

# Hydrogen Atom Abstraction by a Mononuclear Ferric Hydroxide Complex: Insights into the Reactivity of Lipoxygenase

## *Supporting Information*

Christian R. Goldsmith, T. Daniel P. Stack\*

*Contribution from the Department of Chemistry, Stanford University, CA 94305*

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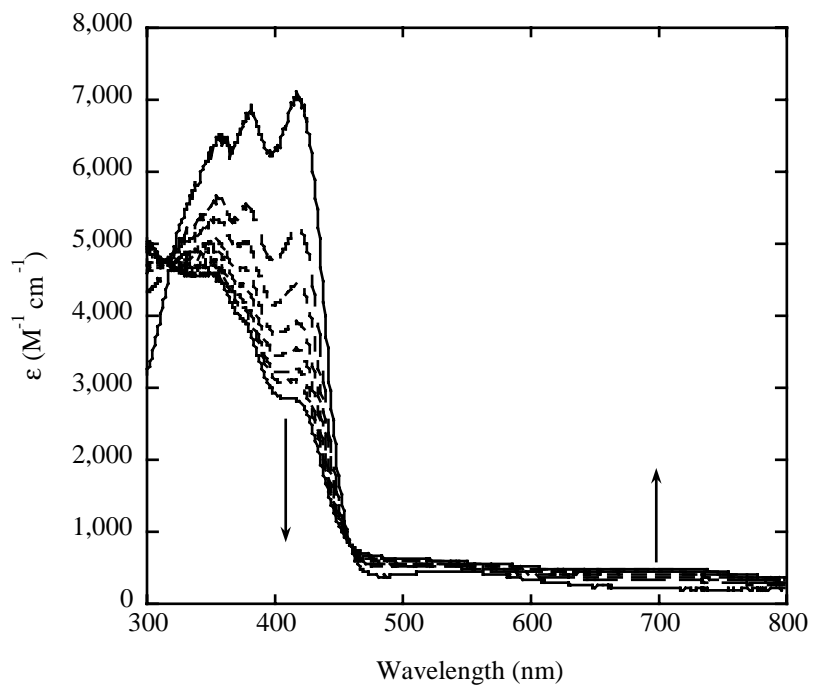
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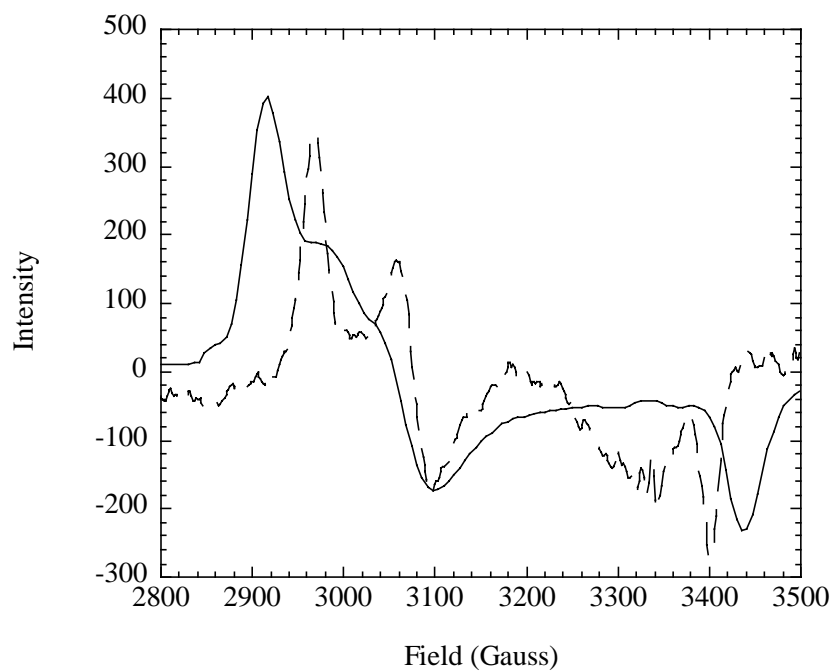
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\*To whom correspondence should be addressed:

