

論文 / 著書情報  
Article / Book Information

題目(和文)	
Title(English)	Analysis of intramolecular electron transfer in tetraheme cytochrome c3 by direct electrochemistry
著者(和文)	
Author(English)	Sim Sanghoon
出典(和文)	学位:博士(理学), 学位授与機関:東京工業大学, 報告番号:甲第10499号, 授与年月日:2017年3月26日, 学位の種別:課程博士, 審査員:朝倉 則行,丹治 保典,中村 聡,三原 久和,蒲池 利章
Citation(English)	Degree:Doctor (Science), Conferring organization: Tokyo Institute of Technology, Report number:甲第10499号, Conferred date:2017/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

## Analysis of intramolecular electron transfer in tetraheme cytochrome $c_3$ by direct electrochemistry

Sim Sanghoon

Biological electron transfer, which is high efficient electron transfer observed in the electron transfer chain, was controlled by each redox protein. Redox protein selects a redox partner and maintains the electron transfer chain. There is an interesting the electron transfer mechanisms arising from redox protein.

Cytochrome  $c_3$  from *Desulfovibrio vulgaris* (Miyazaki F), a redox protein, contains four hemes and has multiple redox state arising from conformational change during intramolecular electron transfer among hemes

Protein film voltammetry (PFV), a direct electrochemical measurement allowing direct observation of the redox reactions of a redox protein, was carried out to observe intramolecular electron transfer in cytochrome  $c_3$

Direct electrochemical measurement shows higher redox potential (-0.095 V vs. SHE) than the other hemes, although the four hemes in cytochrome  $c_3$  are bis-histidyl hemes (-0.350 V ~ -0.200 vs. SHE). The high redox potential of cytochrome  $c_3$  was similar to that observed for the loss of an axial ligand at heme. To investigate the loss of the histidine ligand, the electrochemistry of four cytochrome  $c_3$  Met mutants, in which the sixth coordinated histidine was replaced by methionine, was explored. The electrochemistry of the cytochrome  $c_3$  mutants indicated that Heme III alone undergoes loss of its axial histidine ligand.

In addition, kinetic of an intramolecular electron transfer of cytochrome  $c_3$  was investigated by high speed cyclic voltammetry, showing that conformational change of heme II was rate determining step.

Finally, redox potentials of each heme was successfully clarified by direct electrochemical measurement. To identify the redox potentials of the four hemes, the electrochemistry of four cytochrome  $c_3$  Ala mutants, in which the sixth coordinated histidine was replaced by alanine, was carried out. The cyclic voltammograms arising from the four hemes are complicated but in the mutants, the redox potential of the one heme in which one histidine ligand is replaced with alanine is obviously higher. Thus, the redox potential of the bis-histidyl coordinated each heme can be determined.

In this study, mechanisms of intramolecular electron transfer of cytochrome  $c_3$  were investigated and the roles of cytochrome  $c_3$  during biological electron transfer were clarified.