Supporting Information

Mononuclear Copper Complex Catalyzed Four-Electron Reduction of Oxygen

Shunichi Fukuzumi,[†,‡]* Hiroaki Kotani,[†] Heather R. Lucas,[§] Kaoru Doi,[†]
Tomoyoshi Suenobu,[†] Ryan L. Peterson,[§,‡] and Kenneth D. Karlin[§,‡]*

[†] *Department of Material and Life Science, Graduate School of Engineering, Osaka University, SORST, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan*

[‡] *Department of Chemistry, Division of Nano Sciences, Center for Biomimetic Systems, Ewha Womans University, Seoul 120-750, Korea*

[§] *Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, USA*

* To whom correspondence should be addressed.

E-mail: fukuzumi@chem.eng.osaka-u.ac.jp, karlin@jhu.edu

Experimental Section

Materials. Commercially available reagents, decamethylferrocene (Fc^*), perchloric acid (70%), trifluoroacetic acid, hydrogen peroxide (30%), and NaI (Wako Pure Chemical Industries.) were the best available purity and used without further purification unless otherwise noted. Acetone was dried according to the literature procedures[1] and distilled under Ar prior to use. Copper complex $[(tmpa)Cu^{II}](ClO_4)_2$ (**1**) (tmpa: tris(2-pyridylmethyl)amine) was prepared according to literature procedures.[1]

UV-Vis Spectral Titration. The catalytic reduction of O_2 was observed by the spectral change in the presence of various concentrations of $HClO_4$ at 298 K using a Hewlett Packard 8453 photodiode-array spectrophotometer with a quartz cuvette (path length = 10 mm). Typically, an acetone solution of $HClO_4$ ($0 – 1.44 \times 10^{-3}$ M) was added by means of a microsyringe to an O_2-saturated acetone solution containing **1** (9.0×10^{-5} M) and Fc^* (1.5×10^{-3} M). The concentration of Fc^{*+} was determined from the absorption band at $\lambda_{max} = 780$ nm ($\varepsilon = 4.5 \times 10^2$ M^{-1} cm^{-1}). The ε value of Fc^{*+} was confirmed by the electron-transfer oxidation of Fc^* with $[Ru^{III}(bpy)_3](PF_6)_3$.

The limiting concentration of O_2 in an acetone solution was prepared by a mixed gas flow of O_2 and N_2. The mixed gas was controlled by using a gas mixer (Kofloc GB-3C, KOJIMA Instrument Inc.), which can mix two or more gases at a certain pressure and flow rate.

Reaction Procedure. Gas chromatographic analysis was performed on a Shimadzu GC-17A equipped with an InertCap 5MS/Sil column (GL Science Inc., 30 m) and a mass spectrograph (Shimadzu QP-5000) as a detector. The amount of H_2O_2 was determined by the titration by iodide ion. The diluted acetone solution (× 10) of the reduced product of O_2 was treated with an excess amount of NaI. The amount of I_3^- formed was then determined by the visible spectrum ($\lambda_{max} = 361$ nm, $\varepsilon = 2.5 \times 10^4$ M^{-1} cm^{-1}).

Kinetic Measurements. Kinetic measurements were performed on a UNISOKU RSP-601 stopped-flow spectrometer equipped with a MOS-type highly sensitive photodiode array or a Hewlett Packard 8453 photodiode-array spectrophotometer at 298 K. Rates of electron transfer from Fc^* to **1** were monitored by the rise of absorption bands due to Fc^{*+} and $[(tmpa)Cu^{II}(O_2)Cu^{II}(tmpa)]^{2+}$ (**2**). All kinetic measurements were carried out under pseudo-first-order conditions where concentrations of Fc^* was maintained to be more than in 10-fold excess compared to the concentration of **1**.

References

(1) Tyeklár, Z.; Jacobson, R. R.; Wei, N.; Murthy, N. N.; Zubieta, J.; Karlin, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 2677.

(2) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals,* 5th ed.; Butterworth-Heinemann: Amsterdam, 2003.

