

## Supporting Information

### **Formic Acid Acting as an Efficient Oxygen Scavenger in Four-Electron Reduction of Oxygen Catalyzed by a Heterodinuclear Iridium-Ruthenium Complex in Water**

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## Experimental Section

### Materials.

Commercially available reagents: hydrogen hexachloroiridate,  $\text{H}_2\text{IrCl}_6$  (Tanaka Kikinzoku), *cis*-dichlorobis(2,2'-bipyridine)ruthenium(II) dihydrate,  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{Cl}_2)] \cdot 2\text{H}_2\text{O}$  (Stream Chemicals, Inc.),  $\eta^5$ -pentamethylcyclopentadiene (Kanto Chemical Co., Inc.), 2,2'-bipyrimidine (Johnson Matthey, Inc.), formic acid, sodium hydroxide, diluted sulfuric acid (1.0 M, Wako Pure Chemical Industries.), peracetic acid (9%) in acetic acid solution (Aldrich Chemical Co.),  $\text{D}_2\text{O}$  (99.9% D, Cambridge Isotope Laboratories) were the best available purity and used without further purification unless otherwise noted.  $\text{H}_2$  gas (99.99999%, Japan Air Gases Co.) and a standard gas ( $\text{H}_2$  1.07%,  $\text{CO}_2$  1.07%,  $\text{CO}$  1.06%,  $\text{N}_2$  96.8%; GL Sciences Co., Ltd.) as a reference of GC analysis were used without further purification.

### General Methods.

All experiments were carried out under an Ar or  $\text{N}_2$  atmosphere by using standard Schlenk techniques. Purification of water (18.2  $\text{M}\Omega$  cm) was performed with a Milli-Q system (Millipore; Direct-Q 3 UV).  $^1\text{H}$  NMR spectra were recorded on a JEOL JNM-AL300 spectrometer and a Varian UNITY INOVA600. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments in  $\text{D}_2\text{O}$  were performed by dissolving the samples in  $\text{D}_2\text{O}$  in an NMR tube (diameter = 5.0 mm) with a sealed capillary tube (diameter = 1.5 mm) containing 3-(trimethylsilyl)propionic-2,2',3,3'- $d_4$  acid sodium salt (TSP) (100 mM, as a reference with the methyl proton resonance set at 0.00 ppm) dissolved in  $\text{D}_2\text{O}$  for deuterium lock. UV-vis absorption spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer with a quartz cuvette (path length = 1 mm or 1 cm) at 298 K. Kinetic measurements were performed on a UNISOKU RSP-601 stopped-flow spectrometer equipped with MOS-type highly sensitive photodiodes at 298 K. Electrospray ionization mass spectrometry (ESI-MS) data were obtained by an API 150EX quadrupole mass spectrometer (PE-Sciex) in the positive detection

mode, equipped with an ion spray interface. The sprayer was held at a potential of +5.0 kV, and compressed N<sub>2</sub> was employed to assist liquid nebulization. The orifice potential was maintained at +30.0 V. The filtration with the membrane filter was performed using the membrane filter (Toyo, Roshi Kaisha, Ltd., H100A025A, pore diameter, 1 μm)

### **pH-Adjustment.**

In a pH range of 1.1-7.8, the pH values of the solutions were determined by a pH meter (TOA, HM-20J) equipped with a pH combination electrode (TOA, GST-5725C). The pH of the solution was adjusted by using 1.00–10.0 M NaOH/H<sub>2</sub>O or 1.00 M H<sub>2</sub>SO<sub>4</sub> without buffer.

