

Supporting Information

Lewis Acid-Induced Change from Four- to Two-Electron Reduction of Dioxygen Catalyzed by Copper Complexes Using Scandium Triflate

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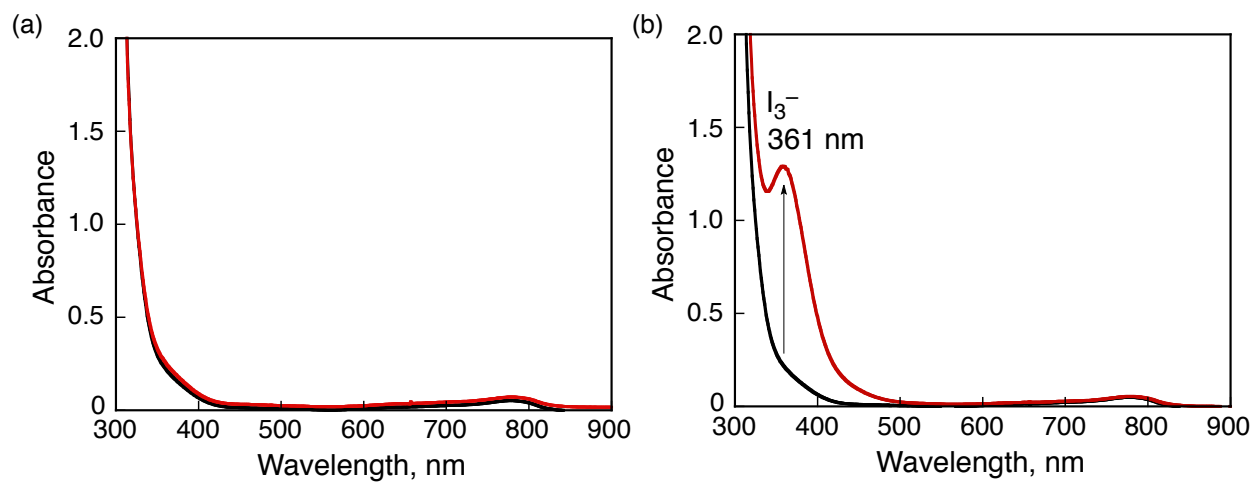


Figure S1. Spectral changes in the reaction of NaI (0.30 M) and 20 times diluted of reduced product of O_2 (0.5 mM) in a 298K acetone solution including Fc^{*+} (2.0 mM), $[(tmpa)Cu^{II}]^{2+}$ (4.0×10^{-5} M), and (a) HOTf (2.0 mM) or (b) $Sc(OTf)_3$ (2.0 mM)

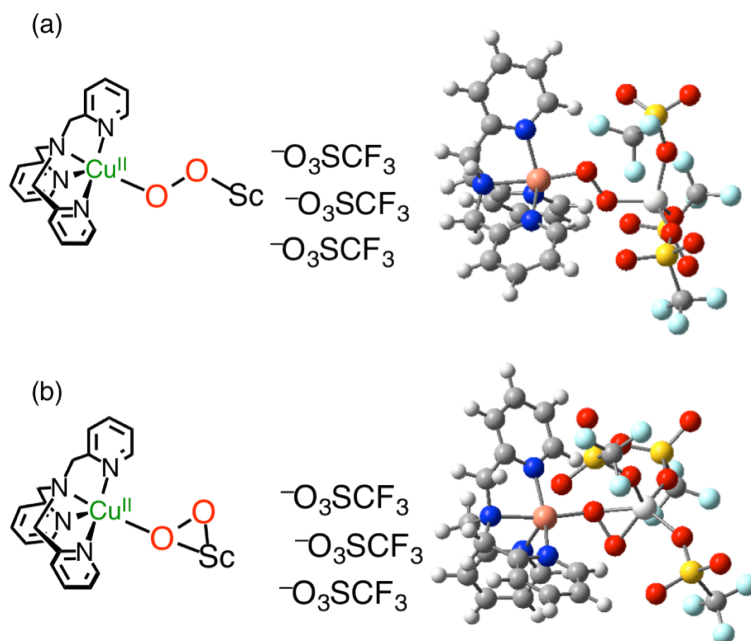


Figure S2. Optimized structures of $[(\text{tmpa})\text{Cu}^{\text{II}}\text{OOSc}(\text{OTf})_3]$ obtained by DFT calculations with the UCAM-B3LYP density-functional and the Lanl2dz basis set. The SOMO orbital is shown in the right panel. (a) The end-on peroxo complex is 19 kcal mol^{-1} more stable than (b) the side-on peroxo complex.