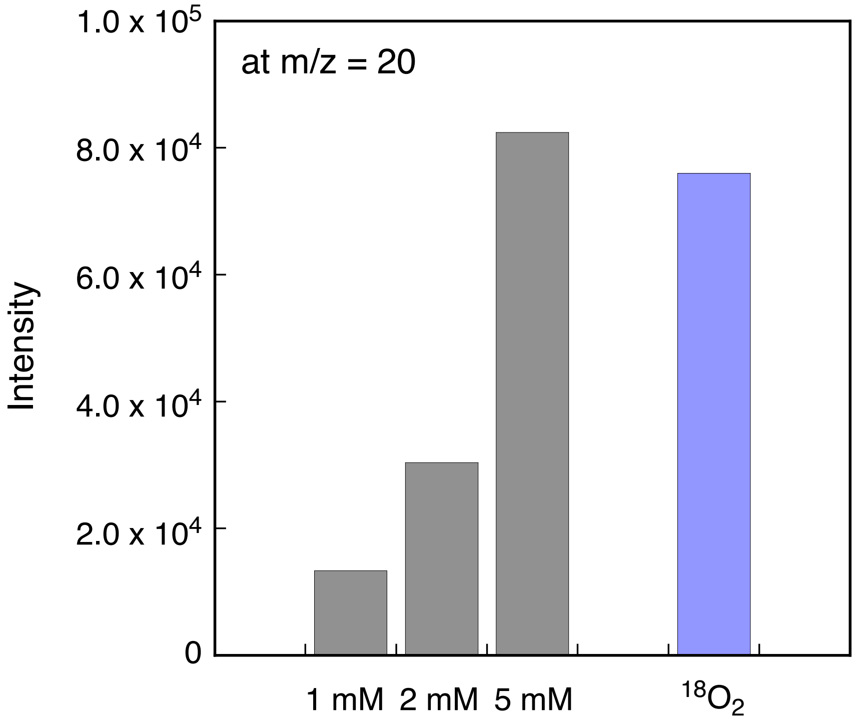

Figure S1. A molecular ion peak at m/z = 20 due to $H_2{}^{18}O$ (gray: 1, 2 and 5 mM) and that observed in the reduction of $^{18}O_2$ (blue) with Fc^* (17 mM) catalyzed by **1** (0.1 mM) in the presence of CF_3COOH (20 mM) in acetone at 298 K after 3h.

Comment: The product of catalytic O_2 reduction was confirmed to be H_2O by using ^{18}O-labeled O_2, because $H_2{}^{18}O$ was formed by the reduction of $^{18}O_2$. Trifluoroacetic acid (CF_3COOH) was used as a proton source instead of $HClO_4$ to avoid inclusion of H_2O.

