

# Supporting Information

## Catalytic Four-Electron Reduction of Dioxygen by Ferrocene Derivatives with a Nonheme Iron(III) TAML Complex

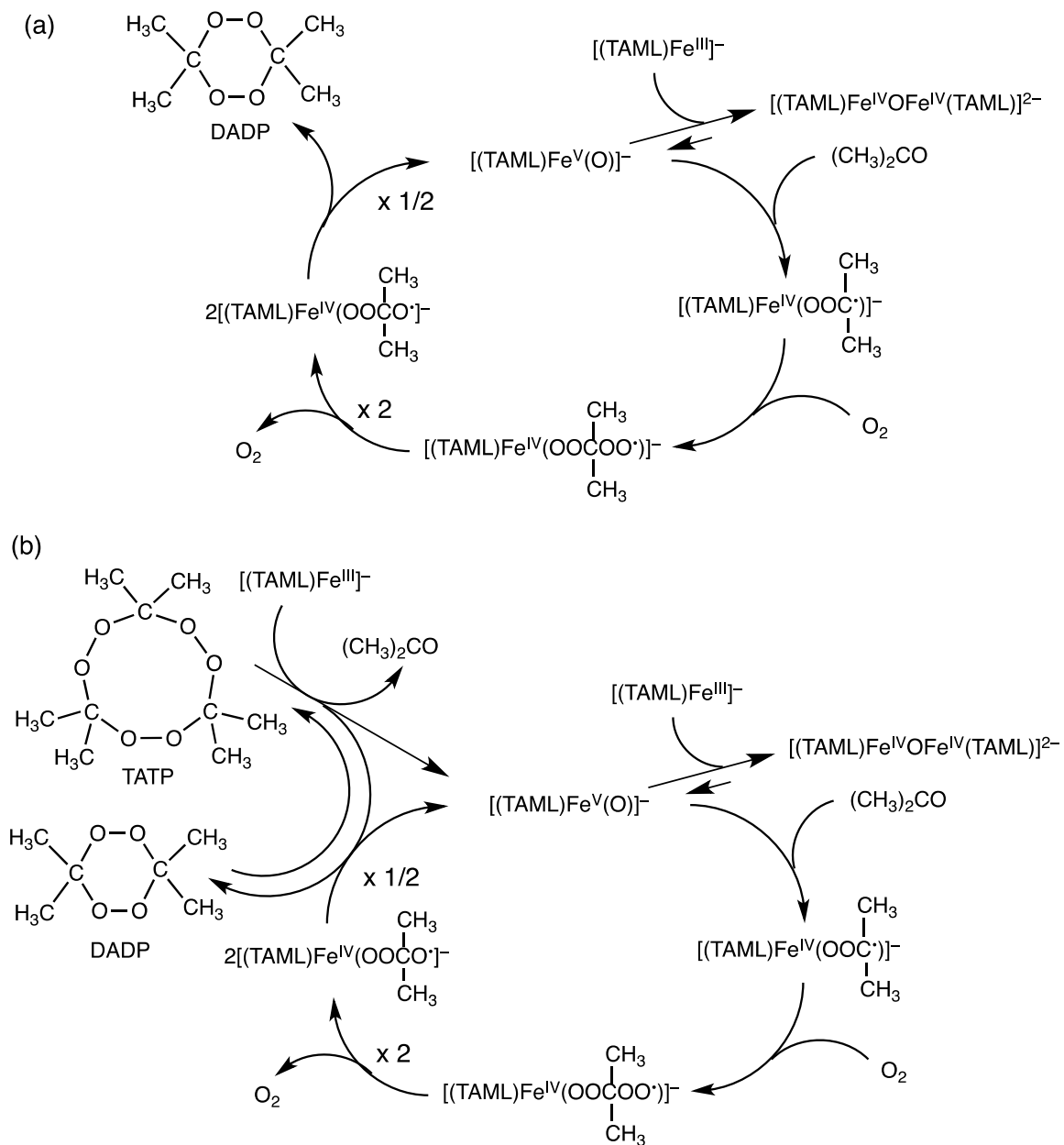
Xiaoyan Lu,<sup>†</sup> Yong-Min Lee,<sup>†</sup> Muniyandi Sankaralingam,<sup>†</sup> Shunichi Fukuzumi,<sup>\*,†,‡</sup> and Wonwoo Nam<sup>\*,†</sup>

