Supporting Information

Formation, stability, and reactivity of a mononuclear nonheme oxoiron(IV) complex in aqueous solution

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Experimental Section

Materials. All chemicals obtained from Aldrich Chemical Co. were the best available purity and used without further purification unless otherwise indicated. Acetonitrile were obtained from Aldrich and distilled with CaH_2 under Ar prior to use. Water used in all the experiments was distilled and deionized (Millipore, Milli-Q). CH_3CO_3H (32% wt %), $KHSO_5$, and H_2O_2 (30% aqueous) were purchased from Aldrich Chemical Co. Iodosylbenzene (PhIO) was prepared from iodobenzene diacetate by a literature method [1]. $[Fe^{II}(N4Py)(ClO_4)_2]$ was synthesized by a literature procedure [2]. $H_2{}^{18}O$ (95% ^{18}O-enriched) was purchased from ICON Services Inc. (Summit, NJ, USA).

Instrumentation. UV-vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer equipped with an Optostat^{DN} variable-temperature liquid-nitrogen cryostat (Oxford instruments) or a circulating water bath. Electrospray ionization mass (ESI-MS) spectra were collected on a Thermo Finnigan (San Jose, CA, USA) LCQ^{TM} Advantage MAX quadrupole ion trap instrument. Product analysis for thioanisole oxidation was performed on DIONEX Pump Series P 580 equipped with a variable wavelength UV-200 detector. Products were separated on Waters Symmetry C18 reverse phase column (4.6 x 250 mm), and detection was made at 215 and 254 nm.

Generation and reactivity studies of $[(N4Py)Fe^{IV}{=}O]^{2+}$ (1). In general, reactions were run at least in triplicate, and the data represent average of these reactions. Treatment of $[Fe^{II}(N4Py)(ClO_4)_2]$ (2 mM) with a stoichiometric amount of oxidant (2 mM) in a solvent mixture (2 mL) of H_2O-CH_3CN or buffered H_2O-CH_3CN (v/v = 3 : 1) afforded the formation of a pale green solution at 25 °C. Then, thioanisole (10 – 40 equiv, diluted in 50 μL of CH_3CN) was added to the reaction solution. All reactions were followed by monitoring UV-vis spectral changes of the reaction solutions, and rate constants were determined by fitting the changes in absorbance at 681 nm. Product analysis was performed by injecting the reaction solution directly into HPLC, and product yields were determined by comparison with standard curves of known authentic samples.

Isotope labeling study with $H_2{}^{18}O$ was carried out by reacting $[Fe^{II}(N4Py)(ClO_4)_2]$ (2 mM) with 2 equiv of CH_3CO_3H (4 mM) in a solvent mixture (0.1 mL) of $H_2{}^{18}O$-CH_3CN (*v*/*v* = 3 : 1) at 25 °C. The ESI MS of **1** was taken by infusing samples directly into the source at 20 μL/min using a syringe pump. The spray voltage was set at 4 kV and the capillary temperature at 70 °C.

References

[1] H. Saltzman and J. G. Sharefkin, *Org. Synth.*, Wiley, New York, 1973, Coll. Vol. V, p. 658.

[2] M. Lubben, A. Meetsma, E. C. Wilkinson, B. Feringa and L. Que, Jr., *Angew. Chem., Int. Ed. Engl.* 1995, **34**, 1512.

Table S1. Pseudo-first-order rate constants determined in the reactions of **1** and *para*-substituted thioanisoles at pH 5 at 10 °C[a]

Substituent of *para*-X-thioanisole	σ_p	k_{obs} (s^{-1})	log (k_{obs}) (s^{-1})	log (k_{rel})[b]
CH_3O	-0.27	9.9 x10^{-3}	-2.0	0.31
CH_3	-0.17	6.8 x10^{-3}	-2.2	0.14
H	0.0	4.9 x10^{-3}	-2.3	0.0
Cl	0.23	2.7 x10^{-3}	-2.6	-0.26
CHO	0.42	1.9 x10^{-3}	-2.7	-0.42
CN	0.66	1.0 x10^{-3}	-3.0	-0.71

[a] All reactions were followed by monitoring UV-vis spectral changes of the reaction solutions. **1** was prepared by reacting [$Fe^{II}(N4Py)(ClO_4)_2$] (2 mM) with $KHSO_5$ (2 mM) at pH 5 in CH_3CN-acetate buffer (0.1 M) (v/v = 1:3) at 10 °C. Then, the substrate (20 equiv, diluted in 50 μL of CH_3CN) was added to the reaction solution. The pseudo-first-order rate constants were determined by fitting the changes in absorbance at 681 nm.