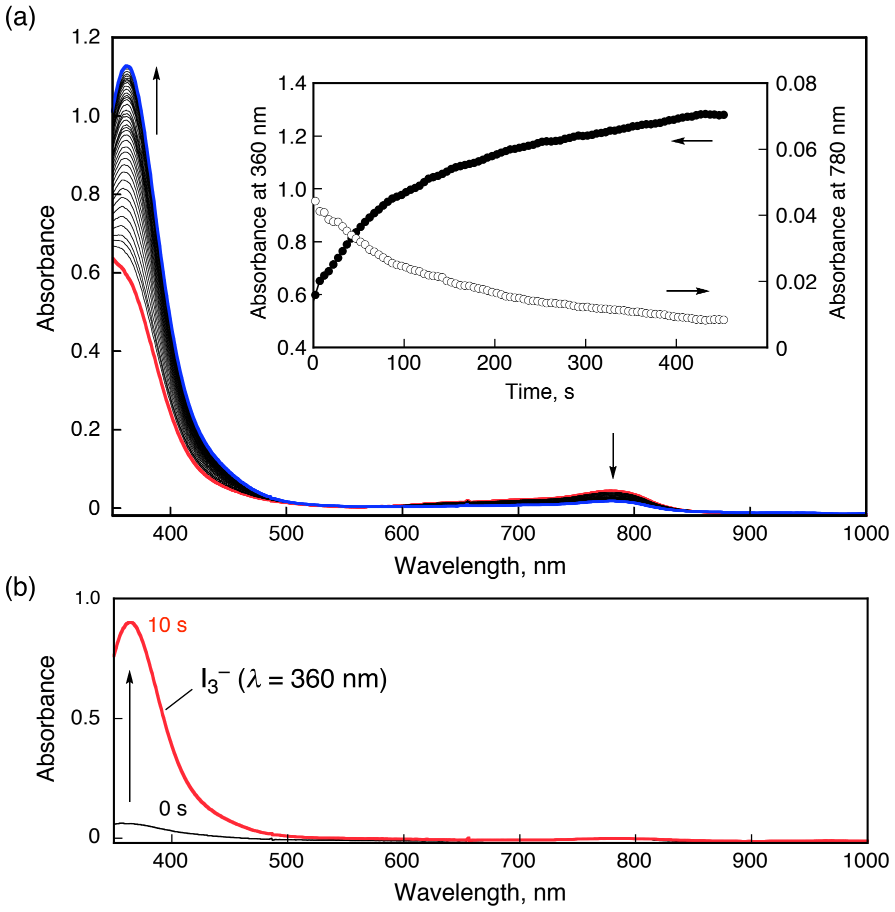

Figure S2. (a) Spectral changes in the reaction of NaI (0.3 M) and reduced product of O_2 (2.2 mM) in acetone solution including Fc^{*+} (0.15 mM), **1** (9.0×10^{-6} M) and $HClO_4$ (0.15 mM). Inset: Time profiles of formation of I_3^- monitored by absorbance at 360 nm and decay of Fc^{*+} at 780 nm. (b) Spectral changes in the reaction of NaI (0.3 M) and H_2O_2 (0.15 mM) in acetone solution.

Comment: The formation of I_3^- was accompanied by the decay of Fc^{*+}, see Figure S2a. This indicates that there is no formation of H_2O_2 in this solution compared to the reaction between NaI and H_2O_2, see Figure S1b.

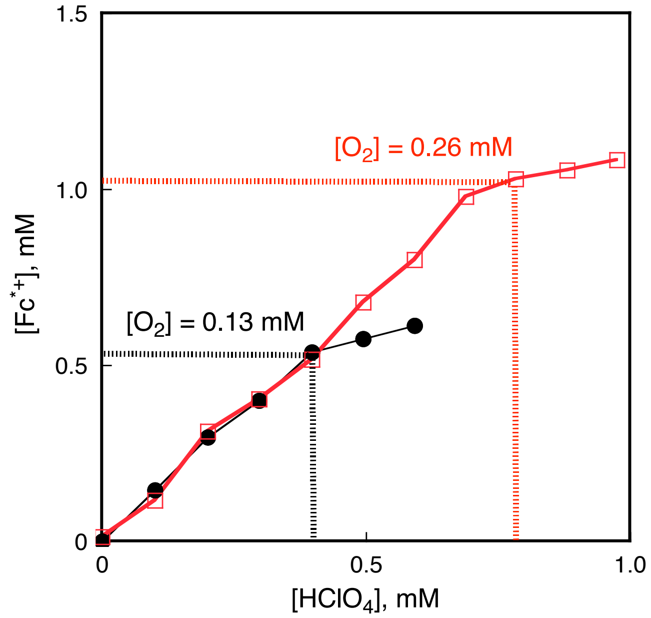

Figure S3. The concentration of Fc^{*+} determined from absorbance at 780 nm vs the concentration of $HClO_4$ in the reduction of O_2 [0.13 mM (●) and 0.26 mM (□)] with Fc^* (2.0 mM) catalyzed by **1** (0.04 mM) in the presence of $HClO_4$ in acetone at 298 K.

Comment: The stoichiometry of O_2 as described in eq 1 was confirmed by using a limiting [O_2] experiment. After the addition of four equiv. of $HClO_4$, four equiv. of Fc^{*+} was formed with respect to the initial concentration of O_2.

The turnover number (TON = 7) was determined from the ratio (moles of Fc^{*+}: 43 μmol)/(moles of **1**: 1.5 μmol) in the catalytic reduction of O_2 (2.2 mM) by Fc^* (10 mM) in the presence of **1** (0.3 mM) and $HClO_4$ (10 mM) in acetone (5 mL) at 298 K. In this case, a stoichiometric amount of $HClO_4$ was added at the beginning.

