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Mononuclear Copper Complex Catalyzed Four-Electron Reduction of Oxygen

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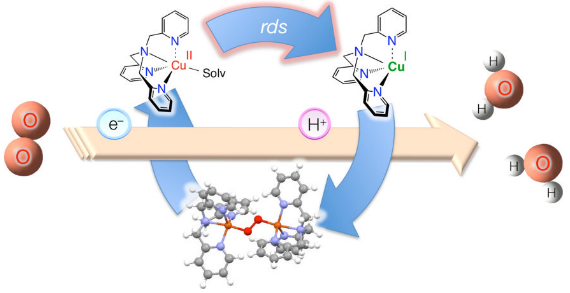
Abstract



A mononuclear Cu^{II} complex acts as an efficient catalyst for four-electron reduction of O_2 to H_2O by a ferrocene derivative via formation of the dinuclear Cu^{II} peroxo complex that is further reduced in the presence of protons by a ferrocene derivative to regenerate the Cu^{II} complex.

Cytochrome *c* oxidases (C*c*Os), with a bimetallic active-site consisting of a heme *a* and Cu (Fe_{a3}/Cu_B), are the terminal enzymes of respiratory chains, catalyzing the reduction of molecular oxygen to water by the soluble electron carrier, cytochrome *c*.[1,2] Synthetic Fe_{a3}/Cu_B analogs have attracted significant attention, because the four-electron reduction of O_2 is not only of great biological interest,[3,4] but also of technological significance such as in fuel cells.[5,6] Multicopper oxidases such as laccase also activate oxygen at a site containing a three-plus-one arrangement of 4 Cu atoms, exhibiting remarkable electroactivity for the four-electron reduction of oxygen at potentials approaching 1.2 V (vs RHE).[7] Such electrocatalytic reduction of O_2 has frequently been used to probe the catalytic reactivity of synthetic C*c*O model complexes[3–5] and some copper (only) complexes have also been investigated.[8–10] However, there has been no report on the copper complex catalyzed four-electron reduction of O_2 employing one-electron reductants in homogeneous solution; such situations are amenable to systematic studies which provide considerable mechanistic insights.[11]

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Supporting Information Available. Experimental section, kinetic analysis, and figures (Figure S1–S7). This material is available free of charge via the Internet at http://pubs.acs.org.

We report herein that a copper complex $[(\mathrm{tmpa})\mathrm{Cu}^{\mathrm{II}}](\mathrm{ClO}_4)_2$ (**1**: tmpa = tris(2-pyridylmethyl) amine)[12] efficiently catalyzes the four-electron reduction of O_2 by one-electron reductants such as ferrocene derivatives in the presence of $HClO_4$ in acetone. As described below, the catalytic mechanism is clarified based on kinetic studies and detection of reactive intermediates.

The addition of a catalytic amount of **1** to an O_2-saturated acetone solution of decamethylferrocene (Fc^*) and $HClO_4$ results in the efficient oxidation of Fc^* by O_2 to afford ferrocenium cation (Fc^{*+}) (see Supporting Information for the experimental section). Figure 1 shows the spectral changes obtained following stepwise addition of $HClO_4$ to this solution. For each time period, the concentration of Fc^{*+} (λ_{max} = 380 and 780 nm)[11] immediately formed is the same as the concentration of $HClO_4$ added. The reduced product of O_2 is confirmed to be H_2O based on the detection of $H_2{}^{18}O$ by ^{18}O-labeled O_2 experiments (Figure S1). It has also been confirmed that no H_2O_2 is detected via iodometric titration experiments (Figure S2).[13] When more than four equiv. of Fc^* relative to O_2 (i.e., limiting $[O_2]$) were employed, only four equiv. Fc^{*+} were formed in the presence of four equiv. $HClO_4$ (Figure S3).[14] Thus, the stoichiometry of the catalytic reduction of O_2 by Fc^* is given by eq 1.[15]

$$4\mathrm{Fc}^* + \mathrm{O}_2 + 4\mathrm{H}^+ \xrightarrow{[(\mathrm{tmpa})\mathrm{Cu}^{\mathrm{II}}]^{2+}} 4\mathrm{Fc}^{*+} + 2\mathrm{H}_2\mathrm{O} \tag{1}$$