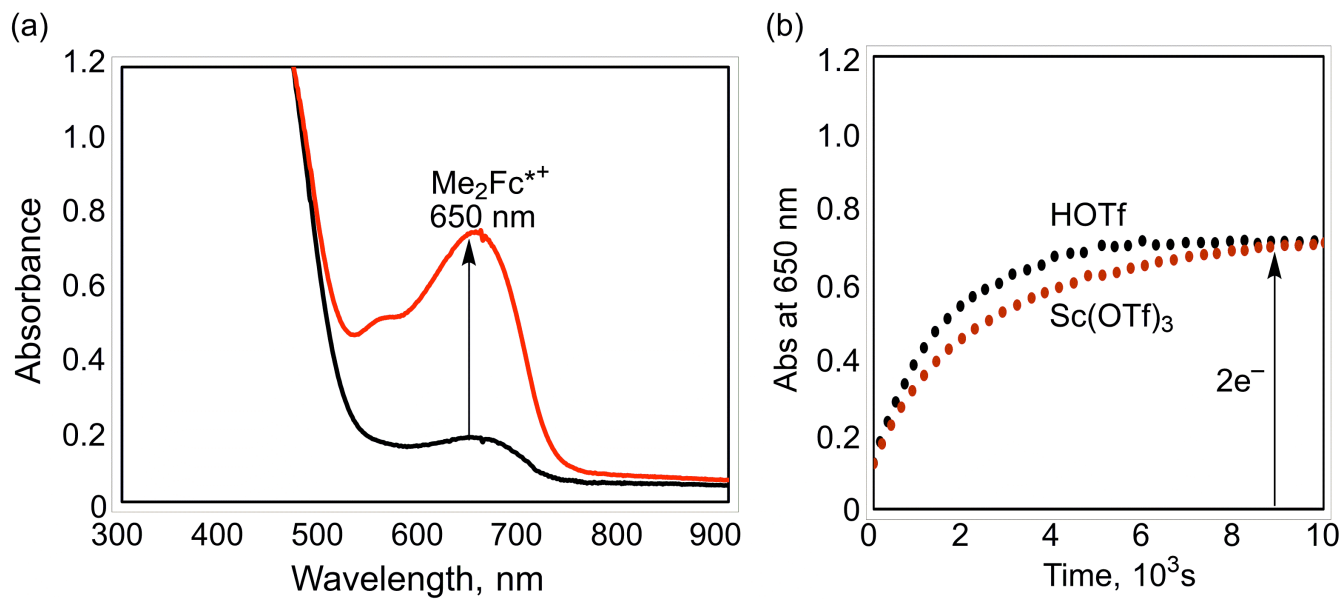


Figure S3. (a) UV-vis spectral changes observed in the two-electron reduction of O₂ (0.9 mM) by Me₂Fc* (10 mM) with Sc(OTf)₃ (10 mM) (red line) and with HOTf (10 mM) (black line), respectively, catalyzed by **1** (40 mM) in acetone at 298 K. (b) Time courses at 650 nm for formation of Me₂Fc⁺ with Sc(OTf)₃ (red dots) and HOTf (black dots).