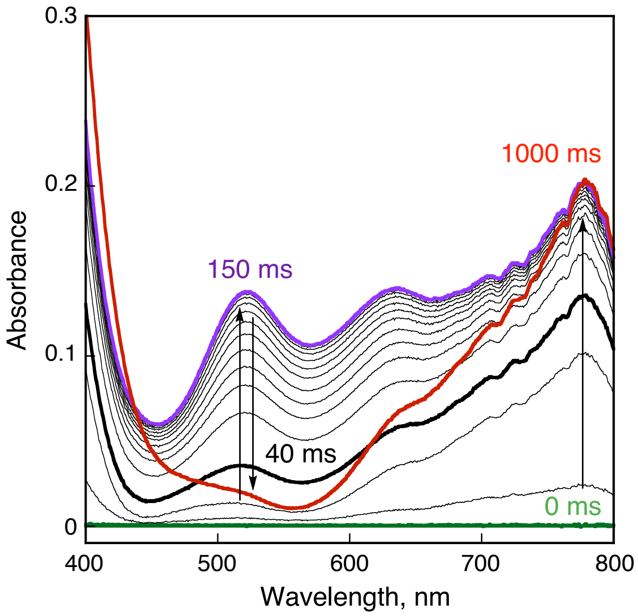

Figure S4. UV-vis spectral change observed in electron transfer from Fc* (1.0 mM) to **1** (0.12 mM) in the presence of $HClO_4$ (0.35 mM) in aerated acetone at 298 K.

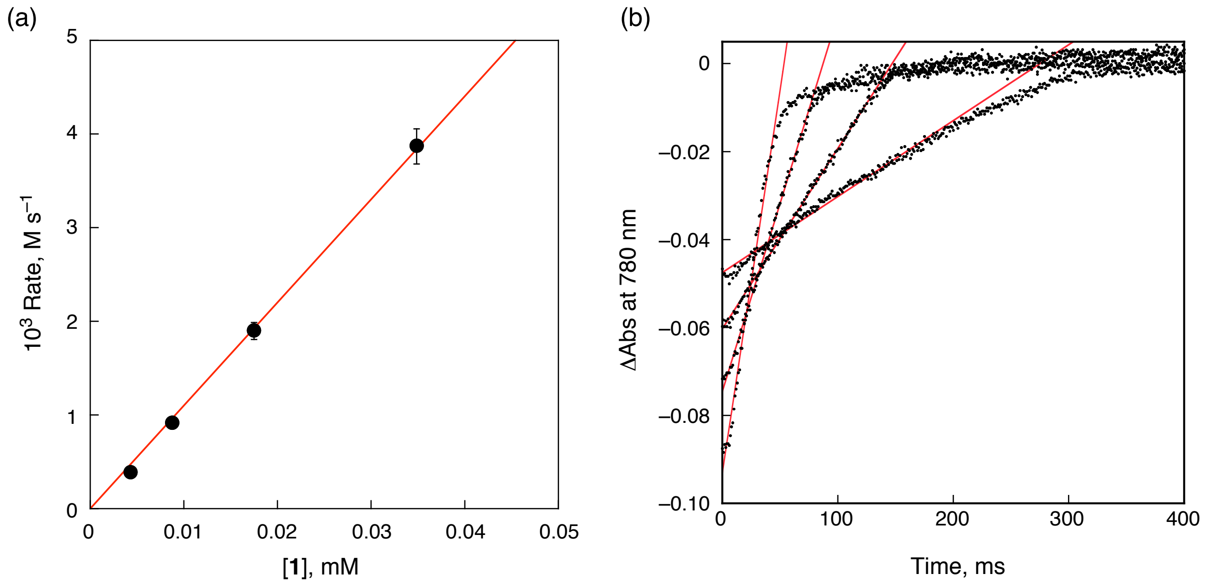

Figure S5. (a) Plot of the constant rate vs [**1**] (0.5 – 3.5 × 10^{-5} M) in an acetone solution containing Fc^* (1.0 mM), O_2 (2.2 mM), and $HClO_4$ (0.1 mM) at 298 K. (b) Time profiles of the absorbance at 780 nm due to Fc^{*+}.

Comment: The constant rate also increased linearly with [Fc^*] (data is not shown) under the conditions ([Fc^*], [O_2] >> [H^+] > [**1**]).

