

Electrocatalytic Water Oxidation by a Monomeric Amidate-Ligated Fe(III)-Aqua Complex

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Experimental Section:

General Methods. All reagents and solvents were purchased from commercial vendors and used without further purification unless otherwise specified. Distilled water was further purified using a Milli-Q Ultrapure water purification system. $[\text{Fe}^{\text{III}}(\text{dpaq})(\text{H}_2\text{O})](\text{ClO}_4)_2$ ¹ and *nanoITO-RVC* electrodes² were prepared according to previously-published procedures. Anhydrous propylene carbonate (Sigma-Aldrich) was housed in a nitrogen-purged sealed container over oven dried molecular sieves prior to use. Propylene carbonate/water mixtures were sonicated for at least 5 minutes to ensure complete mixture homogeneity. Gas chromatography data were obtained using a Shimadzu GC-2014 instrument.

Electrochemical Methods. Electrochemical measurements were performed with a model CHI660D electrochemical workstation (CH instruments) and a three-electrode system consisting of either a glassy carbon or *nanoITO-RVC* working electrode, platinum wire counter electrode, and either a Ag/AgCl (3.5 M NaCl) or SCE reference electrode without *iR* compensation. All potentials are referenced to NHE. Cyclic voltammetry experiments were conducted in a one-compartment cell with 4-6 mL of electrolyte solution, while controlled potential electrolysis measurements were conducted with a total of 15-20 mL of total electrolyte solution in a closed three-compartment anaerobic cell (30 mL total volume, each compartment separated by a fine frit) that had been vigorously purged with N₂ for 30 minutes prior to beginning the CPE experiment. Background CPE experiments were conducted under identical conditions except with the absence of the catalyst to correct for both background current and atmospheric O₂ leakage into the electrolysis cell during these experiments.

Supplementary Figures:

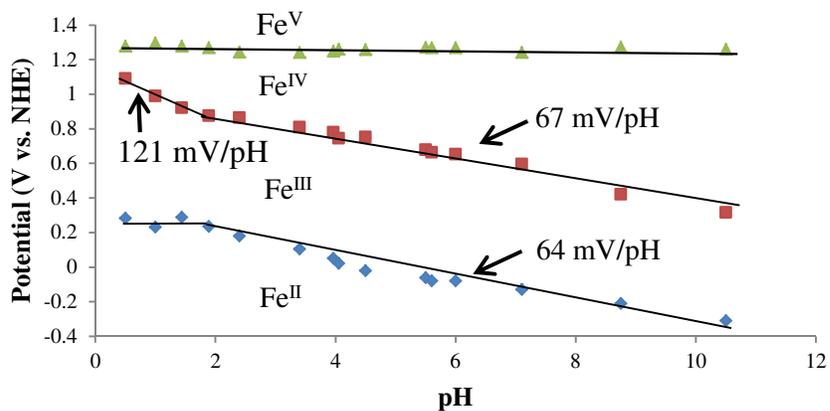


Figure S-1. Pourbaix diagram ($E_{1/2}$ vs. pH) for $[\text{Fe}^{\text{III}}(\text{dpaq})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (**1**).

