Electrochemical surface immobilization triggers intramolecular electron transfer in multi-centre redox metalloproteins: The di-heme protein cytochrome c4

Chi, Qijin; Nazmudtinov, R.R; Bronshtein, M.D.; Zinkicheva, T.T.; Zhang, Jingdong; Ulstrup, Jens

Publication date:
2012

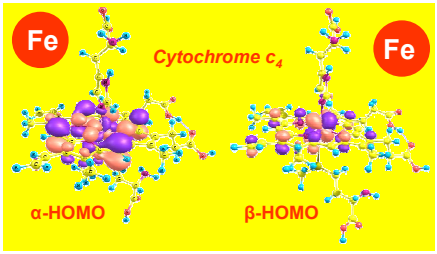
Document Version
Publisher's PDF, also known as Version of record

Electrochemical surface immobilization triggers intramolecular electron transfer in multi-centre redox metalloproteins: The di-heme protein cytochrome c_4

Q. Chi[1*], R.R. Nazmudtinov[2*], M.D. Bronshtein[2], T.T. Zinkicheva[2], J. Zhang[1] and J. Ulstrup[1*]

[1]Dept of Chemistry, Techn. University of Denmark, DK-2800 Kgs. Lyngby, Denmark
[2] Kazan National Research Technol. Univ., Kazan, Tatarstan, Russian Federation.
(E-mails: *cq@kemi.dtu.dk; *nazmutdi@mail.ru; *ju@kemi.dtu.dk)

Protein film and monolayer voltammetry is a powerful tool for mechanistic redox enzyme mapping. A common observation is that composite multi-centre enzymes, e.g. copper oxidases do not themselves give voltammetric signals. Addition of substrate molecules (O_2, NO_2^- etc.), however, triggers strong electrocatalytic signals, still caused by the enzyme, indicating that crucial changes in the enzyme molecules occur on substrate binding or surface immobilization. The di-heme metalloprotein cyt c_4 (*P. stutzeri*) has emerged as a prototype multi-centre metalloprotein that offers clues to these observations. Electron transfer (ET) behaviour of cyt c_4 in homogeneous solution shows clearly that ET between the heme groups is slow. Immobilization on well-defined SAM-modified Au(111)-electrodes, however, open efficient intramolecular ET channels, clearly displayed by the two-ET voltammetric cyt c_4 behaviour.
We present here a comprehensive experimental and theoretical (quantum chemical) analysis of the intramolecular ET behaviour of cyt c_4 in bulk solution and on a SAM-modified electrochemical surface. The electronic coupling between the heme groups is, particularly, exceedingly sensitive to the conformational environment and increases by many orders of magnitude on even tiny, thermally accessible structural fluctuations. Low-energy conformational triggering of electronically based facile ET channels therefore offer a clue to broadly observed metalloenzyme voltammetry.



Two references:

1. Q. Chi, Q., J. Zhang, T. Arslan, L. Borg, G.W. Pedersen, H.E.M. Christensen, R.R. Nazmutdinov, J. Ulstrup, *J. Phys. Chem*. B, 2010, **114**, 5617-5624.
2. R. R. Nazmutdinov, M.D. Bronshtein, T.T. Zinkicheva, Q. Chi, J. Zhang, J. Ulstrup, PCCP (2012), in press.