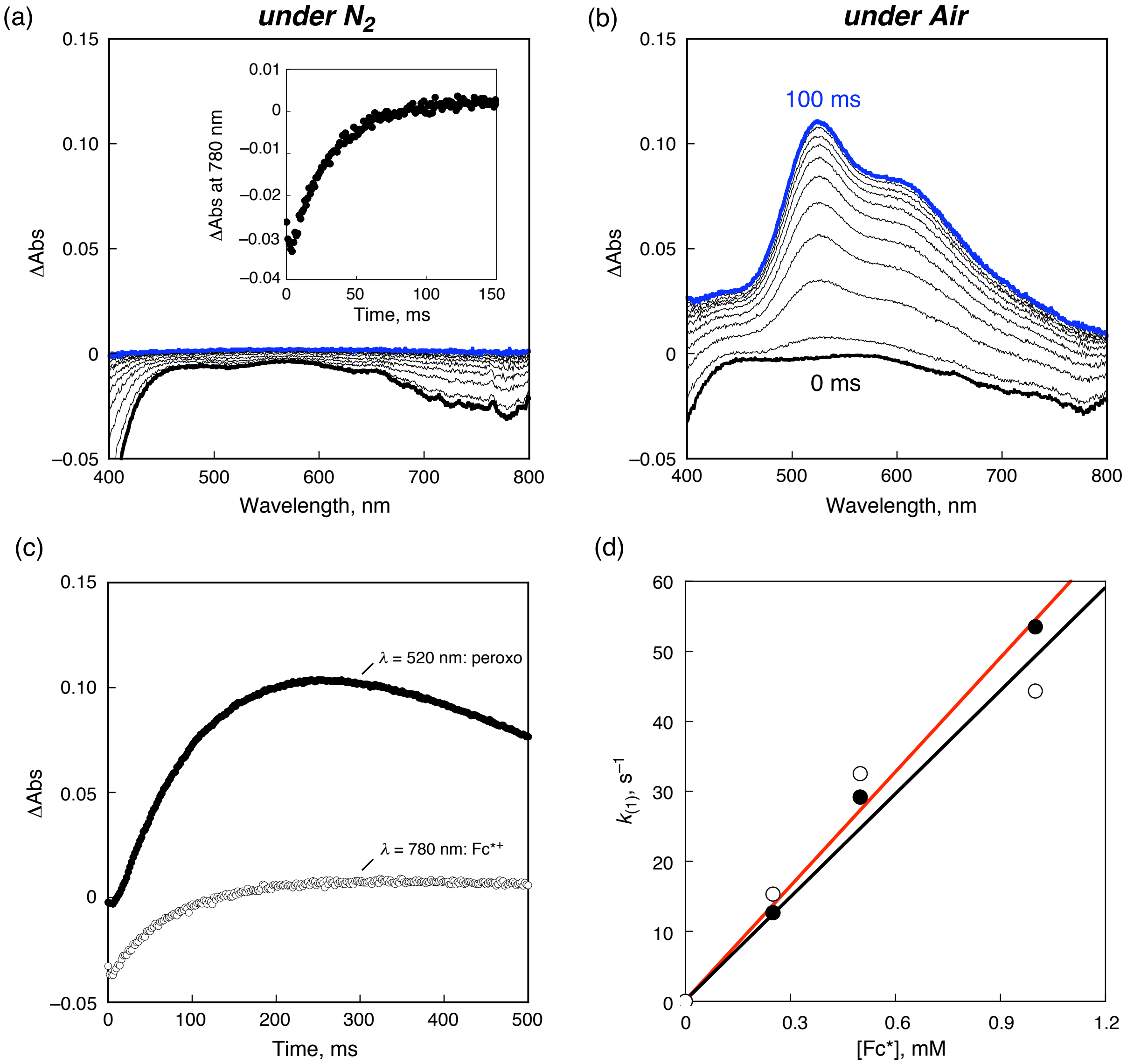

Figure S6. UV-vis spectral change observed in electron transfer from Fc^* (1.0 mM) to **1** (0.05 mM) in (a) deaerated or (b) air saturated acetone solution. Inset: Time profile of absorbance at 780 nm due to Fc^{*+}. (c) Time profiles of formation of **2** and Fc^{*+} monitored by the absorbances at 520 nm and 780 nm in electron transfer from Fc^* (0.5 mM) to **1** (0.05 mM) in aerated acetone at 298 K. (d) Plots of $k_{(1)}$ vs $[Fc^*]$ under N_2 (○) and air (●).