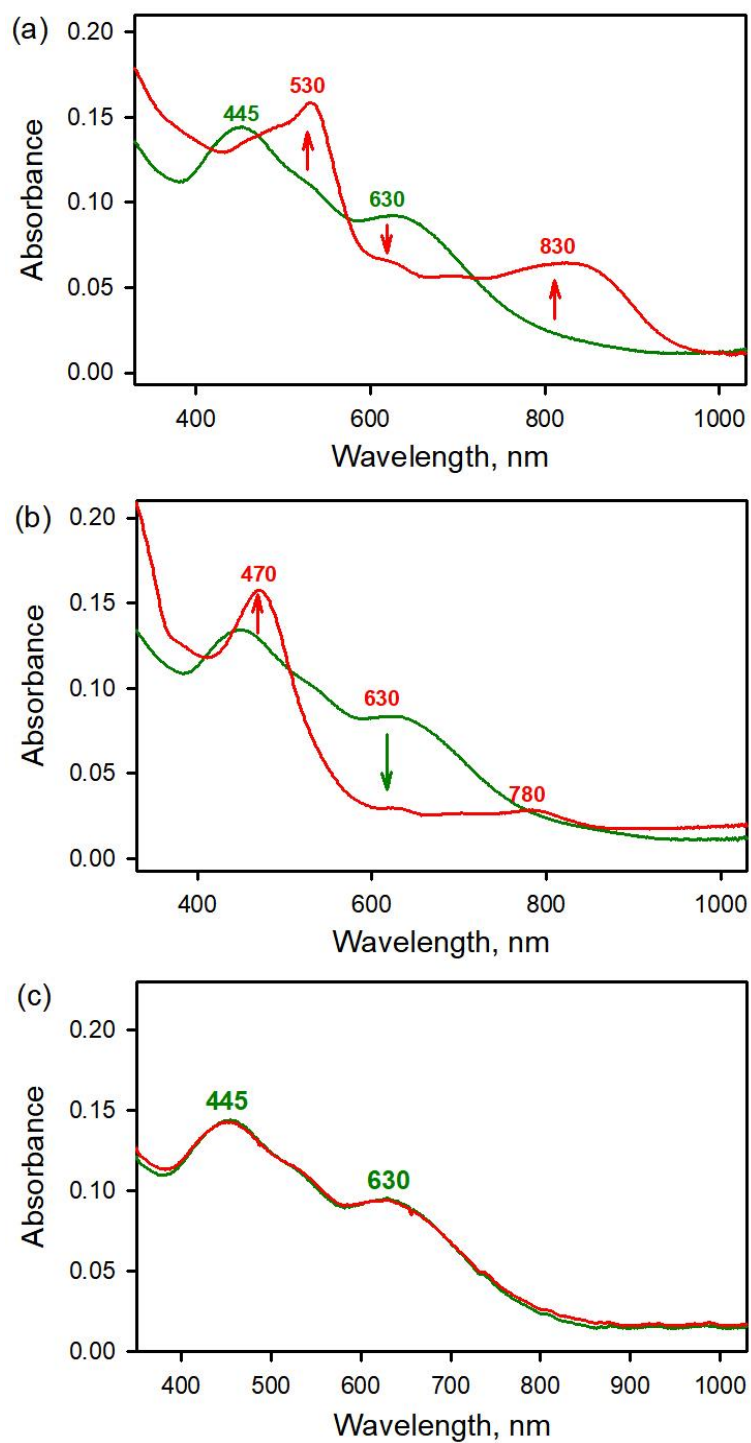
<sup>†</sup> *Department of Chemistry and Nano Science, Ewha Womans University, Seoul 03760, Korea*

<sup>‡</sup> *Faculty School of Science and Engineering, Meijo University, Nagoya, Aichi 468-8502, Japan*

