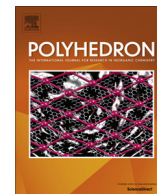




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# Electrocatalytic hydrogen evolution by an iron complex containing a nitro-functionalized polypyridyl ligand

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## ABSTRACT

Iron polypyridyl complexes have recently been reported to electrocatalytically reduce protons to hydrogen gas at  $-1.57$  V versus  $Fc^+/Fc$ . A new iron catalyst with a nitro-functionalized polypyridyl ligand has been synthesized and found to be active for proton reduction. Interestingly, catalysis occurs at  $-1.18$  V versus  $Fc^+/Fc$  for the nitro-functionalized complex, resulting in an overpotential of 300 mV. Additionally, the complex is active with a turnover frequency of  $550$  s $^{-1}$ . Catalysis is also observed in the presence of water with a 12% enhancement in activity.

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## 1. Introduction

One of the great challenges facing the current generation of scientists involves limiting our dependence on fossil fuels. In order to relieve pressure on dwindling fossil fuel reserves, renewable energy must be pursued. Solar energy appears to be a viable long-term source of energy because roughly 400 times the amount of energy needed each year strikes the earth as harvestable solar energy [1]. One method of utilizing solar energy involves the development of systems for artificial photosynthesis (AP). In general, these systems are designed to use solar energy to photochemically split water, converting sunlight into both electricity and fuel in the form of  $H_2$  [2]. Although noble metals can be used to reduce protons to hydrogen gas, the rare nature of these materials limits their widespread use in devices for AP. Therefore, it is critical to develop complexes containing earth-abundant metals that can catalytically reduce protons to hydrogen gas.

Many cobalt glyoxime complexes have been studied and can be tuned to operate at low overpotential [3]. Other cobalt and nickel complexes have been discovered that are remarkably active with turnover frequencies (TOFs) as high as  $10^5$  s $^{-1}$  [4]. However, many of the cobalt and nickel catalysts are unstable and operate in only organic solutions. To circumvent this limitation, polypyridyl ligands have been coordinated to cobalt and molybdenum, result-

ing in highly stable catalysts that can generate hydrogen from aqueous solutions [5]. Although there are many examples of active cobalt, nickel, and molybdenum complexes, there are far fewer examples of molecular iron catalysts that generate hydrogen in the presence of water.

One approach to developing active iron catalysts involves mimicking the active site of hydrogenase enzymes [6]. Functional mimics that are active electrocatalysts for hydrogen generation often operate at potentials that are more cathodic than  $-1.6$  V versus  $Fc^+/Fc$  [6]. Additionally, these catalysts are significantly less active than  $[Fe]H_2ase$  [7,8]. In an effort to develop a water-stable iron catalyst, we have recently reported a mononuclear iron polypyridyl catalyst (Fig. 1) that is active in aqueous solutions [9]. Although the iron polypyridyl catalysts are active and stable, catalysis occurs at  $-1.57$  V versus  $Fc^+/Fc$ , corresponding to an overpotential of 800 mV. We reasoned that functionalizing the ligand with an electron withdrawing group would result in an iron catalyst that operates at a significantly less cathodic potential.

Herein we report the synthesis and characterization of an iron complex (2) containing a nitro-functionalized polypyridyl ligand and its corresponding electrocatalytic activity. The incorporation of an electron withdrawing nitro group on the phenolate ring of the complex results in a catalyst that reduces protons at  $-1.18$  V versus  $Fc^+/Fc$ , corresponding to an overpotential of just 300 mV. This represents a significant improvement over complex 1 and is a promising step towards developing an iron catalyst that is stable, active, and operates at low overpotential.

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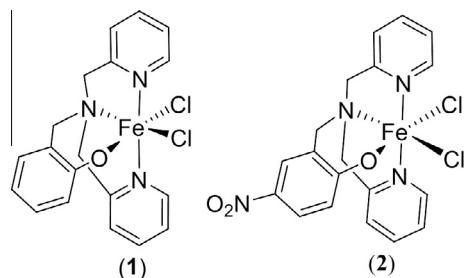


Fig. 1. Left: iron poly(pyridin-2-ylmethyl)amino)methyl-4-nitrophenol complex (1). Right: nitro-functionalized iron poly(pyridin-2-ylmethyl)amino)methyl-4-nitrophenol complex (2).

## 2. Materials and methods

### 2.1. General procedures

2-Hydroxy-5-nitrobenzaldehyde was purchased from Alfa Aesar. Bis(pyridin-2-ylmethyl)amine was purchased from Aldrich. Iron (III) chloride and potassium hydroxide were purchased from Fisher Scientific. Tetra-*n*-butylammoniumhexafluorophosphate (98%), was purchased from Acros Organics. All other reagents were purchased from Fisher Scientific and used without further purification.