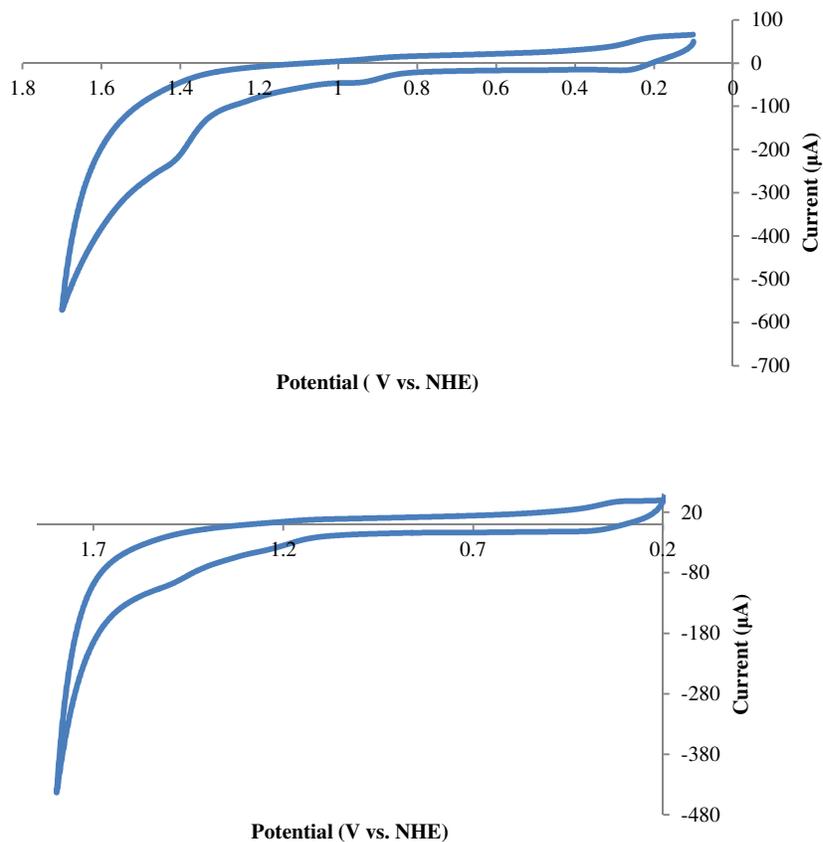


Figure S-2. Cyclic voltammograms (blue) of **1** at pH 1.0 (top, 0.1 M HClO_4 , 0.4 M LiClO_4 , 50 mV/sec) and pH 3.9 (bottom, 0.1 M acetate buffer, 0.4 M LiClO_4 , 20 mV/sec) at a glassy carbon working electrode (0.07 cm^2).

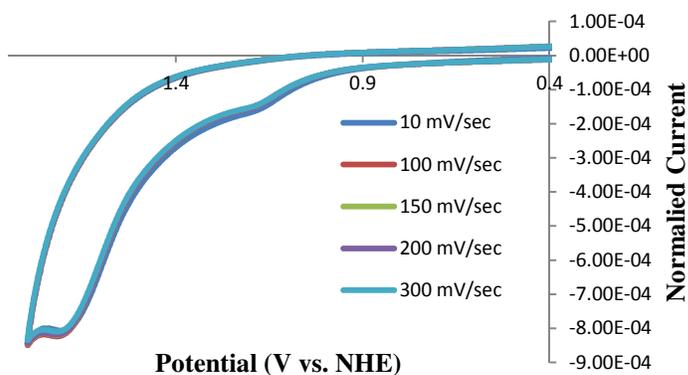


Figure S-3. Scan rate-normalized cyclic voltammograms ($i/v^{1/2}$) of $[\text{Fe}^{\text{III}}(\text{dpag})(\text{H}_2\text{O})](\text{ClO}_4)_2$ at pH 1.0 (0.1 M HClO_4 , 0.4 M LiClO_4 , Ag/AgCl reference, GC working, Pt auxiliary) at room temperature.