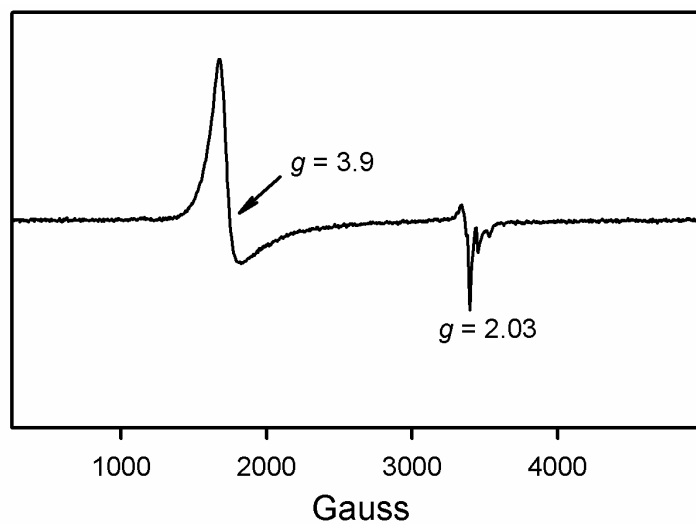
\* E-mails: fukuzumi@chem.eng.osaka-u.ac.jp; wwnam@ewha.ac.kr

**Scheme S1. (a) Autocatalytic Mechanism for the Formation of  $[(\text{TAML})\text{Fe}^{\text{V}}(\text{O})]^-$  and DADP in Acetone and (b) Autocatalytic Mechanism for the Formation of  $[(\text{TAML})\text{Fe}^{\text{V}}(\text{O})]^-$  via TATP in Acetone** (Taken from reference 14 in Text)

