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The Au-S bond in biomolecular adsorption and electrochemical electron transfer

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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, such as gold surfaces by self-assembled molecular monolayers (SAMs), is nearly always required, where pure and functionalized alkanethiols have emerged as core linkers.

We overview first binding and single-molecule long-range electron transfer of some metalloproteins, metalloenzymes, and DNA-based molecules on single-crystal Au(111), Au(100), and Au(100) electrode surfaces, bound either directly by Au-S linking of surface cysteines to the gold surfaces, or indirectly by non-covalent linking to SAMs of pure and functionalized alkanethiols^{1,2}. Core techniques are electrochemistry, surface spectroscopies, and *in situ* STM and AFM under electrochemical potential control, framed by single-molecule charge transport theory and electronic structure computations^{3,4}. Molecular packing, voltammetry and *in situ* STM/AFM are found to be exceedingly sensitive to the structure of the thiol-based SAM molecules, testifying both to the crucial importance of the Au-S binding, and to the SAM linking to the protein²⁻⁵.

A primary focus that has emerged is the electronic structure of the Au-S link and the packing of the SAMs^{3,4}. We have, first disentangled a wealth of data to identify the nature of the core Au-S contact. All data suggest that the electronic Au-S link is dominated by a Au(0)-thiyl radical with strong van der Waals forces and not by a Au(I)-thiolate ionic/covalent unit. Molecular packing is, further crucially determined by the SAM molecular structure and involves binding either to Au-atoms mined out of the surface or directly to a flat single-crystal surface. We illustrate this by high-resolution *in situ* STM of straight, branched, and chiral alkanethiols on Au(111)-electrode surfaces.

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