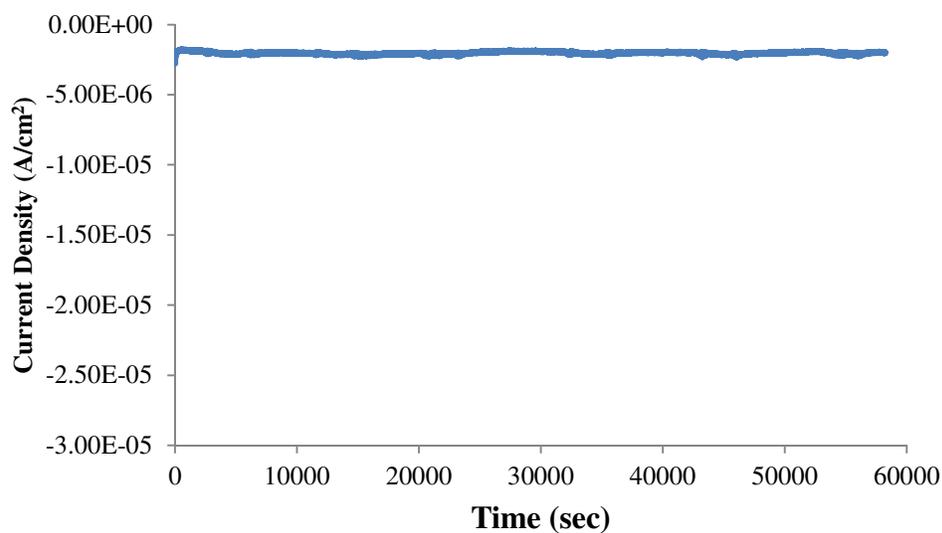


Figure S-4. Current density-time CPE control experiment with propylene carbonate/8% H_2O (0.5 M LiClO_4 , $E = 1.58$ V vs. NHE, *nano*ITO-RVC, 16.5 cm^2).

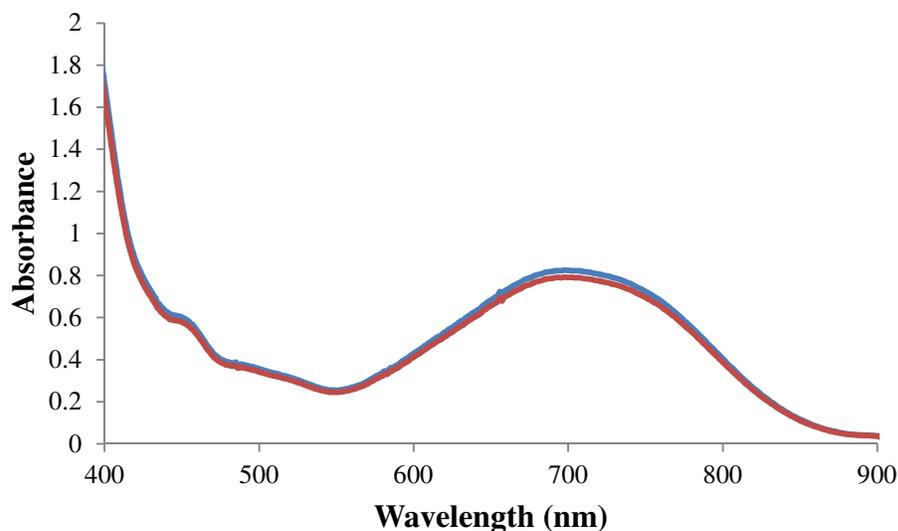


Figure S-5. UV/Vis spectra of $[\text{Fe}^{\text{III}}(\text{dpaq})(\text{H}_2\text{O})](\text{ClO}_4)_2$ in propylene carbonate/8% H_2O before (blue trace) and after (red trace) 15 hours of controlled potential electrolysis at 1.58 V vs. NHE. A 4% decrease in absorbance intensity is observed at 690 nm.