[b] The relative rate constants, k_{rel}, were calculated by dividing k_{obs} of *para*-X-thioanisoles by k_{obs} of *para*-H-thioanisole.

Table S2. Bimolecular rate constants determined in the reactions of **1** and *para*-substituted thioanisoles at pH 5 at 10 °C[a]

Substituent of *para*-X-thioanisole	E^{o}_{ox} vs. SCE (V)[b]	k_2 (M^{-1} s^{-1})	log (k_2) / M^{-1} s^{-1}
CH_3O	1.13	2.1×10^{-1}	-0.67
CH_3	1.24	1.6×10^{-1}	-0.79
H	1.34	8.1×10^{-2}	-1.1
Cl	1.37	7.4×10^{-2}	-1.1

[a] All reactions were followed by monitoring UV-vis spectral changes of the reaction solutions. **1** was prepared by reacting $[Fe^{II}(N4Py)(ClO_4)_2]$ (2 mM) with $KHSO_5$ (2 mM) at pH 5 in CH_3CN-acetate buffer (0.1 M) (v/v = 1:3) at 10 °C. Then, appropriate amounts of substrates (10 - 40 equiv, diluted in 50 μL of CH_3CN) were added to the reaction solution. Pseudo-first-order rate constants were determined by fitting the changes in absorbance at 681 nm, and second-order-rate constants k_2 were determined by plotting k_{obs} against substrate concentration (see Figure S1 as an example).

[b] Data were obtained from Table 1 in Goto et al., *J. Am. Chem. Soc.* 1999, **121**, 9497.

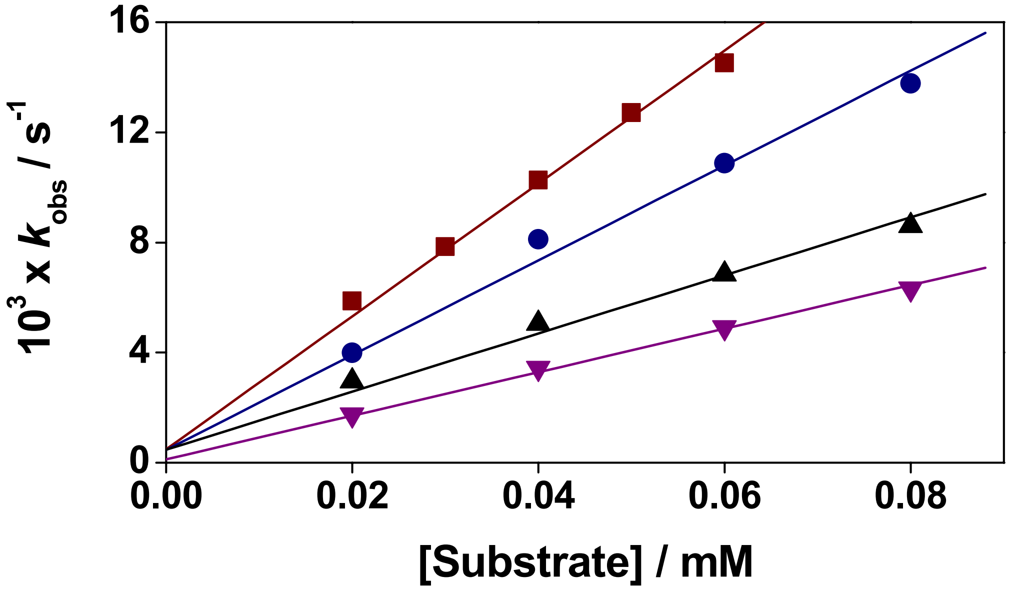

Figure S1 Plot of k_{obs} against *para*-substituted thioanisole concentration for the reaction of **1** and *para*-substituted thioanisole at pH 5. *para*-OCH_3 (■), *para*-CH_3 (●), *para*-H (▲) and *para*-Cl (▼). Reaction conditions: **1** (2 mM) was prepared with $KHSO_5$ (2 mM) in 0.1 M acetate buffer-CH_3CN (*v*/*v* = 3:1) at 10 °C followed by adding the given amounts of thioanisole to the reaction solution of **1**.

