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POSTER PRESENTATION

Biogenesis of Metalloproteins

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Reconstitution of copper ions to the partly expressed aqueous exposed domains from the 45 kda subunit of particulate methane monooxygenase

Zong-Lin Yang, Sunney I. Chan, Steve S.-F. Yu
Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan (ROC). Armaniboy.tw@yahoo.com.tw

The crystal structure of the particulate methane monooxygenase (pMMO) from *Methylococcus capsulatus* (Bath) has been reported recently. Since the aqueous-exposed domains of the 45 kDa subunit (PmoB) have been suggested to be the putative binding domains for the E-cluster copper ions, in *Escherichia coli*, we have cloned and over-expressed the two aqueous-exposed subdomains toward the N- and C-termini of the subunit: the N-terminal subdomain (residues 54–178) and the C-terminal sub-domain (residues 257–394 and 282–414). The recombinant C-terminal water-exposed sub-domain is shown to behave like a Cu(I) sponge, taking up to ca. 10 Cu(I) ions cooperatively when cupric ions are added to the protein fragment in the presence of dithiothreitol or ascorbate. In addition, circular dichroism measurements reveal that the C-terminal sub-domain folds into a β-sheet structure in the presence of Cu(I). The propensity for the C-terminal sub-domain to bind Cu(I) is consistent with the high redox potential(s) determined for the E-cluster copper ions in the pMMO. These properties of the E-clusters are in accordance with the function proposed for these copper ions in the turnover cycle of the enzyme [1].

Reference

1. Yu SS-F, Ji C-Z, Wu YP, Lee T-L, Lai C-H, Lin S-C, Yang Z-L, Wang VC-C, Chen KH-C, Chan SI (2007) Biochemistry 46:13762–13774 (2007)

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Oxidation power of the chlorophyll pair P680 in Photosystem II

Hiroshi Ishikita[1], Ernst-Walter Knapp[2]
[1]Bldg E, Graduate School of Medicine, Kyoto University, Yoshida Konoe-cho, Sakyo-ku, Kyoto 606-8501, Japan.
[2]Takustr. 6, Institute of Chemistry, Free University of Berlin, 14195 Berlin, Germany.
[1]hzi1@usc.edu, [2]knapp@chemie.fu-berlin.de

Atmospheric oxygen is generated by the oxidation of water at the Mn_4Ca cluster of the photosynthetic protein–pigment complex, Photosystem II (PSII). Light-induced charge separation leads to the formation of an oxidized, positively charged radical $P680^+$ chlorophyll *a* (Chl*a*). The redox potential for one-electron oxidation (E_m) of P680 is unusually high 1,100–1,300 mV with respect to the E_m of isolated Chl*a* ($\approx$ca. 700–800 mV). The unusually high E_m enables P680 to act as an electron acceptor for the different Mn_4Ca redox states. To elucidate this known but still unexplained E_m shift in the protein environment of PSII, we calculated E_m in the reaction center of PSII by solving the linearized Poisson–Boltzmann equation for all atoms in the crystal structures under identical computational conditions. The results were compared with those of the corresponding chlorophyll pairs P700 in Photosystem I (PSI) and P870 in the purple bacterial photosynthetic reaction centers (PbRC).

References

1. Ishikita H, Saenger W, Biesiadka J, Loll B, Knapp E-W (2006) Proc Natl Acad Sci USA 103:9855–9860
2. Ishikita H, Biesiadka J, Loll B, Saenger W, Knapp E-W (2006) Angew Chem Int Ed Engl 45:1964–1965