The time profile of the four-electron reduction of O_2 with Fc^* catalyzed by **1** in the presence of $HClO_4$ in acetone at 298 K was examined by stopped-flow measurements. Figure 2a shows the observed absorption spectral change during the catalytic reaction. Under the conditions employed with relative concentrations of reagents as given in the Figure 2 caption, it is only after Fc^{*+} (λ_{max} = 780 nm) is completely formed that the peroxo species, $[(\mathrm{tmpa})\mathrm{Cu}^{\mathrm{II}}(\mathrm{O}_2)\mathrm{Cu}^{\mathrm{II}}(\mathrm{tmpa})]^{2+}$ (**2**: λ_{max} = 520 nm)[16] starts to be produced.[17] This is more clearly seen in Figure 2b, the time profiles for the absorbance at 780 nm due to Fc^{*+}, by comparison to the absorbance at 520 nm due to **2**. Because the concentration of $HClO_4$ is smaller than that of Fc^*, $HClO_4$ has been consumed when the reaction is over. It is well established that $[(\mathrm{tmpa})\mathrm{Cu}^{\mathrm{I}}]^+$ reacts with O_2 affording the superoxo species $[(\mathrm{tmpa})\mathrm{Cu}^{\mathrm{II}}(\mathrm{O}_2{}^-)]^+$ which reacts rapidly with $[(\mathrm{tmpa})\mathrm{Cu}^{\mathrm{I}}]^+$ to produce the peroxo species **2**.[16] Thus, electron-transfer reduction of **1** by Fc^* with O_2 but without $HClO_4$ affords **2**. This is the reason why **2** starts to appear only after $HClO_4$ is all consumed. The stoichiometry of the reaction of Fc^* with **1** and O_2 is given by eq 2.

$$2\mathrm{Fc}^* + 2[(\mathrm{tmpa})\mathrm{Cu}^{\mathrm{II}}]^{2+} + \mathrm{O}_2 \rightarrow 2\mathrm{Fc}^{*+} + [(\mathrm{tmpa})\mathrm{Cu}^{\mathrm{II}}(\mathrm{O}_2)\mathrm{Cu}^{\mathrm{II}}(\mathrm{tmpa})]^{2+} \tag{2}$$

The rate of formation of Fc^{*+} in Figure 2b appears to be constant with respect to the concentration of Fc^{*+}, when the concentration of Fc^* is in large excess compared to that of $HClO_4$. The constant rate ($\mathrm{M\ s^{-1}}$) increases linearly with increasing concentration of **1** and Fc^* (Figure S5). The second-order rate constant (k_{obs}) is determined to be $(1.1 \pm 0.1) \times 10^5$ $\mathrm{M^{-1}\ s^{-1}}$ from the slope of Figure S5, which is divided by the initial concentration of Fc^* (1.0 mM).

The rate of formation of Fc^{*+}, accompanied by formation of **2** via electron transfer from Fc^* to **1** with O_2, was also determined without $HClO_4$, obeying pseudo-first-order kinetics, when the concentration of Fc^* is much larger than that of **1** (Figure S6). This rate constant increases linearly with concentration of Fc^*. From the slope of the linear plot, the second-order rate constant (k'_{obs}) for formation of Fc^{*+} without $HClO_4$ under single turnover conditions is determined to be $(4.9 \pm 0.4) \times 10^4$ $\mathrm{M^{-1}\ s^{-1}}$ (Figure S6). This value is one-half as compared to the rate constant under catalytic conditions with $HClO_4$. This is quite consistent with the stoichiometries of the catalytic reaction (eq 1) and the single turnover reaction (eq 2), because an additional equiv. of Fc^{*+} is formed in the presence of $HClO_4$ under the catalytic conditions following formation of one equiv. of Fc^{*+} under the single turnover reaction (see Supporting Information for the kinetic analysis).