### 2.2. Syntheses

#### 2.2.1. 2-((Bis(pyridin-2-ylmethyl)amino)methyl)-4-nitrophenol (**L-NO<sub>2</sub>**)

This procedure was modified from a literature method [10]. 2-hydroxy-5-nitrobenzaldehyde (500 mg, 3 mmol) was dissolved in 50 mL of methanol and degassed with argon. A degassed solution of bis(pyridin-2-ylmethyl)amine (0.54 mL, 3 mmol) in 5 mL of methanol was transferred to the aldehyde solution using a cannula. Glacial acetic acid was added (3 drops) followed by the dropwise addition of an air-free solution of sodium cyanoborohydride (190 mg, 3 mmol) in 5 mL methanol. The resulting clear, red solution was refluxed for 1 h and then stirred for 24 h at room temperature. 1 M HCl was added to the solution until it reached pH 4. The solution was evaporated to dryness and dissolved in 25 mL of saturated Na<sub>2</sub>CO<sub>3</sub> solution and extracted with chloroform. The organic layers were combined, dried with Na<sub>2</sub>SO<sub>4</sub>, and filtered through celite. The solvents were removed under vacuum to yield a red oil. The ligand was then purified using silica gel chromatography with 9:1 dichloromethane:methanol. The desired compound eluted first and the solvent was removed under vacuum to give 540 mg of the purified product (1.85 mmol, 62% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.58 (d, 2H), δ 8.12 (d, 1H), δ 8.05 (t, 1H), δ 7.66 (t, 2H), δ 7.30 (d, 2H), δ 7.21 (t, 2H), δ 6.95 (d, 1H), δ 3.93 (s, 4H), δ 3.85 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 164.27, δ 157.71, δ 148.69, δ 139.68, δ 137.06, δ 126.54, δ 125.61, δ 123.52, δ 123.08, δ 122.41, δ 117.17, δ 58.67, δ 56.10. *m/z* for C<sub>19</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub>H<sup>+</sup> expected = 351.15, found = 351.15.

#### 2.2.2. [FeCl<sub>2</sub>(**L-NO<sub>2</sub>**)] (**2**)

The complex was synthesized using a modified literature procedure [9]. **L-NO<sub>2</sub>** (100 mg, 0.6 mmol) and triethylamine (83 μL, 0.6 mmol) were dissolved in 10 mL of MeOH and degassed with Ar. FeCl<sub>3</sub>·6H<sub>2</sub>O (162 mg, 0.6 mmol) was dissolved in 10 mL of methanol and degassed with argon. The ligand solution was transferred to the flask containing the iron precursor using a cannula. The solution immediately turned deep purple with a visible precipitate. The reaction was stirred at room temperature for 1 h and was filtered. The filtrate was evaporated to dryness and was washed with cold methanol to give the product as a purple solid

(118 mg, 41% yield). Crystals suitable for X-ray diffraction were grown by diffusion of diethyl ether into a solution of **2** in dichloromethane. *m/z* for C<sub>19</sub>H<sub>17</sub>Cl<sub>2</sub>FeN<sub>4</sub>O<sub>3</sub>Na<sup>+</sup> expected = 497.991934, found = 497.992060. *Anal. calc.* for **2**: C, 47.83; H, 3.80; N, 11.74. Found: C, 47.77, H, 3.83, N, 11.90.

### 2.3. 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.

#### 2.3.1. X-ray diffractometry

A single crystal was mounted on a glass fiber and data was collected with graphite-monochromated Cu Kα radiation (λ = 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.

#### 2.3.2. 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 μm) 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.

#### 2.3.3. 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<sub>3</sub>CN. Cyclic voltammograms (CVs) were obtained at different concentrations of TFA.

#### 2.3.4. Bulk electrolysis

Controlled-potential coulometry (CPC) experiments were conducted in a closed 500 mL four-neck round-bottom flask. Complex **2** (0.5 mg) was added to 50 mL of 0.1 M TBAPF<sub>6</sub> with 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. The solution was purged with argon and TFA was added resulting in a 65 mM solution. A CPC was run at −1.2 V versus Fc<sup>+</sup>/Fc for 1800 s, resulting in a faradaic yield of 98%. No hydrogen was observed when the experiment was performed without catalyst.

#### 2.3.5. 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 50 mV/s to 700 mV/s.

## 3. Results and discussion

The ligand (**L-NO<sub>2</sub>**) was obtained through a simple condensation reaction of 2-hydroxy-5-nitrobenzaldehyde with bis(pyridin-2-ylmethyl) followed by a reduction using sodium cyanoborohydride (62% yield). The phenol group of **L-NO<sub>2</sub>** was deprotonated with triethylamine and the ligand was coordinated

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