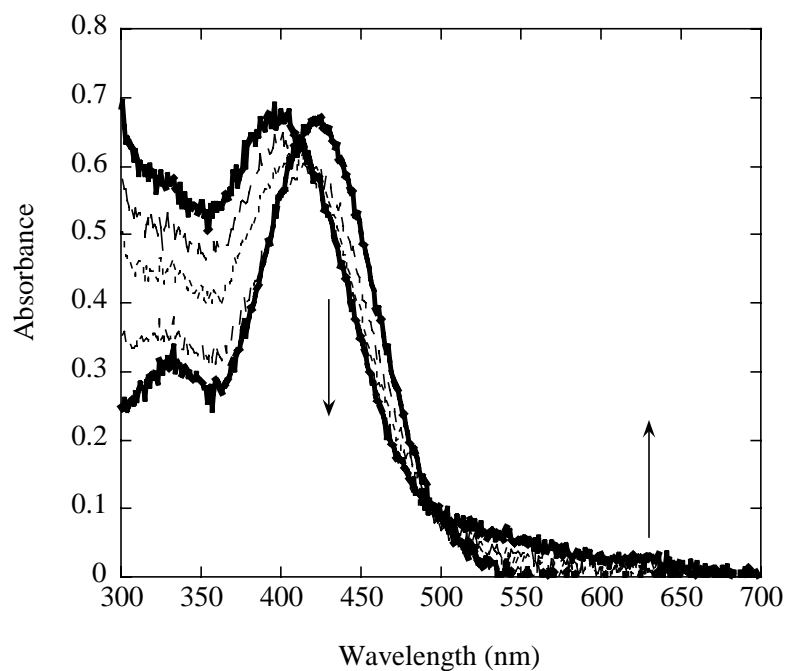
T.D.P.S. at Department of Chemistry, Stanford University, CA 94305, USA; Tel: (650) 725-8736; Fax: (650) 725-0259; email: [stack@stanford.edu](mailto:stack@stanford.edu)



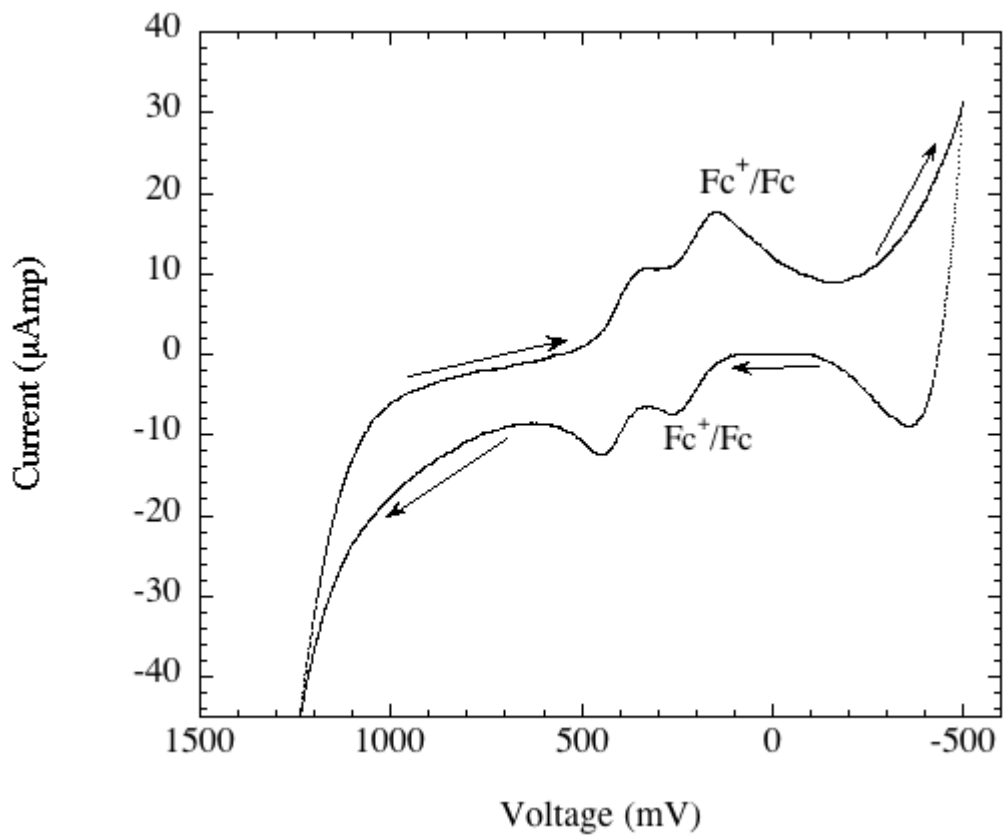
**Figure S1.** MCPBA oxidation of a 0.22 mM solution of  $[\text{Fe}(\text{PY5})(\text{MeCN})]^{2+}$  to a mixture of  $[\text{Fe}(\text{PY5})(\text{OH})]^{2+}$  and  $[\text{Fe}(\text{PY5})(\text{O})]^{2+}$  (710 nm feature) at 233 K in MeCN. Scans are 15 min apart. Arrows indicate spectral changes upon oxidation.



**Figure S2.** Comparative X-band EPR spectra of a 10 mM sample of  $[\text{Fe}^{\text{III}}(\text{PY5})(\text{OH})]^{2+}$  (solid line) and a 1 mM sample of  $[\text{Fe}^{\text{III}}(\text{PY5})(\text{OMe})]^{2+}$  (dashed line) in MeCN at 77 K. The intensities have been normalized to each other.

