

The Au-S bond and SAM-protein contact in long-range electron transfer of pure and biomimetic metalloproteins via functionalized alkanethiol linkers

Chi, Qijin; Ford, Michael J.; Halder, Arnab; Hush, Noel S.; Reimers, Jeffrey R.; Ulstrup, Jens; Zhang, Jingdong

Publication date:
2016

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

[Link back to DTU Orbit](#)

Citation (APA):
Chi, Q., Ford, M. J., Halder, A., Hush, N. S., Reimers, J. R., Ulstrup, J., & Zhang, J. (2016). The Au-S bond and SAM-protein contact in long-range electron transfer of pure and biomimetic metalloproteins via functionalized alkanethiol linkers. Abstract from 67th Annual Meeting of the International Society of Electrochemistry, The Hague, Netherlands.

DTU Library

Technical Information Center of Denmark

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

The Au-S bond and SAM-protein contact in long-range electron transfer of pure and biomimetic metalloproteins via functionalized alkanethiol linkers

Qijin Chi¹, Michael J. Ford², Arnab Halder¹, Noel S. Hush³, Jeffrey R. Reimers^{2,5}, Jens Ulstrup¹ and Jingdong Zhang¹

¹*Department of Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark*

²*School of Mathematic and Physical Sciences, The University of Technology of Sydney, Sydney, NSW 2007, Australia*

³*School of Chemistry F11, The University of Sydney, Sydney, NSW 2006, Australia*

⁴*School of Molecular Bioscience, The University of Sydney, Sydney, NSW 2006, Australia*

⁵*International Centre for Quantum and Molecular Structure, College of Sciences, Shanghai University, Shanghai 200444, China*

E-mail: ju@kemi.dtu.dk

Abstract:

Interfacial electrochemical electron transfer (ET) of redox metalloproteins is long established¹. For the proteins to retain full ET or enzyme activity, modification of the electrode surfaces, say gold surfaces by self-assembled molecular monolayers (SAMs) is nearly always needed, where functionalized alkanethiols have emerged as core linkers. We have studied molecular linking in the long-range ET (LRET) processes in detail using electrochemistry, *in situ* STM and AFM, and electronic structure computations^{2,3}. A focus is the electronic structure of the Au-S link and the SAM packing. We have disentangled a wealth of data to identify the nature of the crucial Au-S contact, all suggesting prevalence of a Au(0)-thiyl radical unit. Molecular packing is further determined by the SAM molecular structure and involves binding either to Au-atoms mined out of the surface or directly to a flat surface. We illustrate this by high-resolution *in situ* STM of straight, branched, and chiral alkanethiols on Au(111)-electrode surfaces.

We discuss next LRET of two SAM immobilized multi-copper enzymes, nitrite reductase and laccase, mapped to single-molecule resolution by *in situ* STM and AFM^{4,5}. The voltammetry is exceedingly sensitive to the structure of the thiol-based SAM molecules, testifying to the crucial importance of SAM packing and Au-S binding, and of the SAM link to the protein. Some of the subtleties are illustrated simpler by similar size (5-6 nm) nanoparticles (NPs)⁶. Biomimetic NPs must possess a certain degree of electronic structure sophistication. At the molecular scale this requirement is met by NPs of the renowned mixed-valence Prussian Blue (PB) assembled on Au(111)-electrode surfaces via functionalized alkanethiols. PBNP SAMs show LRET comparable to metalloproteins. Alkanethiols with different terminal groups exhibit, further intriguing LRET differences, reflecting other subtleties. We discuss the molecular LRET mechanisms and the intrinsic conductivity of the PBNPs.

References:

- [1] J. Zhang, A.M. Kuznetsov, I.G. Medvedev, Q. Chi, T. Albrecht, P.S. Jensen and J. Ulstrup, *Chem. Rev.* 108 (2008) 2737-2791.
- [2] J. Yan, R. Ouyang, P.S. Jensen, E. Ascic, D. Tanner, B. Mao, J. Zhang, C. Tang, N.S. Hush, J. Ulstrup and J.R. Reimers, *J. Am. Chem. Soc.* 136 (2014) 17087-17094, and references there.
- [3] J.R. Reimers, M.J. Ford, A. Halder, J. Ulstrup, and N.S. Hush, *PNAS USA* (2016) in press.
- [4] J. Zhang, Q. Chi, A.G. Hansen, P. S. Jensen, P. Salvatore and J. Ulstrup, *FEBS Letters* 586 (2012) 526-535, and references there.
- [5] V. Climent, J. Zhang, E.P. Friis, L.H. Østergaard and J. Ulstrup, *J. Phys. Chem. C* 116 (2012)1232-1243.
- [6] N. Zhu, S. Han, S. Gan, J. Ulstrup and Q. Chi, *Adv. Funct. Mat.* 23 (2013) 5297-5306.