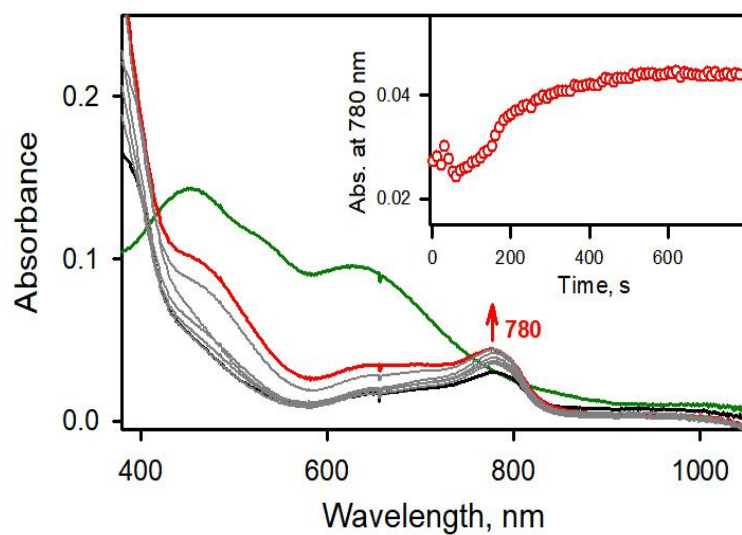




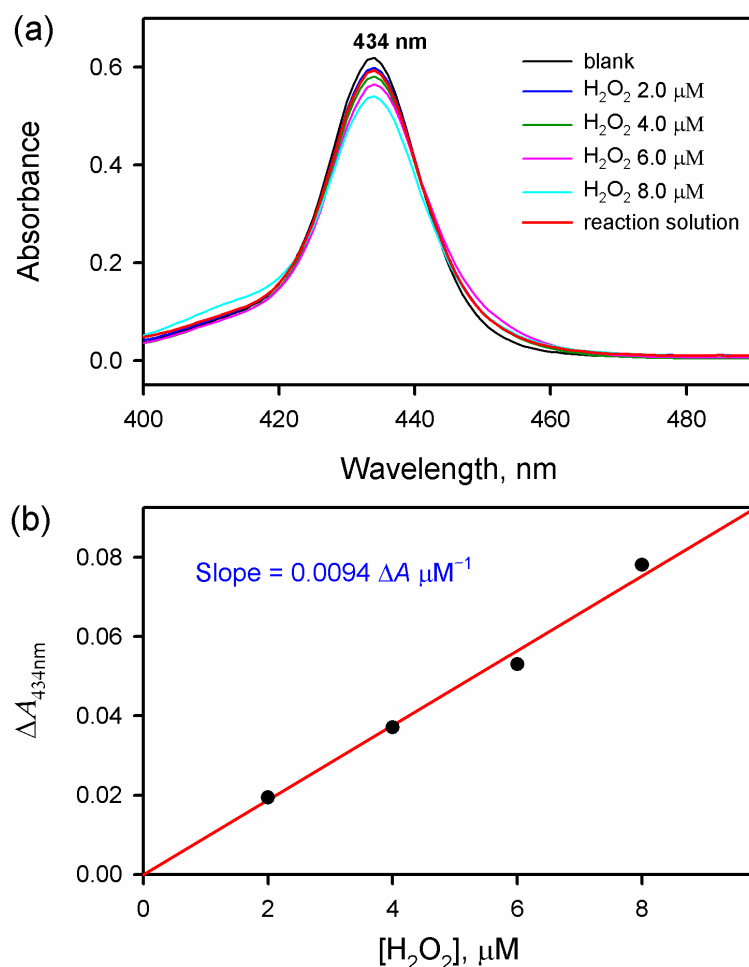
**Figure S1.** UV-visible spectral changes observed upon addition of (a) trifluoroacetic acid (TFA) (0.50 mM), (b) triflic acid (HOTf) (0.50 mM) and (c) acetic acid ( $\text{CH}_3\text{COOH}$ ) (0.50 mM) to an aerated acetone solution of **2** (0.025 mM) at 25 °C.



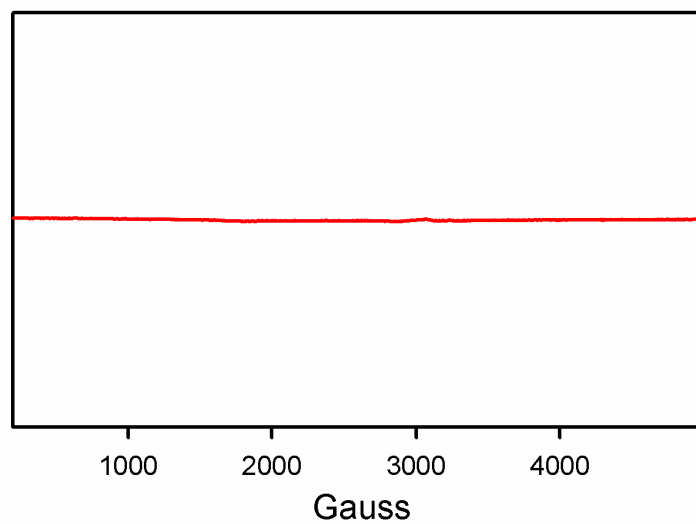
**Figure S2.** X-band CW-EPR spectrum of the reaction solution obtained after the four-electron reduction of  $\text{O}_2$  by  $\text{Me}_{10}\text{Fc}$  (2.0 mM) with **2** (0.20 mM) in the presence of  $\text{CH}_3\text{COOH}$  (6.0 mM) in aerated acetone at 25 °C. The spectrum was recorded at 5 K. The signals with the  $g$  values at 3.9 and 2.03 are assigned due to  $S = 3/2$   $[\text{Fe}^{\text{III}}(\text{TAML})]^-$ .