No further reduction of the peroxo species **2** occurs without an acid. However, the addition of $HClO_4$ facilitates electron-transfer and the further two-electron reduction of **2** to produce two equiv. of Fc^{*+}, accompanied by regeneration of **1**. This was confirmed by low temperature measurements (Figure S7). Thus, the overall catalytic cycle is given in Scheme 1. The initial electron transfer from Fc^* to **1** and reaction with O_2 affords the two-electron reduction of oxygen to produce the peroxo species that can be further reduced in the presence of $HClO_4$ to facilitate the four-electron reduction of O_2 to H_2O by Fc^* (Scheme 1).[18]

In summary, a copper complex **1** acts as an effective catalyst for the four-electron reduction of O_2 by one-electron reductants such as Fc^* in the presence of an acid. The present study opens a new approach and the use of copper ion to develop efficient catalysts for the four-electron reduction of O_2, because the catalytic activity and stability of intermediates can certainly be controlled and tuned by variation of ligands for copper ion.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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17. Note that the spectra recorded were taken as difference spectra in which the final spectrum was subtracted; recovery of bleaching absorption at 780 nm corresponds to the formation of Fc^{*+} (see SI Figure S4)
18. The value of turnover frequency (TOF = 17 s^{-1}) was obtained in the catalytic four-electron reduction of O_2 by Fc^* (1.0 mM) with **1** (5.0×10^{-6} M) in the presence of $HClO_4$ (0.1 mM) in acetone at 298 K at 300 ms (TON = 5) as shown in Figure S5b.