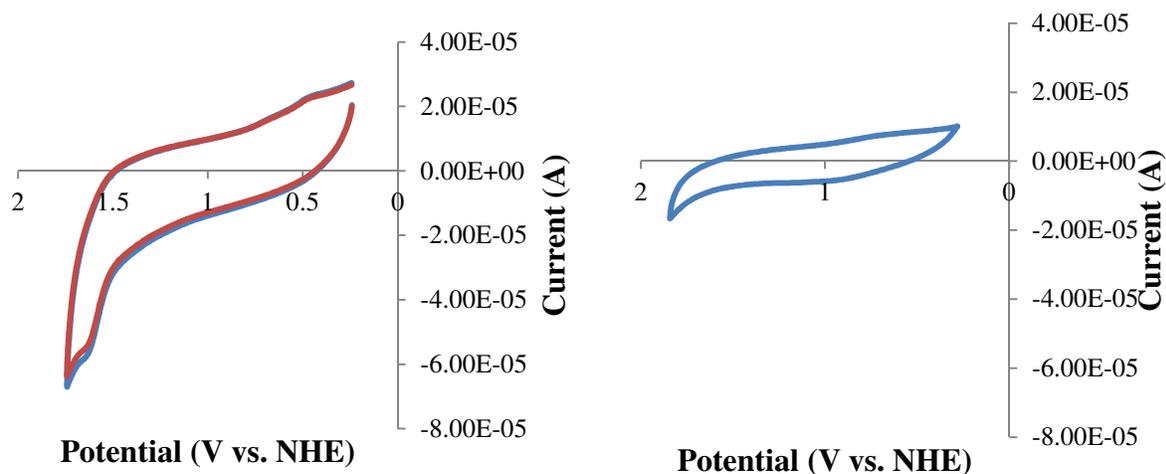


Figure S-6. (Left) CVs of $[\text{Fe}^{\text{III}}(\text{dpaq})(\text{H}_2\text{O})](\text{ClO}_4)_2$ in propylene carbonate/8% H_2O (0.5 M LiClO_4) before (blue trace) and after (red trace) 15 hours of controlled potential electrolysis at 1.58 V vs. NHE. A ~5% loss in catalytic current at 1.58 V is observed. (Right) Background CV of propylene carbonate/8% H_2O (0.5 M LiClO_4 , GC working, Ag/AgCl reference, Pt auxiliary electrodes, 50 mV/sec for all CVs).

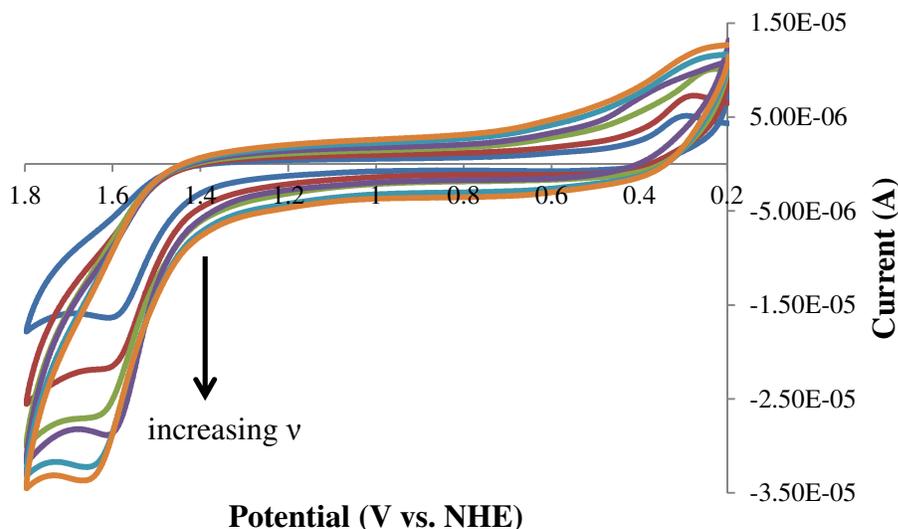


Figure S-7. Cyclic voltammograms at various scan rates of $[\text{Fe}^{\text{III}}(\text{dpaq})(\text{H}_2\text{O})](\text{ClO}_4)_2$ in propylene carbonate/8% H_2O (GC working, Ag/AgCl reference, Pt auxiliary electrodes) at room temperature.