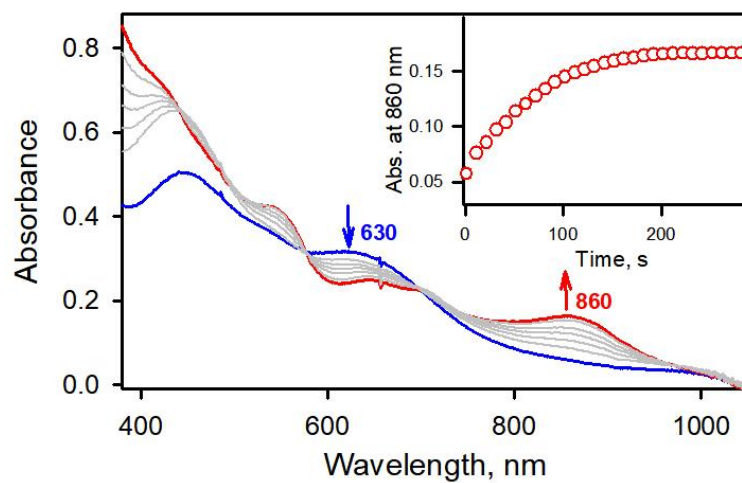
**Figure S3.** UV-vis spectral changes observed in the four-electron reduction of  $O_2$  by  $Me_{10}Fc$  (0.25 mM) with **2** (0.025 mM; green line) in the absence of  $CH_3COOH$  in aerated acetone at 25 °C.



**Figure S4.** (a) Spectroscopic titration by Ti-TPyP for the  $\text{H}_2\text{O}_2$  solutions (0 – 8.0  $\mu\text{M}$ ) and the reaction solution, which was obtained after reduction of  $\text{O}_2$  by  $\text{Me}_{10}\text{Fc}$  (0.25 mM) with **2** (0.025 mM) in the presence of  $\text{CH}_3\text{COOH}$  (0.75 mM) in aerated acetone at 25 °C. A decrease in the absorbance at 434 nm from the blank value is expected if the sample contains  $\text{H}_2\text{O}_2$ .  $\text{H}_2\text{O}_2$  concentration in the sample is related to  $\Delta A_{434\text{ nm}} = A_{\text{blank}} - A_{\text{sample}}$ . (b) Plot of  $\Delta A_{434\text{ nm}}$  against concentration of  $\text{H}_2\text{O}_2$  as a standard curve. The concentration of  $\text{H}_2\text{O}_2$  in the reaction solution was determined to be 2.7  $\mu\text{M}$  by the equation,  $\Delta A_{434\text{ nm}} = (0.0094 \Delta A_{434\text{ nm}} \mu\text{M}^{-1}) \times [\text{H}_2\text{O}_2]$ .