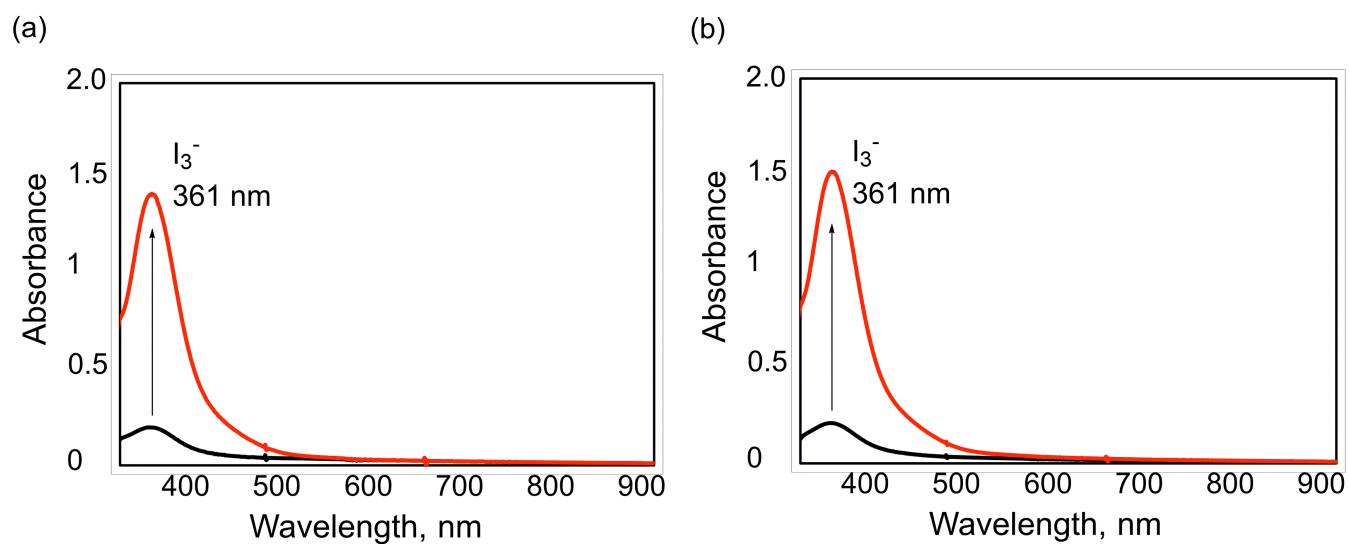


Figure S4. Spectral changes observed in the reaction of NaI (0.30 M) and 20 times diluted of reduced product of O_2 (11 mM) in a 298K acetone solution including Me_2Fc^{*+} (2.0 mM), $[(Cu^{II}BzQ)]^{2+}$ (0.20 mM), and (a) HOTf (0.50 mM) or (b) $Sc(OTf)_3$ (0.50 mM)

