

Electronic Supplementary Information

Autocatalytic dioxygen activation to produce an iron(V)-oxo complex without any reductants

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Experimental section

Materials. Commercially available chemicals and solvents were used without further purification unless otherwise indicated. $\text{Na}(\text{H}_2\text{O})_x[\text{Fe}(\text{III})(\text{TAML})]$ complex was purchased from GreenOx Catalyst Inc. (Pittsburgh, PA, USA). The commercial complex has been recrystallized from isopropanol/ H_2O mixture as previously described for further use.^{S1} Acetonitrile, acetone, hydrogen peroxide, *m*-chloroperbenzoic acid (*m*-CPBA), sulfuric acid and chloroform-*d* were purchased from Aldrich Chemical Co.

Instrumentation. UV-vis spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer equipped with a UNISOKU Scientific Instruments Cryostat USP-203A for low-temperature experiments. X-band EPR spectra were recorded at 5 K using X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM). Low temperature was achieved and controlled with an Oxford Instruments ESR900 liquid He quartz cryostat with an Oxford Instruments ITC503 temperature and gas flow controller. The experimental parameters for EPR measurement were as follows: Microwave frequency = 9.646 GHz, microwave power = 1.0 mW, modulation amplitude = 10 G, gain = 1×10^4 , modulation frequency = 100 kHz, time constant = 40.96 ms, and conversion time = 81.00 ms. ^1H NMR spectra were measured with a Bruker model digital AVANCE III 400 FT-NMR spectrometer.

Formation of iron(V)-oxo intermediate. All the reactions were run in a 1-cm UV cuvette by monitoring UV-vis spectral changes of the reaction solutions. Addition of a catalytic amount of $[(\text{TAML})\text{Fe}^{\text{III}}]^-$ (0.15 mM) to an air-saturated acetone solution resulted in the formation of $[(\text{TAML})\text{Fe}^{\text{V}}(\text{O})]^-$ at 298 K with good yields which were determined using the extinction coefficient at 630 nm ($\epsilon = 4200 \text{ M}^{-1} \text{ cm}^{-1}$) due to $[(\text{TAML})\text{Fe}^{\text{V}}(\text{O})]^-$. The formation $[(\text{TAML})\text{Fe}^{\text{V}}(\text{O})]^-$ was also confirmed by the reaction of $[(\text{TAML})\text{Fe}^{\text{III}}]^-$ with *m*-CPBA according to the published procedure.^{S2}

Triacetone triperoxide (TATP). The triacetone triperoxide (TATP) has been prepared by literature methods.^{S3} Acetone (0.010 mol) was mixed with hydrogen peroxide (30%, 0.010 mol), and the mixture was cooled to 0 °C. Concentrated sulfuric acid (1 drop) was slowly added at the same temperature, and the mixture was allowed to reach room temperature and kept at this

temperature without stirring for 24 h. The resultant precipitate was collected by filtration with air-aided suction to afford the white crystals of TATP. The formation of TATP was confirmed by ^1H NMR (see Fig. S3).

References

- S1. (a) C. P. Horwitz and A. Ghosh, Carnegie Mellon University, PA, USA, 2006; found under <http://igs.chem.cmu.edu/>; (b) T. J. Collins, R. D. Powell, C. Slebodnick and E. S. Uffelman, *J. Am. Chem. Soc.*, 1991, **113**, 8419.
- S2. (a) F. T. de Oliveira, A. Chanda, D. Banerjee, X. Shan, S. Mondal, L. Que, Jr., E. L. Bominaar, E. Münck and T. J. Collins, *Science*, 2007, **315**, 835; (b) E. Kwon, K.-B. Cho, S. Hong and W. Nam, *Chem. Commun.*, 2014, **50**, 5572.
- S3. (a) F. Dubnikova, R. Kosloff, J. Almog, Y. Zeiri, R. Boese, H. Itzhaky, A. Alt and E. Keinan *J. Am. Chem. Soc.*, 2005, **127**, 1146; (b) E. A. Espinosa-Fuentes, L. C. Pacheco-Londoño, M. A. Barreto-Cabán and S. P. Hernández-Rivera, *Propellants Explos. Pyrotech.*, 2012, **37**, 413.

