# Four-Electron Reduction of Dioxygen to Water by Ferrocene Derivatives in the Presence of Perchloric Acid in Benzonitrile, Catalyzed by Cofacial Porphyrins

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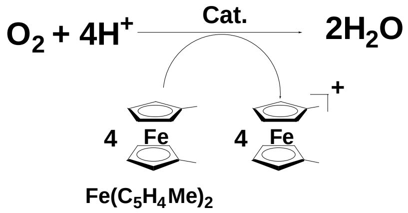
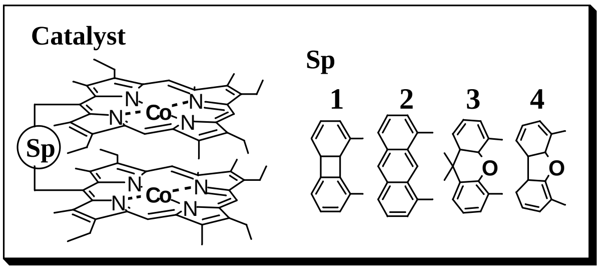
Metalloporphyrin-catalyzed reduction of dioxygen has been extensively studied in electrochemical system in relation with the efficient four-electron reduction of oxygen in respiratory chain, catalyzed by Cytochome c Oxidase.[1] Electrochemical four-electron reduction of dioxygen to water has been achieved using various dimeric cofacial metalloporphyrins.[2] The catalytic two-electron reduction of dioxygen by chemical reductants has also been accomplished.[3] However, little is known about efficient catalytic four-electron reduction of dioxygen by appropriate chemical reductants.

We report herein efficient four-electron reduction of dioxygen by ferrocene derivatives, catalyzed by cofacial dicobalt porphyrins in the presence of perchloric acid ($HClO_4$) in benzonitrile (PhCN) as shown in Scheme 1.

**Scheme 1**





The stoichiometry of the catalytic reduction of dioxygen by 1,1'-dimethylferrocene ($Fe(C_5H_4Me)_2$) using dicobalt porphyrin (**3**) as a catalyst in the presence of perchloric acid in PhCN is determined from the spectral titration by observing the rise of 650 nm due to $Fe(C_5H_4Me)_2^+$ [$\varepsilon$(650nm) = 280 $M^{-1}cm^{-1}$; $Fe(C_5H_4Me)_2^+$]. Four equivalents of $Fe(C_5H_4Me)_2$ are consumed in the reduction of dioxygen.

Typical time courses of the catalytic two- or four-electron reduction of dioxygen by an excess amount of $Fe(C_5H_4Me)_2$ in the presence of catalysts are shown in Figure 1. Upon mixing $Fe(C_5H_4Me)_2$ and catalysts in the presence of $HClO_4$ in air-saturated PhCN at 298 K, the rise of 650 nm due to $Fe(C_5H_4Me)_2^+$ is observed. The selective two-electron reduction of dioxygen occurs in the case of mono-cobalt porphyrin [(OEP)Co], whereas the selective four-electron reduction of dioxygen occurs in the case of cofacial dicobalt porphyrin (**3**). The other cofacial dicobalt porphyrins (**1**, **2** and **4**) also catalyze the two-electron reduction of dioxygen, but the four-electron reduction is not as efficient as the case of **3**.

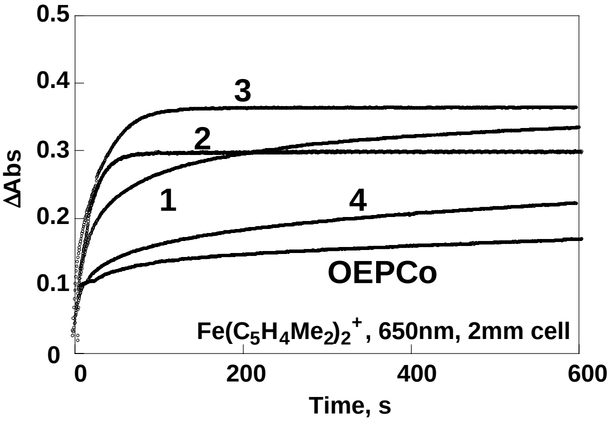


**Figure 1.** Time course of absorbance change at $\lambda$ = 650 nm due to $Fe(C_5H_4Me)_2^+$ in the reduction of dioxygen by $Fe(C_5H_4Me)_2$ (0.1 M) in the presence of **1**- **4** (1 x $10^{-5}$ M), (OEP)Co (2 x $10^{-5}$ M) and $HClO_4$ (0.02 M) in air-saturated PhCN.

The $\mu$-superoxo species of cofacial dicobalt porphyrins were produced by the reactions cofacial dicobalt(II) porphyrins with dioxygen in the presence of a bulky base and the subsequent one-electron oxidation of the resulting peroxo species by iodine. The superhyperfine structure due to two equivalent cobalt nulei was observed in the ESR spectra of the $\mu$-superoxo species. The superhyperfine coupling constant of the $\mu$-superoxo species of **3** is the largest among those of cofacial dicobalt porphyrins. This indicates that the efficient catalysis of **3** for the four-electron reduction of dioxygen by $Fe(C_5H_4Me)_2$ results from the strong binding of the reduced oxygen with **3** which has a suitable distance between two cobalt nuclei for the oxygen binding.

Mechanisms of the catalytic two-electron and four-electron reduction of dioxygen by ferrocene derivatives will be discussed on the basis of detailed kinetics studies on the overall catalytic reactions as well as on each redox reaction in the catalytic cycle.

## References

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