### **Syntheses.**

[Ir<sup>III</sup>(Cp<sup>\*</sup>)(Cl)<sub>2</sub>]<sub>2</sub>:<sup>1</sup> To H<sub>2</sub>IrCl<sub>6</sub> (1.02 g, 3.87 mmol) in 6 mL of methanol was added excess η<sup>5</sup>-pentamethylcyclopentadiene (1.5 mL). The mixture was stirred under reflux for 37 h. After the mixture was cooled to 0 °C, the product was isolated by filtration and washing with ether to yield an yellow blown powder of [Ir<sup>III</sup>(Cp<sup>\*</sup>)(Cl)<sub>2</sub>]<sub>2</sub>, which was dried in vacuo {Yield: 73% based on H<sub>2</sub>IrCl<sub>6</sub>}. <sup>1</sup>H NMR (300 MHz, in CDCl<sub>3</sub>, 298 K): δ (ppm) 1.60 (s, η<sup>5</sup>-C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>, 15H). Anal. Calcd for [Ir<sup>III</sup>(Cp<sup>\*</sup>)(Cl)<sub>2</sub>]<sub>2</sub>: C<sub>20</sub>H<sub>30</sub>Cl<sub>4</sub>Ir<sub>2</sub>: C, 30.15%; H, 3.80%. Found: C, 30.14 %; H, 3.72 %.

[Ir<sup>III</sup>(Cp<sup>\*</sup>)(H<sub>2</sub>O)<sub>3</sub>](SO<sub>4</sub>):<sup>2</sup> A solution of [Ir<sup>III</sup>(Cp<sup>\*</sup>)(Cl)<sub>2</sub>]<sub>2</sub> (0.96 g, 1.32 mmol) and Ag<sub>2</sub>SO<sub>4</sub> (0.83 g, 2.66 mmol) in H<sub>2</sub>O (70 mL) was stirred at ambient temperature for 5 h in the dark, and then the solution was filtered with membrane filter. The filtrate was evaporated under reduced pressure to yield an orange powder of [Ir<sup>III</sup>(Cp<sup>\*</sup>)(H<sub>2</sub>O)<sub>3</sub>](SO<sub>4</sub>), which was dried in vacuo {Yield: 86 % based on [Ir<sup>III</sup>(Cp<sup>\*</sup>)(Cl)<sub>2</sub>]<sub>2</sub>}. <sup>1</sup>H NMR (300 MHz, in DMSO-*d*<sub>6</sub>, 298 K): δ (ppm) 1.68 (s, η<sup>5</sup>-C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>, 15H), 3.31 (br, 3(H<sub>2</sub>O), 6H). Anal. Clad for [Ir<sup>III</sup>(Cp<sup>\*</sup>)(H<sub>2</sub>O)<sub>3</sub>](SO<sub>4</sub>): C<sub>10</sub>H<sub>21</sub>O<sub>7</sub>SIr: C, 25.15 %; H, 4.43 %. Found: C, 25.39 %; H, 4.48 %.

[Ru<sup>II</sup>(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](SO<sub>4</sub>): A solution of [Ru<sup>II</sup>(bpy)<sub>2</sub>(Cl)<sub>2</sub>]•2H<sub>2</sub>O (3.1 g, 6.0 mmol) and Ag<sub>2</sub>SO<sub>4</sub> (1.87 g, 6.0 mmol) in H<sub>2</sub>O (20 mL) was stirred at ambient temperature for 12 h and then the solution was filtered with membrane filter. The filtrate was evaporated under reduced pressure to yield a red powder of [Ru<sup>II</sup>(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](SO<sub>4</sub>), which was dried in vacuo

{Yield: 90 % based on  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{Cl}_2)] \cdot 2\text{H}_2\text{O}$ }.  $^1\text{H}$  NMR (300 MHz, in  $\text{D}_2\text{O}$ , reference to TSP in  $\text{D}_2\text{O}$ , 298 K):  $\delta$  (ppm) 7.06 (t,  $J = 7$  Hz, 2H, bpy), 7.70 (d,  $J = 6$  Hz, 2H, bpy), 7.74 (t,  $J = 8$  Hz, 2H, bpy), 7.88 (t,  $J = 7$  Hz, 2H, bpy), 8.23 (t,  $J = 8$  Hz, 2H, bpy), 8.34 (d,  $J = 8$  Hz, 2H, bpy), 8.56 (d,  $J = 8$  Hz, 2H, bpy), 9.36 (d,  $J = 5$  Hz, 2H, bpy). Anal. Calcd for  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2](\text{SO}_4) \cdot \text{H}_2\text{O}$ :  $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_6\text{SRu} \cdot \text{H}_2\text{O}$ : C, 42.63 %; H, 3.93 %; N, 9.94 %. Found: C, 42.53 %; H, 3.67 %; N, 9.95 %.

