## **Supporting Information**

## Proton-Promoted Oxygen Atom Transfer vs Proton-Coupled Electron Transfer of a Non-Heme Iron(IV)-Oxo Complex

Jiyun Park,<sup>†</sup> Yuma Morimoto,<sup>‡</sup> Yong-Min Lee,<sup>†</sup> Wonwoo Nam,<sup>\*,†</sup> and Shunichi Fukuzumi<sup>\*,†,‡</sup>

<sup>†</sup>Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea <sup>‡</sup>Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871,

Japan

E-mail: fukuzumi@chem.eng.osaka-u.ac.jp, wwnam@ewha.ac.kr

**Table S1.** One-Electron Oxidation Potentials ( $E_{ox}$ ) of *para*-X-Substituted Thioanisoles and One-Electron Reductants and Second-Order Rate Constants of Sulfoxidation and Electron-Transfer Reactions with [(N4Py)Fe<sup>IV</sup>(O)]<sup>2+</sup> in MeCN at 298K

thioanisole or one- electron reductant	E <sub>ox</sub>	$k_2 \text{ or } k_{\text{et}},  \mathrm{M}^{-1}  \mathrm{s}^{-1}$		10 mM HClO <sub>4</sub>
		without HClO <sub>4</sub>	10 mM HClO <sub>4</sub>	$\log (k_2, \mathbf{M}^{-1}  \mathbf{s}^{-1})$
para-X-thioanisoles				
<i>p</i> -Me	1.24	$1.3 \pm 0.1$	$(3.2 \pm 0.2) \times 10^3$	3.5
<i>р</i> -Н	1.34	$(8.7 \pm 0.4) \times 10^{-1}$	$(1.5 \pm 0.1) \times 10^3$	3.2
p-Cl	1.37	$(8.7 \pm 0.4) \times 10^{-1}$	$(7.2 \pm 0.4) \times 10^2$	2.8
<i>p</i> -Br	1.41	$(1.5 \pm 0.1) \times 10^{-1}$	$(8.4 \pm 0.4) \times 10^2$	2.9
<i>p</i> -CN	1.61	$(4.4 \pm 0.2) \times 10^{-2}$	$(6.2 \pm 0.3) \times 10$	1.8
one-electron reductant				
$\left[Fe^{II}(Me_2bpy)_3\right]^{2+}$	0.92	NR <sup>a</sup>	$(3.2 \pm 0.2) \times 10^2$	2.5
$\left[Ru^{II}(Me_2bpy)_3\right]^{2+}$	1.10	$NR^{a}$	$(1.2 \pm 0.1) \times 10^2$	2.1
[Fe <sup>II</sup> (Clphen) <sub>3</sub> ] <sup>2+</sup>	1.17	$\mathbf{NR}^{\mathrm{a}}$	$(2.1 \pm 0.1) \times 10$	1.3
[Ru <sup>II</sup> (Clphen) <sub>3</sub> ] <sup>2+</sup>	1.36	NR <sup>a</sup>	$1.4 \pm 0.1$	$1.6  imes 10^{-1}$

<sup>a</sup>NR : No Reaction



**Figure S1.** ESI-MS spectrum of the final products obtained in the reaction of  $[(N4Py)Fe^{IV}(O)]^{2+}$  (0.5 mM) with thioanisole (5.0 mM) in the presence of HClO<sub>4</sub> (10 mM) in MeCN at 298 K. Peaks at *m/z* of 231.9 and 522.0 correspond to  $[Fe^{II}(N4Py)(MeCN)]^{2+}$  (calcd *m/z* 232.1) and  $[Fe^{II}(N4Py)(ClO_4)]^+$  (calcd *m/z* 522.1), respectively. Inset shows the observed isotope distribution patterns for  $[Fe^{II}(N4Py)(MeCN)]^{2+}$ .



**Figure S2.** Plots of the pseudo-first-order rate constants ( $k_1$ ) vs concentrations of *para*-X-thioanisoles to determine the second-order rate constants ( $k_{obs}$ ) in the sulfoxidation of *para*-X-thioanisoles by [(N4Py)Fe<sup>IV</sup>(O)]<sup>2+</sup> (0.25 mM) in the presence of HClO<sub>4</sub> (10 mM) in MeCN at 298 K.



**Figure S3**. <sup>1</sup>H NMR spectrum of thioanisole (5.0 mM) in the presence of  $HClO_4$  (20 mM) in CD<sub>3</sub>CN at 298 K. A broadened Ph-S<sup>+</sup>(H)-CH<sub>3</sub> peak appeared in the range of 8.1 – 9.1 ppm, indicating that there is an equilibrium between thioanisole and protonated thioanisole in the presence of  $HClO_4$ . Number of scan was 2048.



**Figure S4.** Plots of concentration of  $[Ru^{III}(Clphen)_3]^{3+}$  produced in PCET from  $[Ru^{II}(Clphen)_3]^{2+}$  to  $[(N4Py)Fe^{IV}(O)]^{2+}$  (0.25 mM) in the presence of various HClO<sub>4</sub> concentrations (black line; 5.0 mM, red line; 7.5 mM, blue line; 15 mM and green line; 20 mM) in deaerated MeCN at 298 K vs initial concentration of  $[Ru^{II}(Clphen)_3](PF_6)_2$ ,  $[[Ru^{II}(Clphen)_3](PF_6)_2]_0$ .



**Figure S5.** Visible spectral changes observed in the reaction of  $[(N4Py)Fe^{IV}(O)]^{2+}$  (0.25 mM) with  $[Fe^{II}(Me_2bpy)]^{2+}$  (5.0 mM) in the presence of HClO<sub>4</sub> (10.0 mM) in MeCN at 298 K (left panel). Right panel shows time course monitored at 695 nm due to the decay of  $[(N4Py)Fe^{IV}(O)]^{2+}$ .



**Figure S6.** Plot of the pseudo-first-order rate constant  $(k_1)$  vs concentration of  $[\text{Fe}^{II}(\text{Me}_2\text{bpy})]^{2+}$  to determine the second-order rate constant  $(k_{obs})$  of PCET from  $[\text{Fe}^{II}(\text{Me}_2\text{bpy})]^{2+}$  to  $[(\text{N4Py})\text{Fe}^{IV}(\text{O})]^{2+}$  (0.25 mM) in the presence of HClO<sub>4</sub> (10 mM) in MeCN at 298 K.