\text{FeCl}_3$  as a photocatalyst with Fl and TEA yielded significantly less hydrogen (see SI).

## 8. Conclusions

In conclusion, we have developed an iron catalyst for electrocatalytic proton reduction that is synthesized from commercially available materials in high yield. The complex is synthesized at room temperature affording  $> 80\%$  yield with an overall materials cost of roughly \$25 USD per gram of catalyst. The tridentate 3 N complex lacks the phenolate moiety present in the previously reported system, yet retains similar catalytic activity to the polypyridyl monophenolate catalysts reported in our laboratory. The complex operates at an over-potential of 800 mV with a  $K_{\text{obs}} = 8400 \text{ M}^{-1}\text{s}^{-1}$  and a  $\text{TOF} = 16 \text{ s}^{-1}$ . When paired with fluorescein as a chromophore and triethylamine as a sacrificial source of electrons, this complex is an active pre-catalyst for photocatalytic hydrogen generation. The presence of an induction period in the photocatalytic experiments suggests that the pre-catalyst is less stable under photocatalytic conditions than the polypyridyl

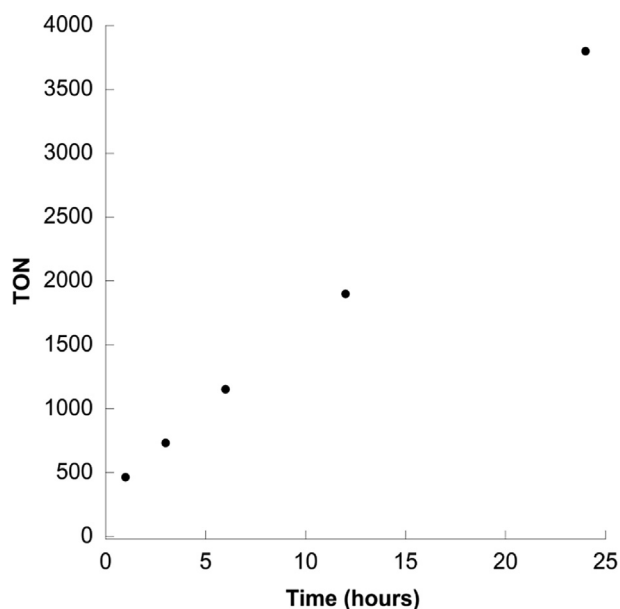


Fig. 6. Hydrogen evolution over 24 h period with: 2  $\mu$ M **4**, with 1.9 mM FI in 1:1 EtOH:H<sub>2</sub>O with 5% TEA.

monophenolate complexes. The observed instability in the photocatalytic system is likely a result of decreasing the coordination number of the ligand set. Although less stable under photocatalytic conditions, the low cost of the complex and comparable electrocatalytic activity to other established iron electrocatalysts represents a promising step toward developing an iron electrocatalyst for widespread use.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ica.2019.119394>.

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