$[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{bpm})](\text{SO}_4)$ : A solution of  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2](\text{SO}_4)$  (0.6 g, 1.1 mmol) and 2,2'-bipyrimidine (137 mg, 1.1 mmol) in  $\text{H}_2\text{O}$  (40 mL) was stirred at ambient temperature for 5 h. The mixture was chromatographed on a Sephadex (G-10) column using  $\text{H}_2\text{O}$  as an eluent. The product was evaporated under reduced pressure to yield an orange powder of  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{bpm})](\text{SO}_4)$ , which was dried in vacuo {Yield: 92% based on  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2](\text{SO}_4)$ }.  $^1\text{H}$  NMR (300 MHz, in  $\text{D}_2\text{O}$ , reference to TSP in  $\text{D}_2\text{O}$ , 298 K):  $\delta$  (ppm) 7.41 (t,  $J = 7$  Hz, 2H, bpy), 7.45 (t,  $J = 7$  Hz, 2H, bpy), 7.60 (t,  $J = 5$  Hz, 2H, bpm), 7.80 (d,  $J = 5$  Hz, 2H, bpy), 7.94 (d,  $J = 5$  Hz, 2H, bpm), 8.09 (t,  $J = 8$  Hz, 2H, bpy), 8.12 (t,  $J = 8$  Hz, 2H, bpm), 8.24 (dd,  $J = 6, 2$  Hz, 2H, bpm), 8.57 (d,  $J = 8$  Hz, 2H, bpm), 8.58 (d,  $J = 7$  Hz, 2H, bpy), 9.09 (dd,  $J = 5, 2$  Hz, 2H, bpm). Anal. Calcd for  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{bpm})](\text{SO}_4) \cdot 4\text{H}_2\text{O}$ :  $\text{C}_{28}\text{H}_{22}\text{N}_8\text{O}_4\text{SRu} \cdot 4\text{H}_2\text{O}$ : C, 45.46 %; H, 4.09 %; N, 15.15 %. Found: C, 45.39 %; H, 4.06 %; N, 15.36 %.

$[\text{Ir}^{\text{III}}(\text{Cp}^*)(\text{H}_2\text{O})(\text{bpm})\text{Ru}^{\text{II}}(\text{bpy})_2](\text{X})_n$  [ $\mathbf{1}(\text{X})_n$ , where  $\text{X} = \text{SO}_4$  ( $n = 2$ ) or  $\text{PF}_6$  ( $n = 4$ ):  $[\text{Ir}^{\text{III}}(\text{Cp}^*)(\text{H}_2\text{O})_3](\text{SO}_4)$  (115 mg, 0.24 mmol) was added to an aqueous solution (10 mL) of  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{bpm})](\text{SO}_4)$  (163 mg, 0.24 mmol) and stirred for a few minutes. The product was evaporated under reduced pressure to yield quantitatively a green powder of  $\mathbf{1}(\text{SO}_4)_2$ , which was dried in vacuo.  $^1\text{H}$  NMR (300 MHz, in  $\text{D}_2\text{O}$ , reference to TSP in  $\text{D}_2\text{O}$ , 298 K):  $\delta$  (ppm) 1.71 (s, 15H,  $\eta^5\text{-C}_5(\text{CH}_3)_5$ ), 7.42 (t,  $J = 7$  Hz, 2H, bpm), 7.50 (t,  $J = 7$  Hz, 1H, bpy), 7.55 (t,  $J = 7$  Hz, 1H, bpm), 7.70 (d,  $J = 5$  Hz, 1H, bpy), 7.75 (d,  $J = 7$  Hz, 1H, bpm), 7.95 (t,  $J = 6$  Hz, 1H, bpm), 7.97 (t,  $J = 6$  Hz, 1H, bpm), 8.05-8.14 (m, 5H, bpm and bpy), 8.18 (t,  $J = 8$  Hz, 1H, bpm), 8.47 (d,  $J = 5$  Hz, 1H, bpm), 8.53 (d,  $J = 6$  Hz, 1H, bpm), 8.54-8.62 (m, 4H, bpm