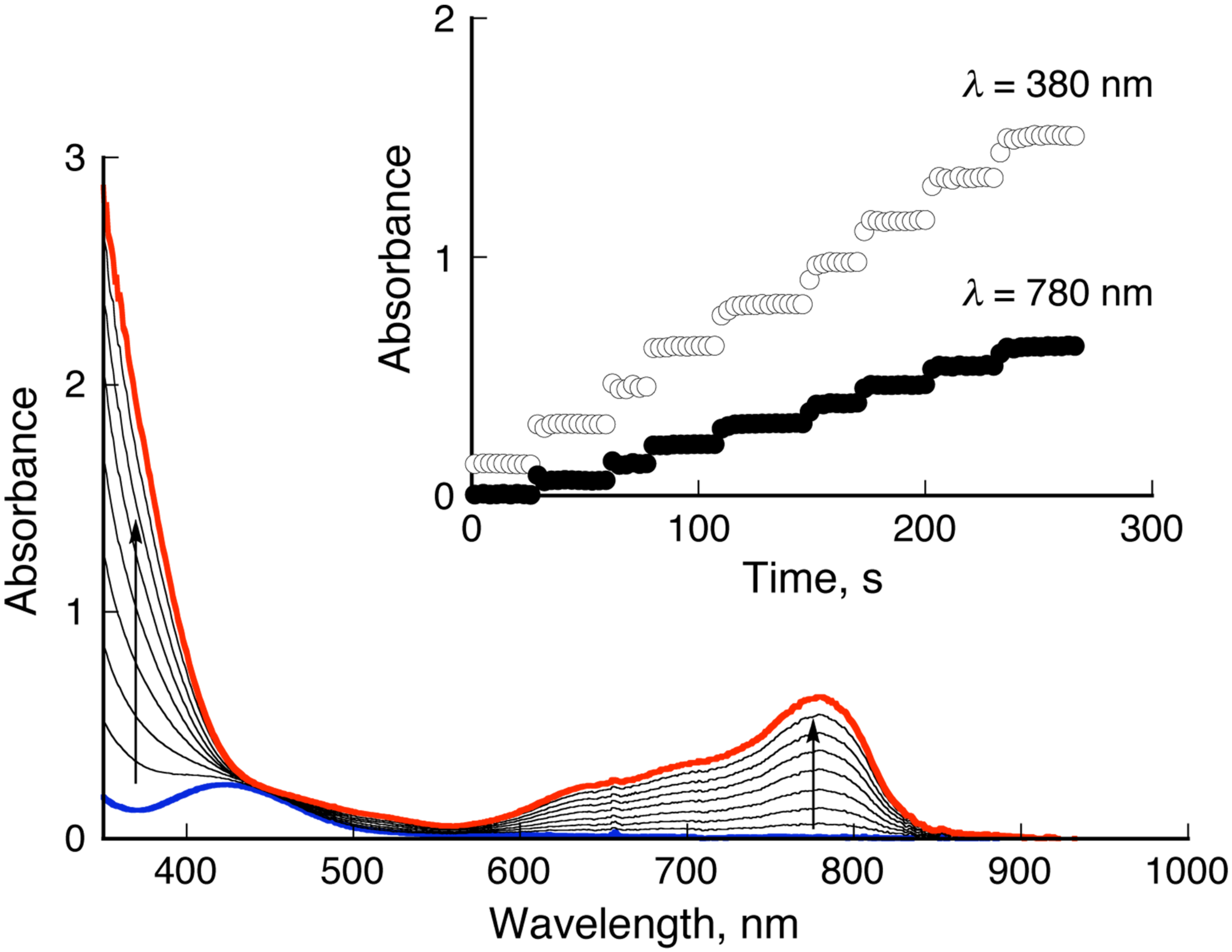


Figure 1.
UV-vis spectral change in four-electron reduction of O_2 by Fc* (1.5 mM) with **1** (9.0×10^{-5} M) in the presence of $HClO_4$ in acetone at 298 K. Inset shows the change in absorbance at 380 and 780 nm due to Fc^{*+} by stepwise addition of $HClO_4$ (0.18 – 1.44 mM) to an O_2-saturated acetone solution ($[O_2]$ = 11 mM) of Fc* and **1**.