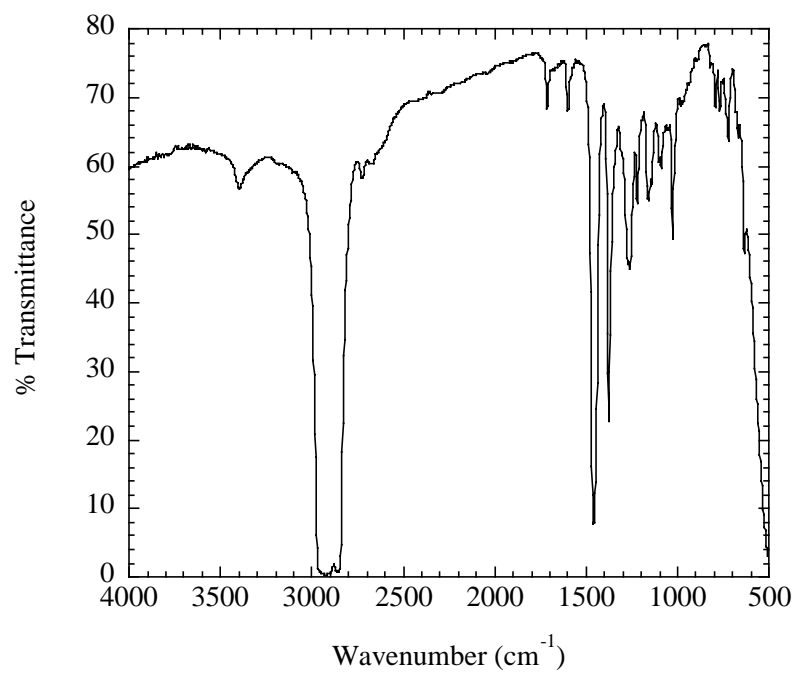


**Figure S3.** Titration of a 0.33 mM bromocresol green solution in DMSO with a 9.2 mM solution of [Fe(PY5)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> in DMSO. Arrows indicate growth of protonated bromocresol green species. The end point spectrum corresponds to 39 equiv of Fe<sup>II</sup>LH<sub>2</sub>O added (~95% conversion). Spectra are taken at 298 K with a 1 mm pathlength.