Comment: The second-order rate constant (k'_{obs}) for formation of Fc^{*+} in the presence of O_2 is virtually the same value as compared to that in the absence of O_2. This indicates that a rate-determining step for formation of **2** was the electron-transfer reaction from Fc^* to **1**.

Kinetic Analysis

Assuming that electron transfer from Fc^* to **1** with O_2 is the rate-determining step in the catalytic cycle, the rate of formation of Fc^{*+} under catalytic conditions in Figure 2b is given by eq 1, where the observed second-order rate constant k_{obs} corresponds to $2k_{et}$ (k_{et} is the rate constant of electron transfer from Fc^* to **1**), because four equiv. of Fc^{*+} are formed once electron transfer from Fc^* to **1** occurs. Equation 1 can be replaced by eq 2, where $[Fc^*]_0$ is the initial concentration of Fc^*. Because the concentration of Fc^*, $[Fc^*]$, is larger than the concentration of $HClO_4$, the final concentration of Fc^{*+} ($[Fc^{*+}]_\infty$) is given by $[Fc^{+*}]_\infty = [HClO_4]_0$. Equation 3 is derived by integration of eq 2. The slope of the linear plot of $\ln\{[Fc^*]_0 - [Fc^{*+}]\}$ vs t affords $k_{obs}[\mathbf{1}]$. Alternatively, the initial rate corresponds to $k_{obs}[Fc^*][\mathbf{1}]$: k_{obs} corresponds to $2k_{et}$, because two equiv. of Fc^{*+} are formed once electron transfer from Fc^* to **1** occurs according to Scheme 1.

$$d[Fc^{*+}]/dt = k_{obs}[Fc^*][\mathbf{1}] \tag{1}$$

$$d[Fc^{*+}]/dt = k_{obs}\{[Fc^*]_0 - [Fc^{*+}]\}[\mathbf{1}] \tag{2}$$

$$\ln\{[Fc^*]_0 - [Fc^{*+}]\} = \ln[Fc^*]_0 - k_{obs}[\mathbf{1}]t \tag{3}$$

The rate of formation of Fc^{*+} under single turnover conditions in Figure S4 (S5) is given by eq 4, where the observed second-order rate constant (k'_{obs}) corresponds to k_{et}, because two equiv. of Fc^{*+} are formed once electron transfer from Fc^* to **1** occurs. Because $[Fc^*]$ is much larger than $[\mathbf{1}]$, the rate obeys pseudo-first-order kinetics with respect to $[Fc^{*+}]$. Equation 4 is rewritten using eq 5, because $[\mathbf{1}] = [\mathbf{1}]_0 - [Fc^{*+}]$; $[\mathbf{1}]_0$ is the initial concentration of **1**.

$$d[Fc^{*+}]/dt = k'_{obs}[Fc^*][\mathbf{1}] \tag{4}$$

$$d[Fc^{*+}]/dt = k'_{obs}[Fc^*]\{[\mathbf{1}]_0 - [Fc^{*+}]\} \tag{5}$$

Equation 6 is derived by integration of eq 5.

$$\ln\{[\mathbf{1}]_0 - [Fc^{*+}]\} = \ln[\mathbf{1}]_0 - k'_{obs}[Fc^*]t \tag{6}$$

The slope of the pseudo-first-order plot affords $k'_{obs}[Fc^*]$. $k_{obs} = 2k'_{obs} = 2k_{et}$.

