

## Enhancing Medical or Biological Functions of Laccase by Cyanide-Bridged Cu(II)-Fe(III) Bimetallic Complexes Mediators

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### Short Communication

Drug Rescue is a useful method to obtain biologically active substances via biochemical reactions in the field of pharmaceutical science [1]. For example, laccase, scavenging active oxygen may be an appropriate enzyme because it can oxidize substrate simultaneously [2]. In this context, we have focused on metal complexes as mediators for modeling cathode systems of biofuel cells to enhance electron transfer reactions of laccase [3]. We have carried out studies with the aim of application to metal complex mediators which are useful as a cathode electrode of the biofuel cells. Some of the cathode electrode mediators smooth the electron transfer between electrode and enzyme (e.g. laccase). Complex which improves the reaction that laccase reduce by four-electron from oxygen to water in catalytic ability is desirable.

Ferricyanide ion is used as the mediator of the cathode because standard electrode potential of it is about 0.36 V and it is relatively inexpensive among metal complex [3]. Therefore, we thought gradual electron transfer can be taken place by making a copper(II) cyanide-bridged bimetallic complex such as molecular magnetic materials showing a mixed valence. Smoother electron transfer between the electrode and the enzyme can be expected. We report on synthesis of cyanide metal complex materials for cathode which are effective for laccase and evaluation of electrochemical properties.

Two complexes,  $[\text{CuL}_2]_3[\text{Fe}(\text{CN})_6]_2$  (L=N-ethylethylenediamine or (1R,2R)-cyclohexanediamine) were prepared (Figure 1).

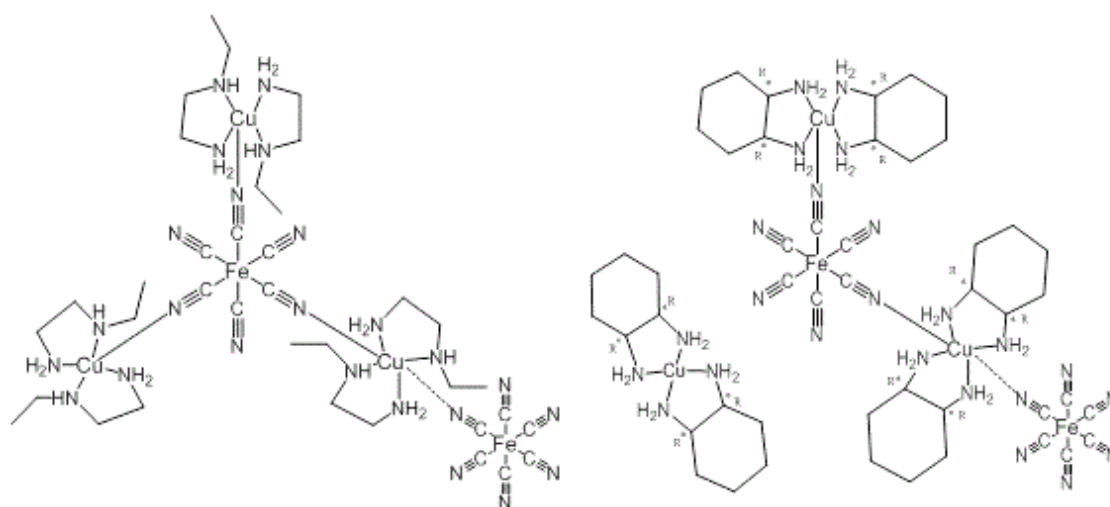
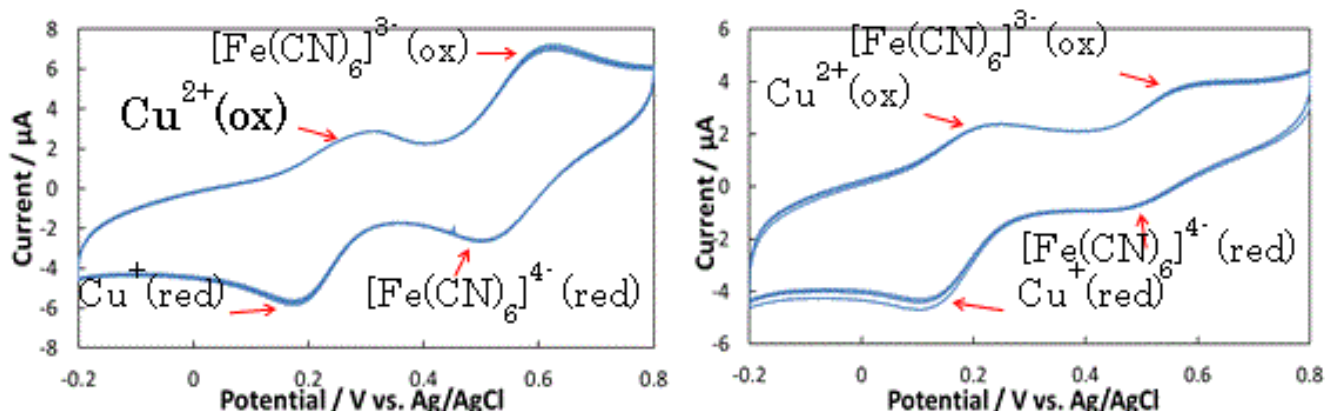