and bpy), 9.45 (td,  $J = 5$  Hz, 2H, bpm).  $^{13}\text{C}$  NMR (300 MHz, in  $\text{D}_2\text{O}$ , reference to TSP in  $\text{D}_2\text{O}$ , 298 K):  $\delta$  (ppm) 10.97 ( $\eta^5\text{-C}_5(\underline{\text{C}}\text{H}_3)_5$ ), 93.54 ( $\eta^5\text{-C}_5(\underline{\text{C}}\text{H}_3)_5$ ), 127.76, 127.31, 127.39, 127.58, 130.00, 130.25, 130.32, 130.52, 130.79, 131.03, 154.49, 154.61, 155.15, 156.31, 159.03, 159.75, 159.76, 159.88, 160.20, 160.49, 164.56, 164.77, 169.08, 169.23 (bpm and bpy). Addition of an aqueous saturated solution of  $\text{KPF}_6$  into an aqueous solution (4.0 mL) of  $\mathbf{1}(\text{SO}_4)_2$  (44.4 mg, 40  $\mu\text{mol}$ ) gave a yellow powder of  $\mathbf{1}(\text{PF}_6)_4$  {Isolated yield: 61% based on  $\mathbf{1}(\text{SO}_4)_2$ }. Anal. Calcd for  $\mathbf{1}(\text{PF}_6)_4$ :  $\text{C}_{38}\text{H}_{39}\text{N}_8\text{OP}_4\text{F}_{24}\text{RuIr}$ : C, 30.49 %; H, 2.63 %; N, 7.49 %. Found: C, 30.75 %; H, 2.73 %; N, 7.76 %. ESI-MS in MeOH:  $m/z = 1027$   $[\text{Ir}^{\text{III}}(\text{Cp}^*)(\text{OCH}_3)(\text{bpm})\text{Ru}^{\text{II}}(\text{bpy})_2](\text{SO}_4)^+$

$[\text{Ir}^{\text{III}}(\text{Cp}^*)(\text{H})(\text{bpm})\text{Ru}^{\text{II}}(\text{bpy})_2]_2(\text{SO}_4)_3$  [ $\mathbf{3}_2(\text{SO}_4)_3$ ]:  $\text{HCOOH}$  solution (8.3 mL, 0.11 mol) was added to the solution of  $\mathbf{1}(\text{SO}_4)_2$  (1.0 mg, 6.0  $\mu\text{mol}$ ) in deaerated  $\text{H}_2\text{O}$  (0.4 mL) at pH 2.0. The pH was adjusted by using  $\text{H}_2\text{SO}_4$  solution. The mixture was heated at 333 K for 1 min.  $^1\text{H}$  NMR (300 MHz, in  $\text{D}_2\text{O}$ , reference to TSP in  $\text{D}_2\text{O}$ , 298 K):  $\delta$  (ppm) -11.4 (s, Ir-H), 1.91 (s, 15H,  $\eta^5\text{-C}_5(\text{CH}_3)_5$ ), 7.41-7.55 (m, 4H, bpm and bpy), 7.65-7.75 (m, 2H, bpm and bpy), 7.86 (d,  $J = 5$  Hz, 1H, bpy), 7.98 (d,  $J = 7$  Hz, 1H, bpy), 8.05-8.20 (m, 5H, bpm and bpy), 8.32 (m, 1H, bpy), 8.45-8.65 (m, 6H, bpm and bpy), 9.27 (d,  $J = 5$  Hz, 2H, bpm).

