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The Structural Regulation of the Redox Potential in Cytochrome c_3

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Cytochrome c_3 (cyt c_3) isolated from a sulfate-reducing bacterium, possesses four *c*-type heme groups per molecule. It is involved in the electron-transport system in the bacteria, as a partner of hydrogenase. The properties of cyt c_3 have been investigated extensively and shown to be very different from those of other *c*-type cytochromes. The redox potentials of this protein are significantly lower than those of mitochondrial cytochromes *c*. The heterogeneous electron-transfer at various electrodes is very rapid. The electric conductance of a dry film of ferrocycytochrome c_3 is as high as 0.02 S cm^{-1} in the fully reduced state. The ionization potential of solid state ferricytochrome c_3 is 0.7 eV, which is lower than that of ferricytochrome *c*.

Since cyt c_3 has four redox centers, four macroscopic formal redox potentials and thirty-two microscopic formal redox potentials ("formal" is deleted hereafter for simplicity) can be defined. Many efforts have been made to determine its macroscopic redox potentials and microscopic redox potentials. Correlations between the microscopic redox potentials and the crystal structure has been reported for cyt c_3 from *D. vulgaris* Miyazaki F, *D. vulgaris* Hilden borough. Since the crystal structure of *DvMF* cyt c_3 is available at 0.18 nm resolution, the relationship between its structure and redox behavior can be discussed in detail. We have tried to elucidate the structural factors that determine the redox potentials of each of the four hemes, which are the important regulation factors in the electron transfer.