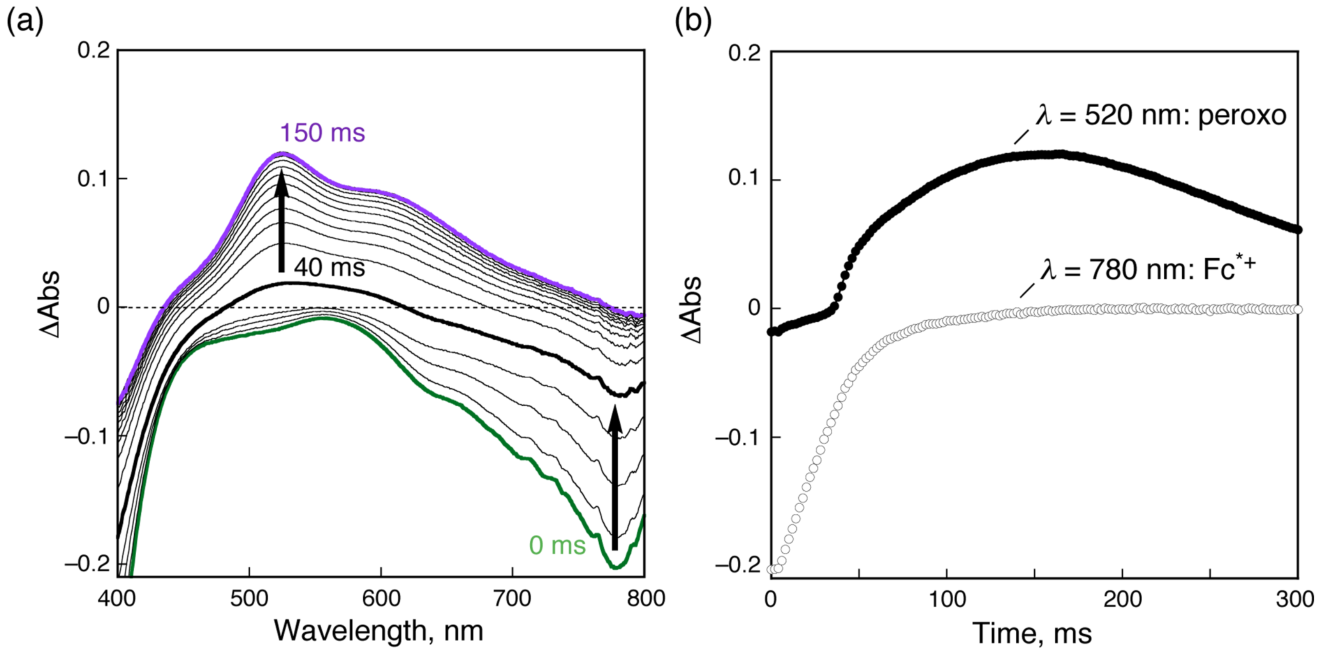
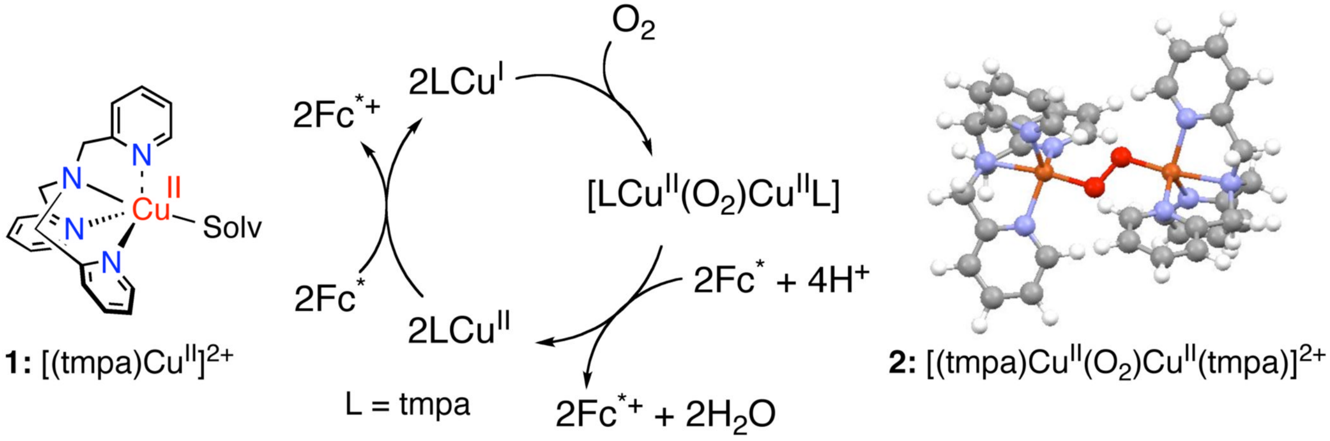


Figure 2.

(a) Formation of the peroxo species **2** (λ_{max} = 520 nm) 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. (b) Time profile of the absorbance at 520 nm (●) and 780 nm (○) due to **2** and Fc^{*+}, respectively.


1: $[(tmpa)Cu^{II}]^{2+}$
N
N
N
N
Cu^{II}
Solv
O_2
$2LCu^{I}$
$2Fc^{*+}$
$[LCu^{II}(O_2)Cu^{II}L]$
$2Fc^{*}$
$2LCu^{II}$
$2Fc^{*} + 4H^{+}$
$2Fc^{*+} + 2H_2O$
L = tmpa
2: $[(tmpa)Cu^{II}(O_2)Cu^{II}(tmpa)]^{2+}$

Scheme 1.