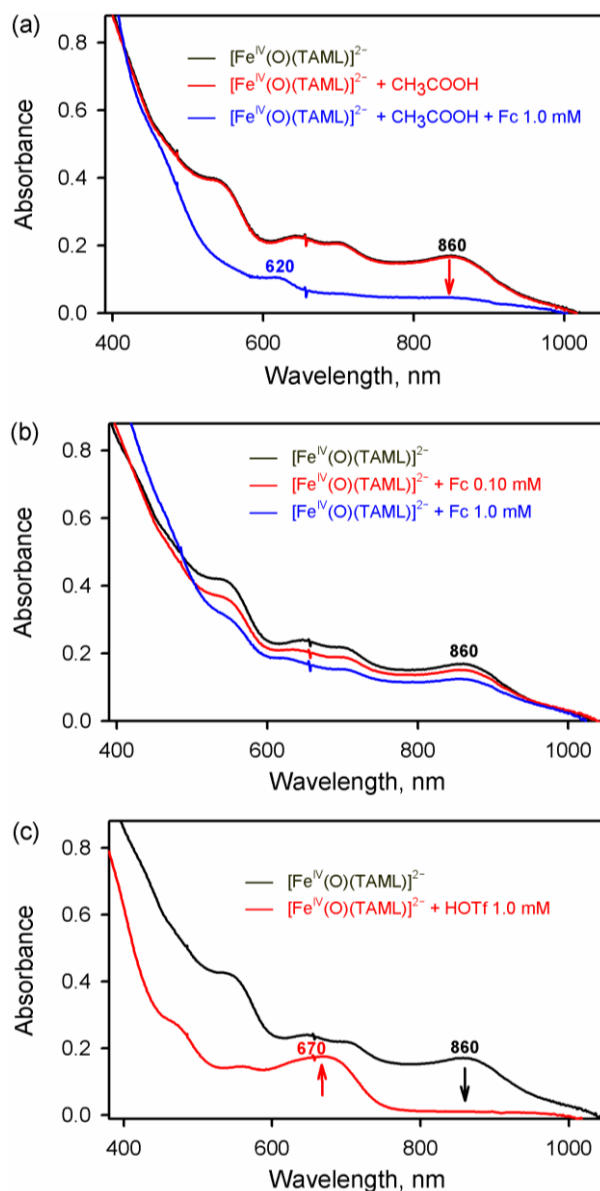


**Figure S5.** X-band CW-EPR spectrum of the complete reaction solution obtained in the reaction of **2** (0.20 mM) and BrFc (4.0 mM) in the presence of CH<sub>3</sub>COOH (4.0 mM) in aerated acetone at 25 °C. The spectrum was recorded at 5 K.

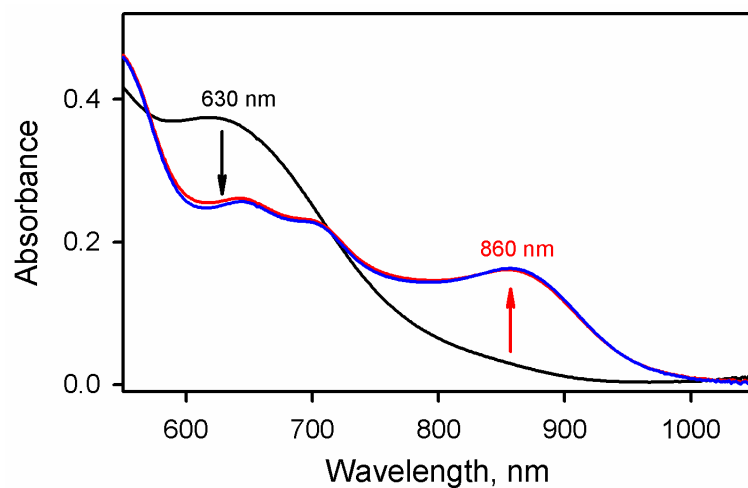


**Figure S6.** UV-vis spectral changes obtained in the reduction of **2** (0.10 mM; blue line) by BrFc (1.0 mM) in the absence of acid in aerated acetone at 25 °C. Inset shows the time profile of absorbance change at 860 nm due to  $[(\text{TAML})\text{Fe}^{\text{IV}}(\text{O})]^{2-}$ .