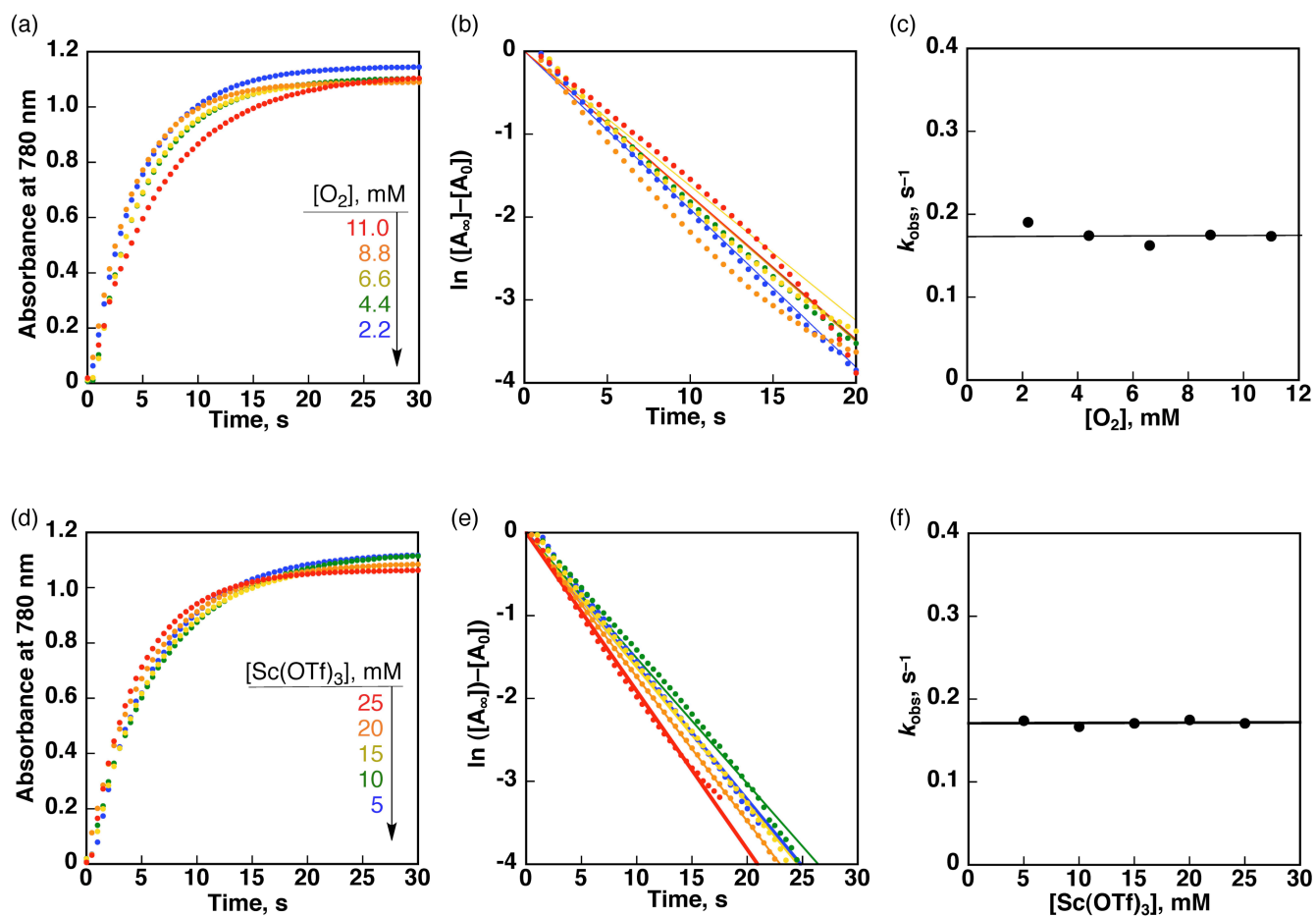


Figure S5. (a) Time profiles of formation of Fc^{*+} monitored by absorbance at 780 nm ($\epsilon = 500 \text{ M}^{-1} \text{ s}^{-1}$) in electron transfer oxidation of Fc^* (2.0 mM) by O_2 (2.2 - 11 mM), catalyzed by $[(\text{tmpa})\text{Cu}^{\text{II}}]^{2+}$ (**1**) (0.002 mM) in the presence of $\text{Sc}(\text{OTf})_3$ (10 mM) in acetone at 298 K. (b) Pseudo-first order plots. (c) Plots of k_{obs} vs $[\text{O}_2]$. (d) Time profiles of formation of Fc^{*+} in electron transfer oxidation of Fc^* (2.0 mM) by O_2 (11 mM), catalyzed by $[(\text{tmpa})\text{Cu}^{\text{II}}]^{2+}$ (**1**) (0.002 mM) in the presence of $\text{Sc}(\text{OTf})_3$ (5 - 25 mM) in acetone at 298 K. (e) Pseudo-first order plots. (f) Plot of k_{obs} vs $[\text{O}_2]$.