Figure 1: Molecular structures of  $[\text{CuL}_2]_3[\text{Fe}(\text{CN})_6]_2$  (L=N-ethylethylenediamine [left] or (1R,2R)-cyclohexanediamine [right]).

Characterizations of them were carried out by IR and diffuse reflection electron spectra, etc. [4,5]. Cyclic voltammetry scans of these cyanide-bridged bimetallic complexes were carried out by using a carbon paste electrode and redox potentials were measured (Figure 2).

Cyclic voltammetry scans of composite system of laccase and complex was carried out to see the electrochemical characteristics

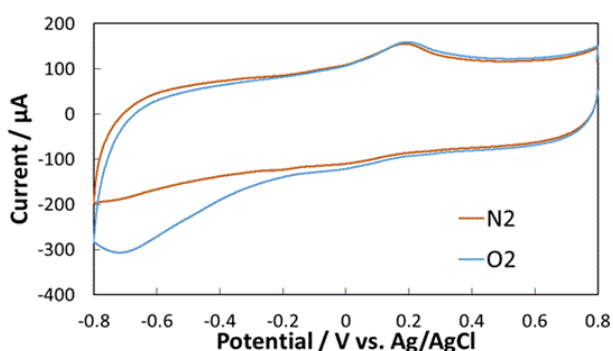
when mixed with enzymes and complex. That was performed by coating the carbon nanotube and complex on glassy carbon electrode under nitrogen and oxygen. The presence or absence of a reduction ability improvement of laccase in the presence of complex was observed.



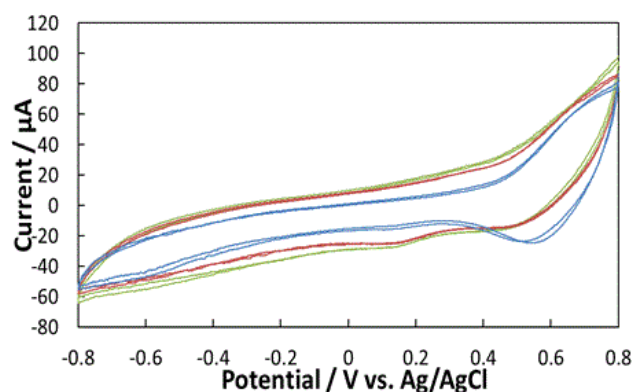
**Figure 2:** Cyclic voltammetry ( $50 \text{ mVs}^{-1}$ , 200 mM acetate buffer, pH 5.0, with 3-20 nm carbon nanotubes under oxygen) of only  $[\text{CuL}_2]_3[\text{Fe}(\text{CN})_6]_2$  (L=N-ethylethylenediamine [left] or (1R,2R)-cyclohexanediamine [right]).

Cyclic voltammetry scans on glassy carbon electrode were measured for a preliminary test. Because of the gradual redox peaks around 0.5 - 0.6 V, these complexes considered to be utilized as a mediator between cathode electrode and enzyme.

Furthermore, in the cyclic voltammogram of glassy carbon electrode coated by the carbon nanotube and laccase, increase of reduction peak was observed in the presence of oxygen (Figure 3), and coated by the carbon nanotube, laccase and complex, reducing ability of laccase seemed to have improved especially only for the complex of L=N-ethylethylenediamine (Figure 4).



**Figure 3:** Cyclic voltammetry ( $50 \text{ mVs}^{-1}$ , 200 mM acetate buffer, pH 5.0, with 3-20 nm carbon nanotubes under oxygen (blue) or nitrogen (red)) of only laccase.



**Figure 4:** Cyclic voltammetry ( $50 \text{ mVs}^{-1}$ , 200 mM acetate buffer, pH 5.0, with 3-20 nm carbon nanotubes under air (green), nitrogen (red), oxygen (blue)) of laccase and  $[\text{CuL}_2]_3[\text{Fe}(\text{CN})_6]_2$  (L=N-ethylethylenediamine).

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