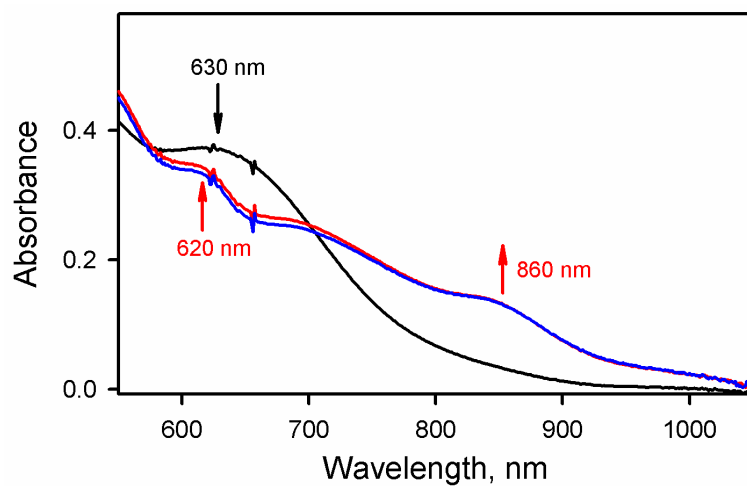




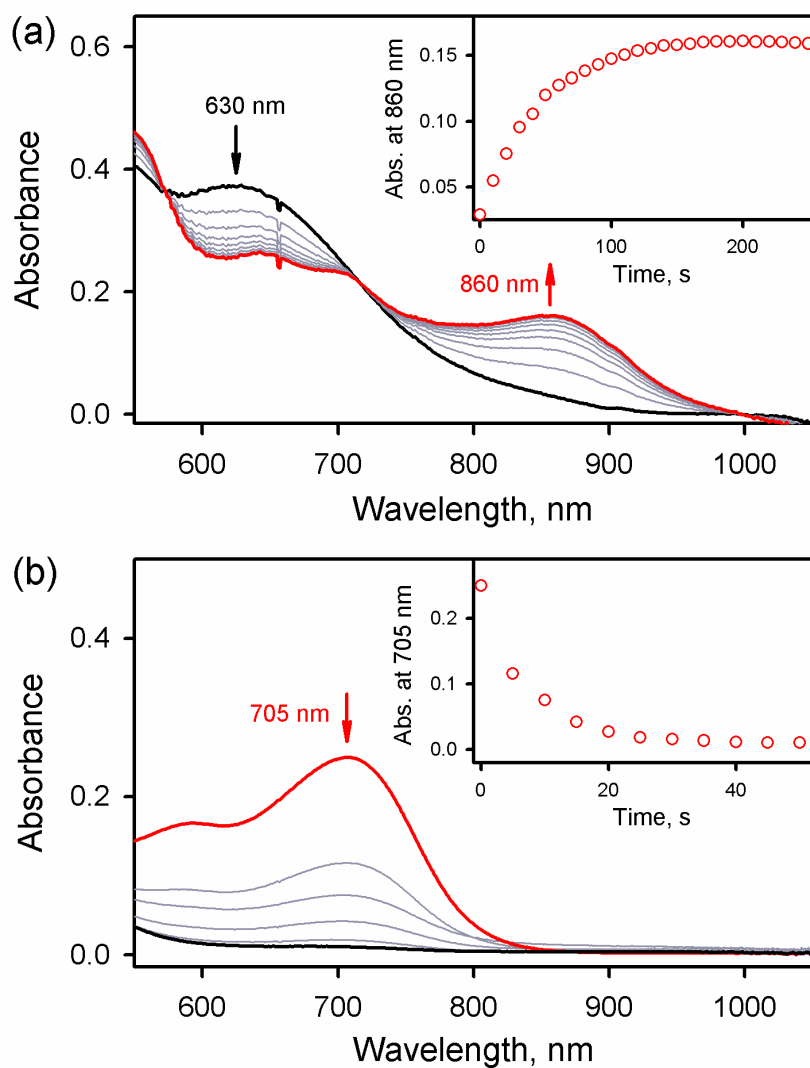
**Figure S7.** (a) UV-vis spectral change from black line to red line observed upon addition of  $\text{CH}_3\text{COOH}$  (300 mM) to a solution of  $[(\text{TAML})\text{Fe}^{\text{IV}}(\text{O})]^{2-}$  (0.10 mM; black line), which was generated by reacting  $[(\text{TAML})\text{Fe}^{\text{V}}(\text{O})]^-$  (0.10 mM) and  $\text{BrFc}$  (1.0 mM) in the absence of acid at 25 °C. For the full formation of  $[(\text{TAML})\text{Fe}^{\text{IV}}(\text{O})]^{2-}$ , 10 equiv of  $\text{BrFc}$  (1.0 mM) was used. The blue line was formed right away upon addition of  $\text{Fc}$  (1.0 mM), which is a stronger reductant than  $\text{BrFc}$ , to a solution containing  $[(\text{TAML})\text{Fe}^{\text{IV}}(\text{O})]^{2-}$  with  $\text{CH}_3\text{COOH}$  at 25 °C. The formation at 620 nm is due to  $\text{Fc}^+$ . (b) UV-vis spectral changes observed upon addition of  $\text{Fc}$  [0.10 (red line) and 1.0 mM (blue line)] to a solution of  $[(\text{TAML})\text{Fe}^{\text{IV}}(\text{O})]^{2-}$  (0.10 mM; black line) in the absence of acid at 25 °C. (c) UV-vis spectral changes observed upon addition of  $\text{HOTf}$  (1.0 mM) to a solution of  $[(\text{TAML})\text{Fe}^{\text{IV}}(\text{O})]^{2-}$  (0.10 mM; black line) at 25 °C, showing further reaction of  $[(\text{TAML})\text{Fe}^{\text{IV}}(\text{O})]^{2-}$  with residual  $\text{BrFc}$  to produce  $\text{Fe}^{\text{III}}$  species and  $\text{BrFc}^+$ , because 10 equiv of  $\text{BrFc}$  (1.0 mM) was used for the full formation of  $[(\text{TAML})\text{Fe}^{\text{IV}}(\text{O})]^{2-}$ . The formation at 670 nm is due to  $\text{BrFc}^+$ .