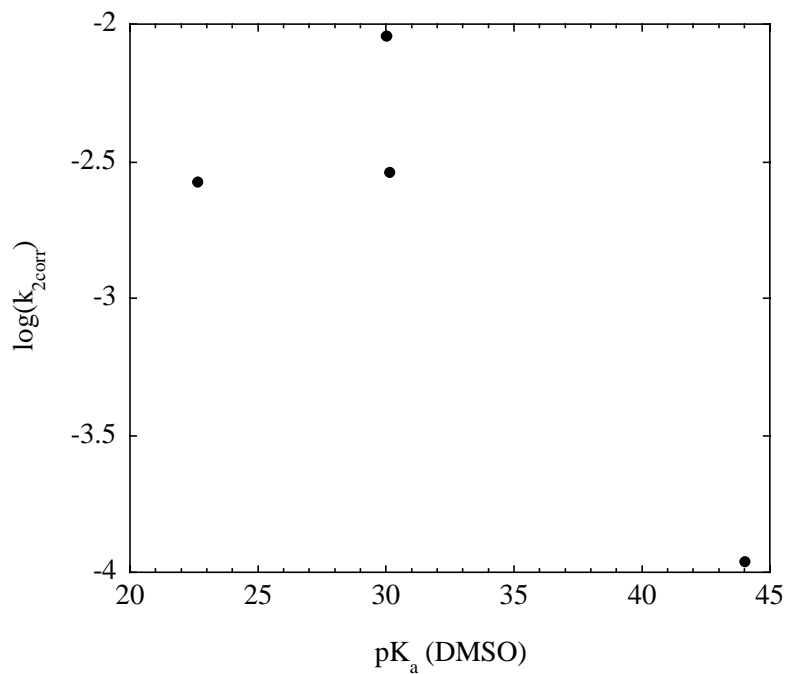


**Figure S4.**

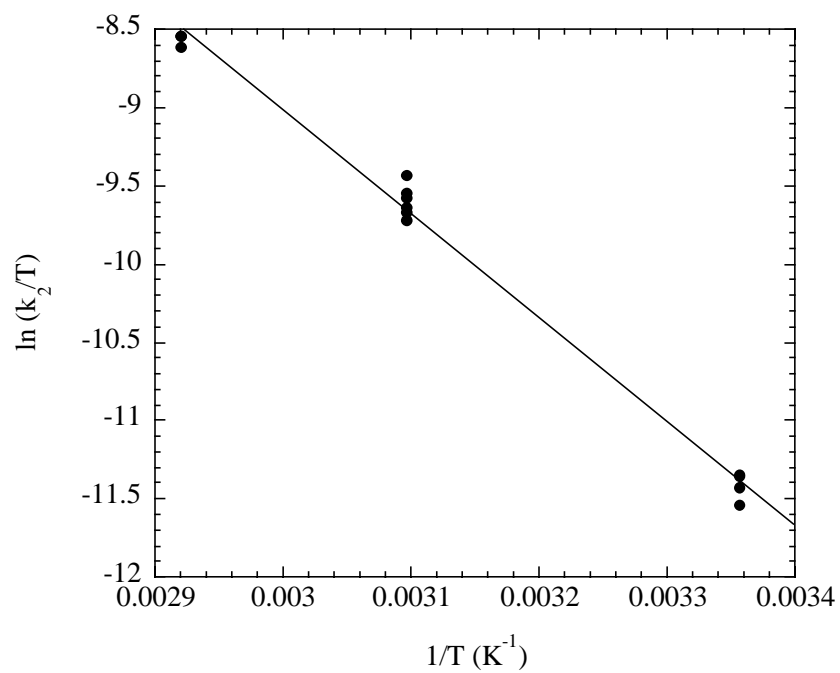
Cyclic voltammetry of  $[\text{Fe}^{\text{III}}(\text{PY5})(\text{OH})]^{2+}$  in 0.10 M tetrabutylammonium perchlorate solution in DMSO. The arrows indicate the direction of the scan. The peaks at 440 mV (anodic current) and 330 mV (cathodic current) are due to the added ferrocene reference.



**Figure S5.** Infrared spectrum of  $[\text{Fe}^{\text{III}}(\text{PY5})(\text{OH})]^{2+}$  as a Nujols mull. The peak at  $3398 \text{ cm}^{-1}$  is assigned as the O-H stretch of the exogenous hydroxide.

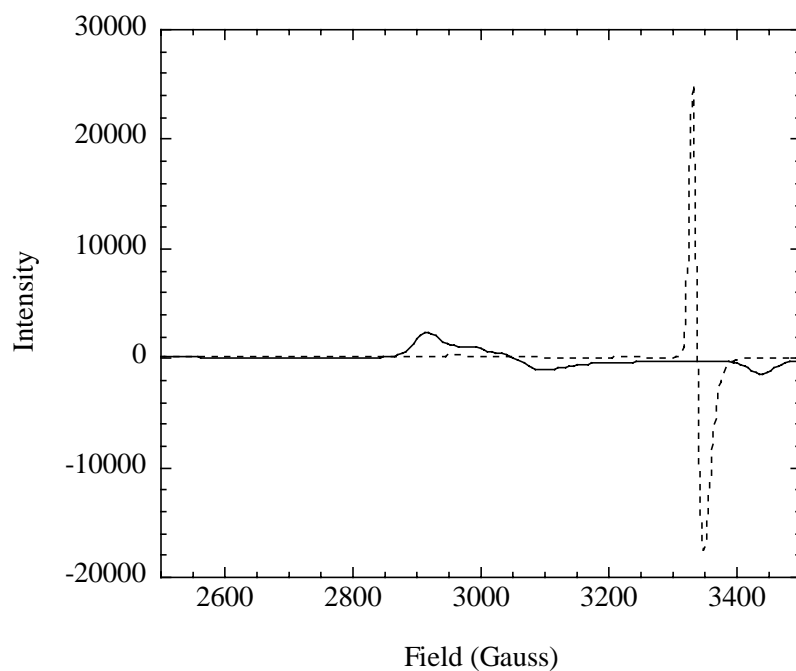


**Figure S6.** Plot of the log of the corrected rate constants  $k_{2corr}$  against substrate  $pK_a$  (DMSO). The following substrates are represented on the plot ( $pK_a$  in parentheses): fluorene (22.6); xanthene (30.0); 9,10-dihydroanthracene (30.1); and ethylbenzene (44, Ref 18). All  $pK_a$  values are from Ref 16 except where noted. Kinetic data are measured at 323 K.



**Figure S7.** Eyring plot for the reduction of 0.7-1.5 mM  $[\text{Fe}^{\text{III}}(\text{PY5})(\text{OH})]^{2+}$  by excess (>40 equiv) 9,10-dihydroanthracene (298-343 K) in anaerobic MeCN.





**Figure S8.** EPR spectra of  $[\text{Fe}^{\text{III}}(\text{PY5})(\text{OH})]^{2+}$  before (solid line) and after (dashed line) addition of 10 equiv of 2,4,6-tri-*t*-butylphenol (TTBP). The reaction is performed in MeCN at 298 K while the spectra are taken at 77 K. Integration of the signals indicates that the concentration of the TTBP radical is ~30% that of the original solution of  $[\text{Fe}^{\text{III}}(\text{PY5})(\text{OH})]^{2+}$ .