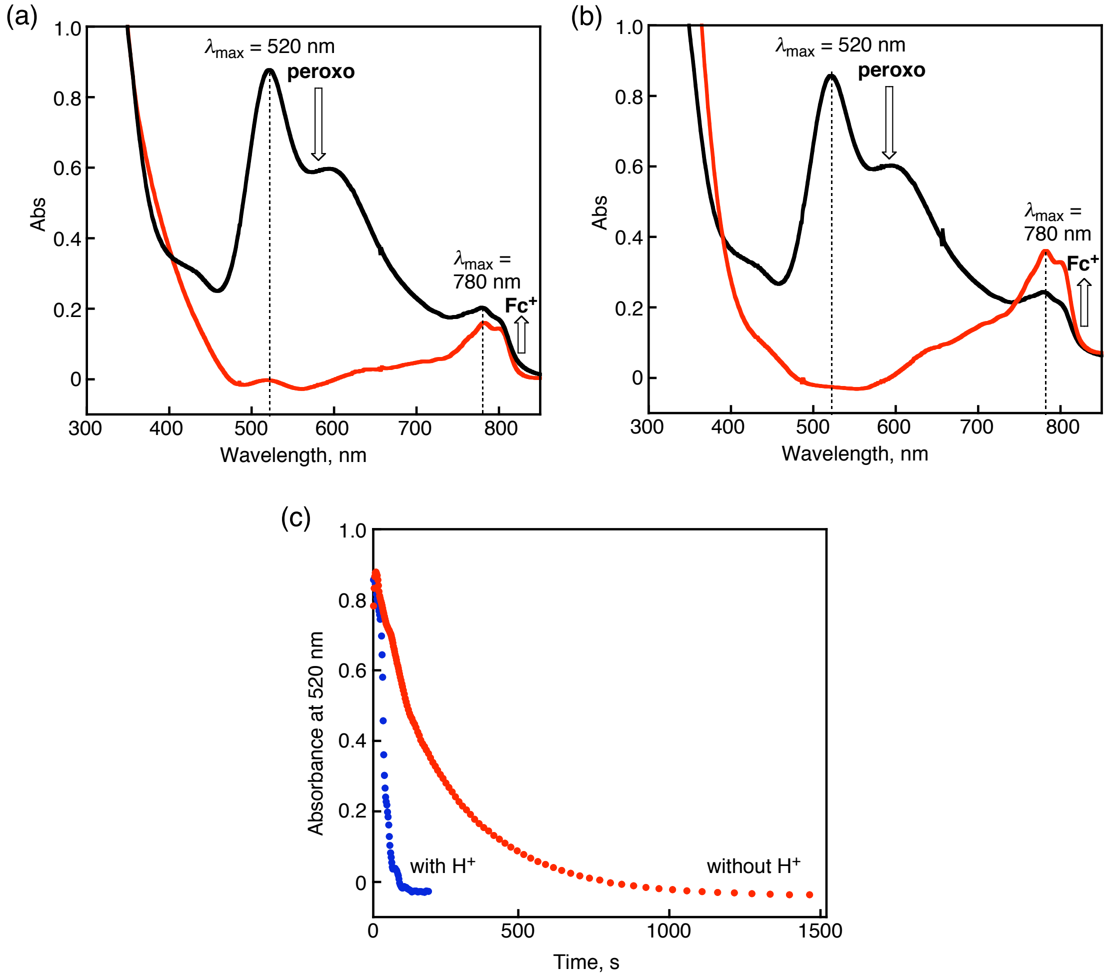

Figure S7. (a) UV-Vis spectrum of the peroxo species, $[(\mathrm{tmpa})\mathrm{Cu}^{\mathrm{II}}(\mathrm{O}_2)\mathrm{Cu}^{\mathrm{II}}(\mathrm{tmpa})]^{2+}$ (black line) observed upon mixing (t = 0 s) an acetone solution of **1** (0.2 mM) with that of Fc^* (2.0 mM) and that observed at t = 1000 s (red line) in the absence of $HClO_4$ in O_2-saturated acetone at 193 K. (b) UV-Vis spectrum of the peroxo species, $[(\mathrm{tmpa})\mathrm{Cu}^{\mathrm{II}}(\mathrm{O}_2)\mathrm{Cu}^{\mathrm{II}}(\mathrm{tmpa})]^{2+}$ (black line) observed upon mixing of acetone solution of **1** (0.2 mM) with that of Fc^* (2.0 mM) and that observed after addition (t = 0 s) of 0.4 mM $HClO_4$ at t = 150 s (red line) in O_2-saturated acetone at 193 K. (c) Time profiles of the absorption at 520 nm due to **2** in the presence or absence of $HClO_4$.