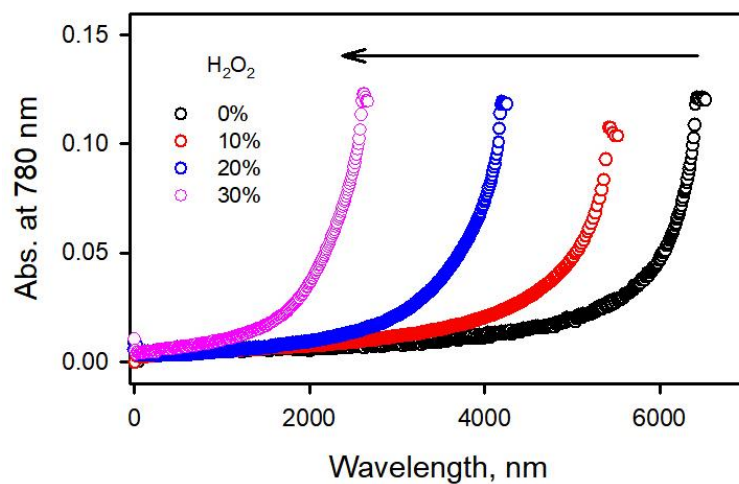
**Figure S8.** UV-vis spectral changes observed in the reduction of **2** (0.10 mM; black line) by BrFc [0.50 mM (red line) and 1.0 mM (blue line)] in the presence of CH<sub>3</sub>COOH (0.20 mM) in aerated acetone at 25 °C. The formation at 860 nm is due to [(TAML)Fe<sup>IV</sup>(O)]<sup>2-</sup>.



**Figure S9.** UV-vis spectral changes observed in the reduction of **2** (0.10 mM, black line) by Fc [0.10 mM (red line) and 1.0 mM (blue line)] in the presence of CH<sub>3</sub>COOH (0.20 mM) in aerated acetone at 25 °C. One equiv of Fc was enough to complete electron transfer from Fc to **2**. The formation at 620 and 860 nm are due to Fc<sup>+</sup> and [(TAML)Fe<sup>IV</sup>(O)]<sup>2-</sup>, respectively.



**Figure S10.** (a) UV-vis spectral changes observed in the reduction of **2** (0.10 mM; black line) by  $\text{Br}_2\text{Fc}$  (1.0 mM) in the presence of  $\text{CH}_3\text{COOH}$  (0.20 mM) in aerated acetone at 25 °C. Inset shows the time profile of absorbance at 860 nm due to  $[(\text{TAML})\text{Fe}^{\text{IV}}(\text{O})]^{2-}$ . (b) UV-vis spectral changes of  $\text{Br}_2\text{Fc}^+$  showing the natural decay in acetone at 25 °C.  $\text{Br}_2\text{Fc}^+$  was produced by reacting  $\text{Br}_2\text{Fc}$  (2.0 mM) with cerium(IV) ammonium nitrate (CAN) in acetone at 25 °C.



**Figure S11.** Time profiles of absorbance changes at 780 nm due to  $\text{Me}_{10}\text{Fc}^+$  observed in the reduction of  $\text{O}_2$  by  $\text{Me}_{10}\text{Fc}$  (0.25 mM) with **1** (0.025 mM) in the presence of  $\text{CH}_3\text{COOH}$  (0.75 mM) and catalytic amount of  $\text{H}_2\text{O}_2$  (0 – 30% based on **1** used) in aerated acetone at 25 °C.