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

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Abstract:

Interfacial electrochemical electron transfer (ET) of redox metalloproteins is long established[1]. 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.

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