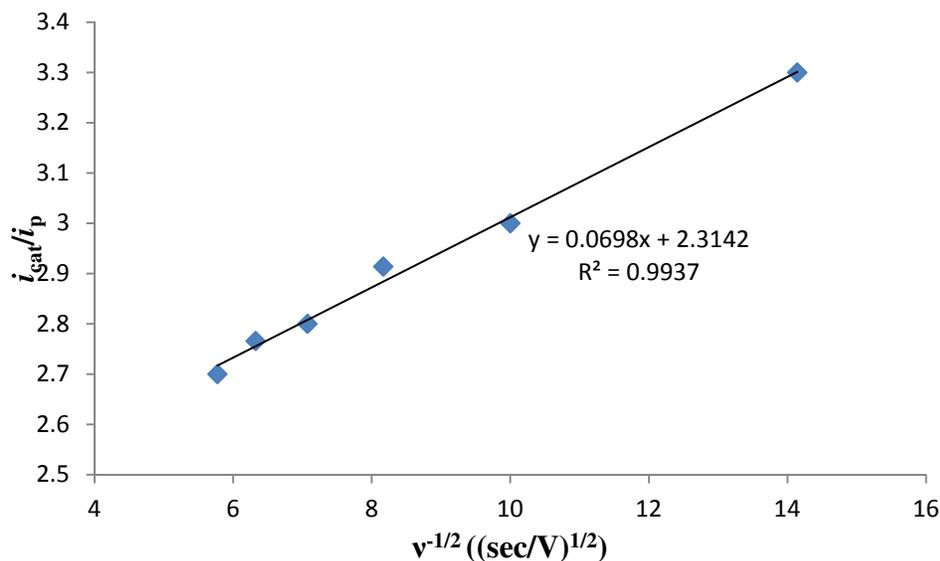


Figure S-8. Plot of $i_{\text{cat}}/i_{\text{p}}$ (i_{cat} and i_{p} were taken as the current at 1.58 and -0.14 V vs. NHE, respectively) versus the inverse square root of scan rate from variable scan rate cyclic voltammograms of $[\text{Fe}^{\text{III}}(\text{dpaq})(\text{H}_2\text{O})](\text{ClO}_4)_2$ in propylene carbonate/8 % H_2O (GC working, Ag/AgCl reference, Pt auxiliary electrodes) at room temperature.

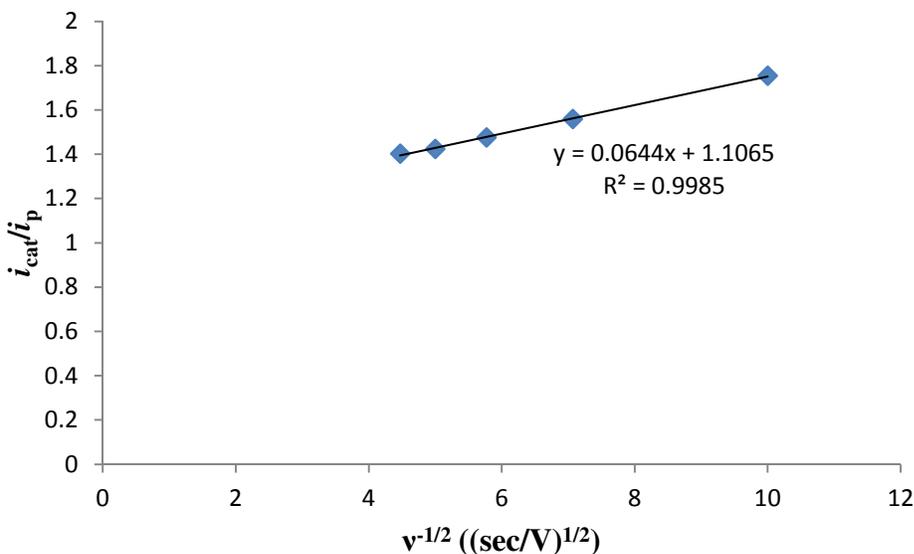


Figure S-9. Plot of i_{cat}/i_p (i_{cat} and i_p were taken as the current at 1.58 and -0.14 V vs. NHE, respectively) versus the inverse square root of scan rate from variable scan rate cyclic voltammograms of $[\text{Fe}^{\text{III}}(\text{dpaq})(\text{H}_2\text{O})](\text{ClO}_4)_2$ in propylene carbonate/8% D_2O (GC working, Ag/AgCl reference, Pt auxiliary electrodes) at room temperature.

References:

- 1) Hitomi, Y.; Arakawa, K.; Funabiki, T.; Kodera, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 3448-3452.
- 2) Méndez, M. A.; Alibabaei, L.; Concepcion, J. J.; Meyer, T. J. *ACS Catal.* **2013**, *3*, 1850-1854.