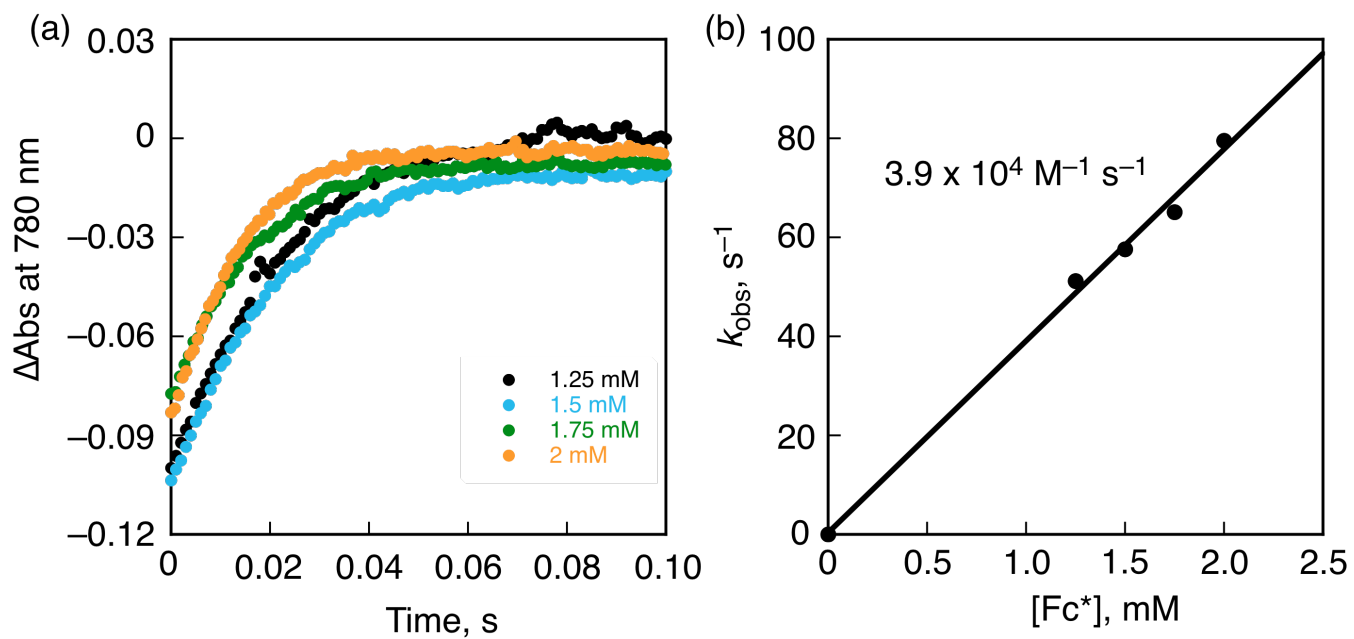


Figure S6. (a) Time courses of difference absorption spectra observed in electron transfer from Fc^* (1.25, 1.50, 1.75 and 2.00 mM) to **1** in the presence of $\text{Sc}(\text{OTf})_3$ in argon saturated acetone at 298 K. (b) Plot of pseudo-first-order rate constant vs $[\text{Fc}^*]$.

Derivation of $k_{\text{cat}} = 2k_{\text{et}}$

According to Scheme 1, where the rate-determining step is electron transfer from Fc^* to $[(\text{tmpa})\text{Cu}^{\text{II}}]^{2+}$, the rate of formation of Fc^{*+} is given by eq S1,

$$d[\text{Fc}^{*+}]/dt = 2k_{\text{et}}[\text{Fc}^*][\text{Cu}^{\text{II}}] \quad (\text{S1})$$

where k_{et} is the rate constant of electron transfer from Fc^* to $[(\text{tmpa})\text{Cu}^{\text{II}}]^{2+}$. Thus, the observed second-order rate constant $k_{\text{obs}} = 2k_{\text{et}}$, because two equivalents of Fc^{*+} are formed once electron transfer from Fc^* to $[(\text{tmpa})\text{Cu}^{\text{II}}]^{2+}$ occurs, followed by the fast reaction of $[(\text{tmpa})\text{Cu}^{\text{I}}]^+$ with O_2 and rapid electron transfer from Fc^* to $[(\text{tmpa})\text{Cu}(\text{O}_2^{\cdot-})]$ with Sc^{3+} to produce another equivalent of Fc^{*+} in Scheme 1.