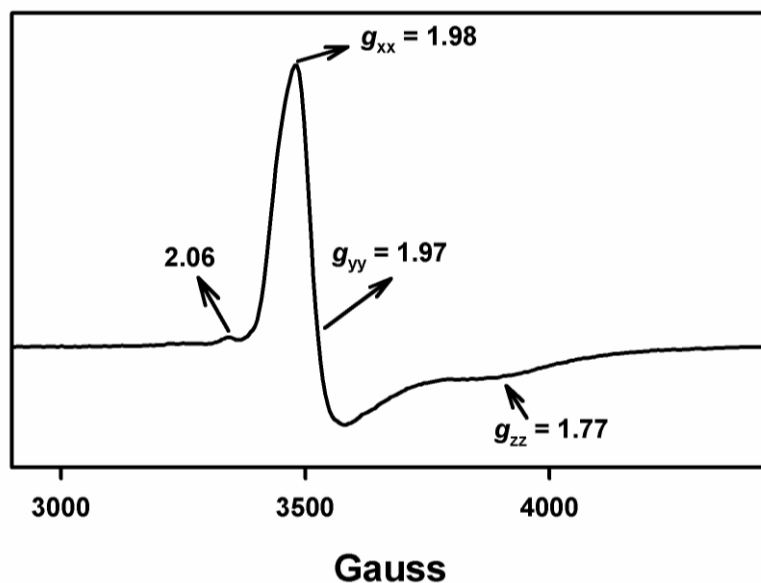


Fig. S1 X-band CW-EPR spectrum of $[(\text{TAML})\text{Fe}^{\text{V}}(\text{O})]^-$ (0.25 mM) species produced by autocatalytic dioxygen activation with $[(\text{TAML})\text{Fe}^{\text{III}}]^-$ in air-saturated acetone at 298 K. EPR spectrum was recorded at 5 K. The major anisotropic EPR signals with $g_{xx} = 1.98$, $g_{yy} = 1.97$, and $g_{zz} = 1.77$ in EPR spectrum belong to $S = 1/2$ $[(\text{TAML})\text{Fe}^{\text{V}}(\text{O})]^-$ species (see reference: F. T. de Oliveira, A. Chanda, D. Banerjee, X. Shan, S. Mondal, L. Que, Jr., E. L. Bominaar, E. Münck and T. J. Collins, *Science*, 2007, **315**, 835). The signals with the g value of 2.06 originated from the minor species.