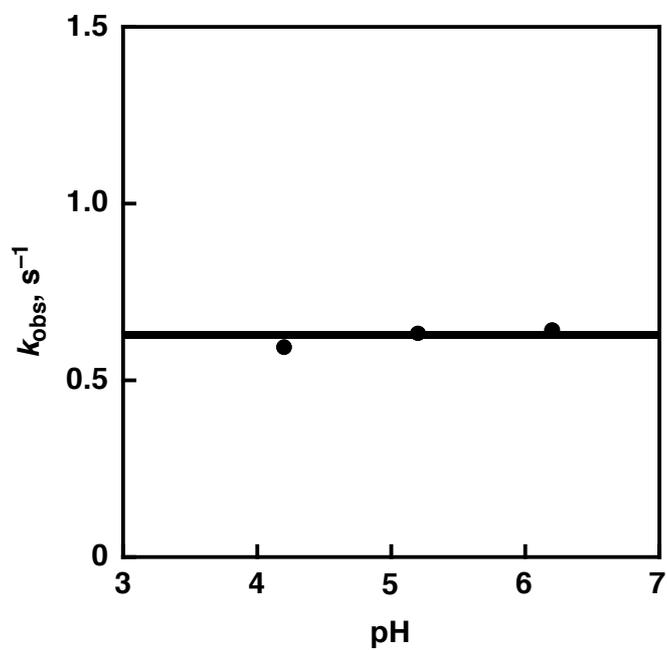
$[\text{Ir}^{\text{I}}(\text{Cp}^*)(\text{bpm})\text{Ru}^{\text{II}}(\text{bpy})_2](\text{SO}_4)$  [ $\mathbf{4}(\text{SO}_4)$ ]: 5 M  $\text{HCOOH}/\text{HCOONa}$  solution (1.2  $\mu\text{L}$ , 6.0  $\mu\text{mol}$ ) was added to the solution of  $\mathbf{1}(\text{SO}_4)_2$  (1.3 mg, 0.90  $\mu\text{mol}$ ) in deaerated  $\text{D}_2\text{O}$  (0.6 mL) at pD 6.5. The mixture was heated at 313 K for 15 min.  $^1\text{H}$  NMR (300 MHz, in  $\text{D}_2\text{O}$ , reference to TSP in  $\text{D}_2\text{O}$ , 298 K):  $\delta$  (ppm) 1.88 (s, 15H,  $\eta^5\text{-C}_5(\text{CH}_3)_5$ ), 6.14 (dd,  $J = 7, 4$  Hz, 2H, bpm), 7.06 (d,  $J = 5$  Hz, 2H, bpm), 7.30 (t,  $J = 6$  Hz, 2H, bpy), 7.36 (t,  $J = 7$  Hz, 2H, bpy), 7.89 (d,  $J = 5$  Hz, 2H, bpy), 8.03 (t,  $J = 7$  Hz, 2H, bpy), 8.05 (t,  $J = 6$  Hz, 2H, bpy), 8.07 (d,  $J = 5$  Hz, 2H, bpy), 8.52 (d,  $J = 6$  Hz, 2H, bpy), 8.54 (d,  $J = 5$  Hz, 2H, bpy), 8.76 (d,  $J = 7$  Hz, 2H, bpm).  $^{13}\text{C}$  NMR (600 MHz, in  $\text{D}_2\text{O}$ , reference to TSP in  $\text{D}_2\text{O}$ , 298 K):  $\delta$  (ppm) 11.57 ( $\eta^5\text{-C}_5(\underline{\text{C}}\text{H}_3)_5$ ), 90.21 ( $\eta^5\text{-C}_5(\underline{\text{C}}\text{H}_3)_5$ ), 110.65, 126.52, 129.62, 129.95, 140.32, 144.97, 150.75, 154.67, 154.73, 157.40, 159.86, 160.21 (bpm and bpy).