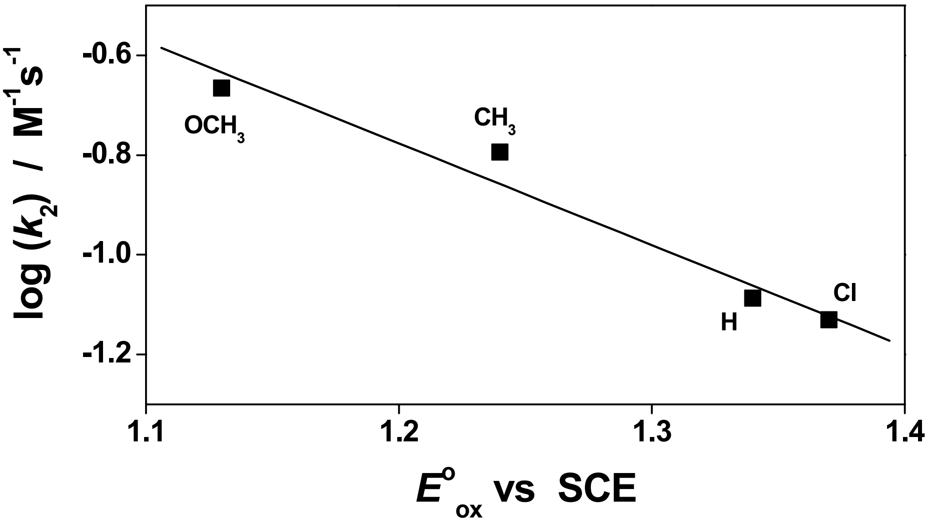

Figure S2 Plot of k_2 against the one-electron oxidation potentials (E^o_{ox}) of thioanisoles at pH 5 in 0.1 M acetate buffer-CH_3CN (v/v = 3:1) at 10 °C. Data are reported in Table S2, and see the detailed experimental procedures in Table S2, footnotes a and b.

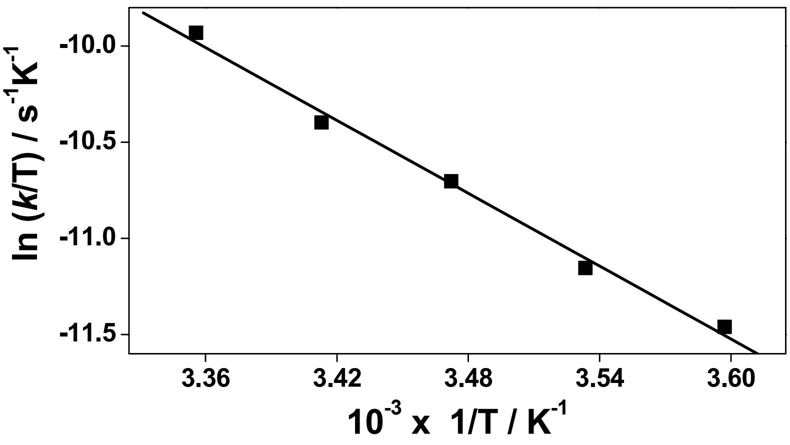

Figure S3 Determination of activation parameters for the oxidation of thioanisole by **1** at pH 5. Reaction conditions: **1** (2 mM) was prepared with $KHSO_5$ (2 mM) at pH 5 in 0.1 M acetate buffer-CH_3CN (*v*/*v* = 3:1) at the given temperatures. Then, thioanisole (10 equiv to **1**, diluted in 50 μL of CH_3CN) was added to the reaction solution of **1**.