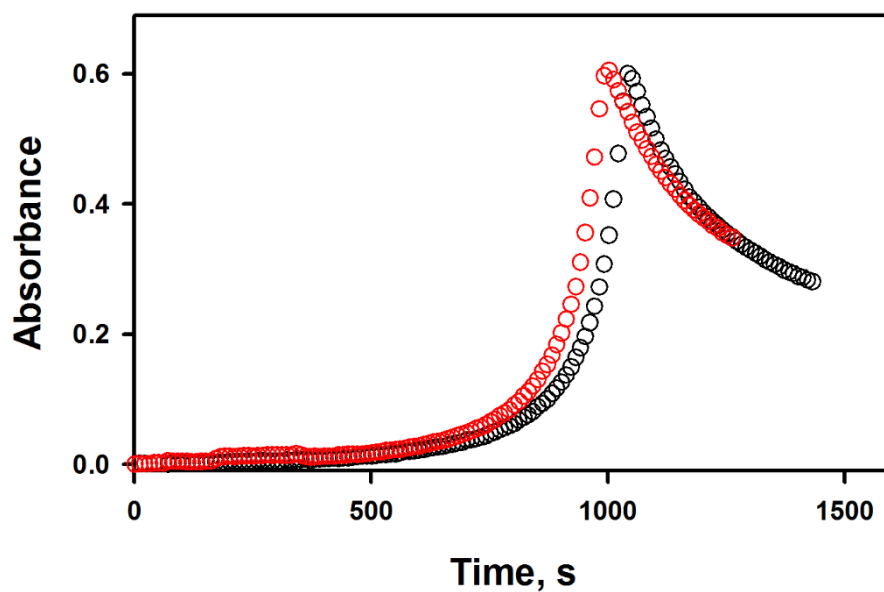


Fig. S2 Time profiles of absorbance at 630 nm due to $[(\text{TAML})\text{Fe}^{\text{V}}(\text{O})]^-$ observed in the oxygenation of $[(\text{TAML})\text{Fe}^{\text{III}}]^-$ (0.15 mM) with O_2 in aerated acetone (black circles) and O_2 -saturated acetone (red circles) at 298 K.

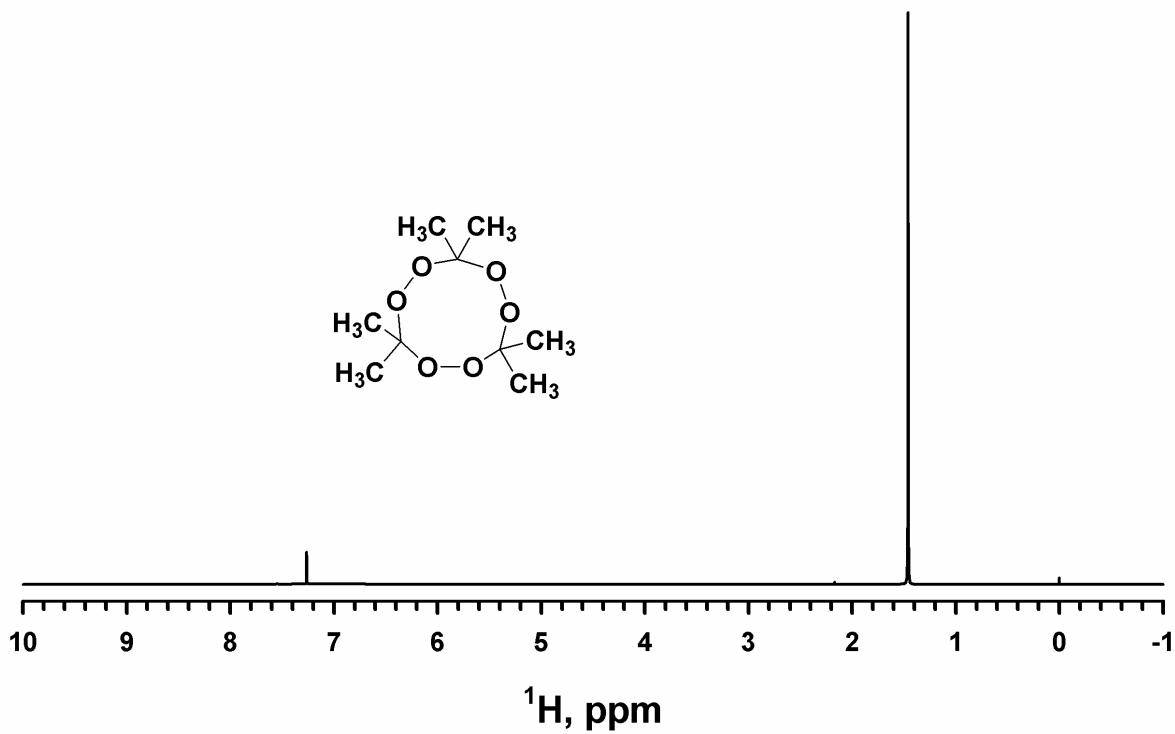


Fig. S3 ^1H NMR spectrum of TATP in CDCl_3 at 298 K. TATP was prepared by mixing acetone (0.010 mol) and hydrogen peroxide (0.010 mol) in the presence of the catalytic amount of sulfuric acid at 273 K.