### Catalytic Oxygen Reduction.

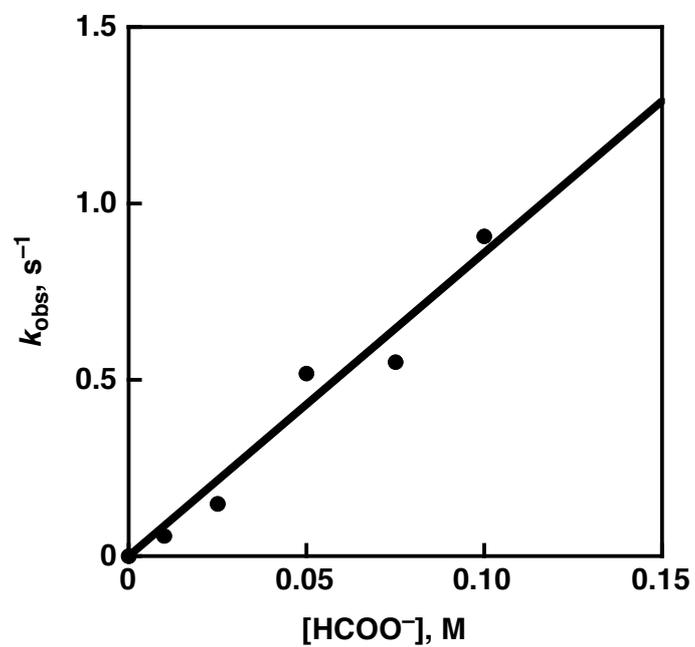
Typically, an aqueous 5 M HCOOH/HCOONa solution (0.4 mL, 2.0 mmol) was added to the solution of  $\mathbf{1}(\text{SO}_4)_2$  (1.2  $\mu\text{mol}$ ) in aerated  $\text{H}_2\text{O}$  (2.0 mL) at pH 3.6 at 298 K. The volume of dead space in the reaction vessel is 595  $\mu\text{L}$ . The amounts of evolved gases ( $\text{H}_2$  and  $\text{CO}_2$ ) were analyzed by a Shimadzu GC-14B gas chromatograph { $\text{N}_2$  carrier, active carbon with a particle size of 60-80 mesh at 353 K} equipped with a thermal conductivity detector. The amounts of evolved  $\text{O}_2$  gas was analyzed by a Shimadzu GC-17A gas chromatograph [Ar carrier, HP-molesieve capillary column (19095P-MS0), 30 m  $\times$  0.53 mm, Agilent Technology at 313 K] equipped with a thermal conductivity detector. The amount of dissolved dioxygen was monitored with a Clark-type oxygen electrode (YSI, Inc., Model 5300A).

#### **References.**

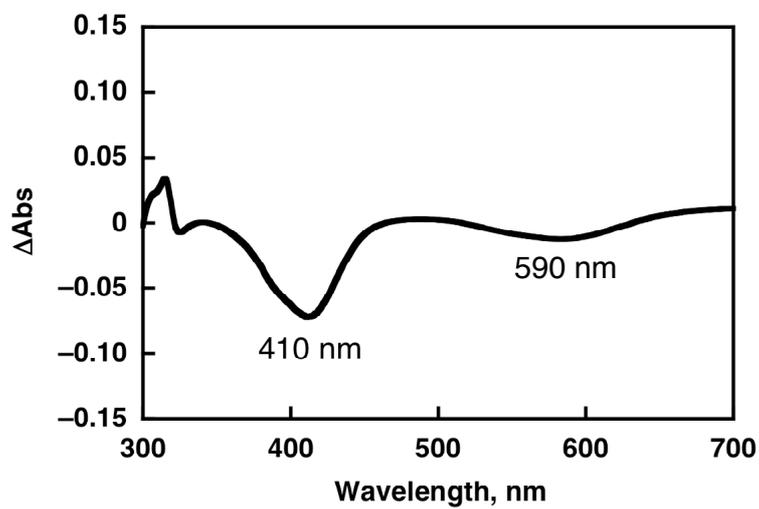
- (1) Ogo, S.; Fukuzumi, S.; Isobe, K. *Jpn. Kokai Tokkyo Koho JP* **2005**, 281169.
- (2) Ogo, S.; Makihara, N.; Watanabe, Y. *Organometallics* **1999**, *18*, 5470.



**Figure S1.** Plot of the pseudo-first-order rate constant for formation of an intermediate **B** ( $k_{\text{obs}}$ ) vs pH in the reduction of  $\text{O}_2$  (0.13 mM) by **3** (0.10 mM) in the presence of HCOOH/HCOONa (10 mM) in  $\text{H}_2\text{O}$  at 298 K.



**Figure S2.** Plot of the pseudo-first-order rate constant ( $k_{\text{obs}}$ ) vs concentration of  $\text{HCOO}^-$  for the reaction of an intermediate **B** with  $\text{HCOO}^-$  in the reduction of  $\text{O}_2$  (0.13 mM) by **3** (0.10 mM) in  $\text{H}_2\text{O}$  at pH 5.2 at 298 K.



**Figure S3.** Difference absorption spectrum by subtracting the spectrum of an aqua complex **1** from that observed after the reaction of **1** ( $95 \mu\text{M}$ ) with  $\text{CH}_3\text{C}(\text{O})\text{OOH}$  ( $67 \text{ mM}$ ) in the presence of  $\text{CH}_3\text{COOH}$  ( $0.64 \text{ M}$ ) at pH 2.1 at 298 K taken at 20 min after mixing.