Charge Transport Properties of Cytochrome b_{562} on Gold Interfaces

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INTRODUCTION

The fundamental processes that drive life, such as respiration, photosynthesis, and various enzymatic catalytic activities, are based on electron transfer reactions facilitated by redox proteins. One such protein, cytochrome b_{562} (Fig. 1) found in *Escherichia coli*, is a metalloprotein, which contains one redox-active heme ($Fe^{2+/3+}$) cofactor covalently bonded to the protein matrix. The central iron cation at the redox site is coordinated with axial histidine (His102) and methionine (Met7) ligands (Fig. 2). The conductive properties of single cytochrome b_{562} adsorbed on gold surfaces were recently investigated using Electrochemical Scanning Tunneling Microscopy (EC-STM) . Here, we examine the related adsorption structures by computational techniques to elucidate the charge transport properties and mechanism.

METHODOLOGY

We employ various computational approaches to study these properties. Classical molecular dynamics (MD) is used for examining the structural aspects of the protein and its configurations on the gold surfaces. On the other hand, the quantum mechanical (QM) approach based on Density Functional Theory (DFT) is applied to investigate the electronic states at the protein/metal interfaces and junctions. [2], [3] These are then used to compute the conductive properties.

PROTEIN ADSORPTION

Following the experimental setup [1], we focus on mutated cytochrome b_{562} (Fig. 3). After validating the stability of a dried protein structure, we simulate spontaneous adsorption to the flat gold (111) surface. The obtained physisorbed structures are statistically analyzed and representative geometries are selected for further study. These are then chemisorbed and used for the preparation of the cytochrome junction between gold contacts.

TRANSPORT PROPERTIES

For the transport at bio/metallic interfaces, electronic-state alignment is crucial. We use the DFT+Σ approach for its prediction, followed by the interfacial electronic coupling calculations by the Projector Operator-Based Diabatization (POD) method. These are then used for tunneling current evaluation within the Landauer formalism. [3], [4] For comparison, we also compute the incoherent electronic flux through the heme redox site to show that this mechanism, also dominant in solution, is not competitive with the coherent tunneling in junction configuration. These findings are in accord with previously studied multi-heme cytochrome junctions [4] and have important consequences for the design of novel bioelectronic devices and material development.

REFERENCES

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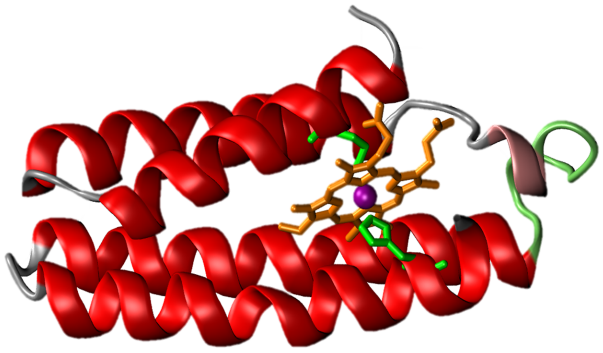

Fig. 1. Crystal structure of the Cytochrome b_{562} protein (PDB id 2BC5)

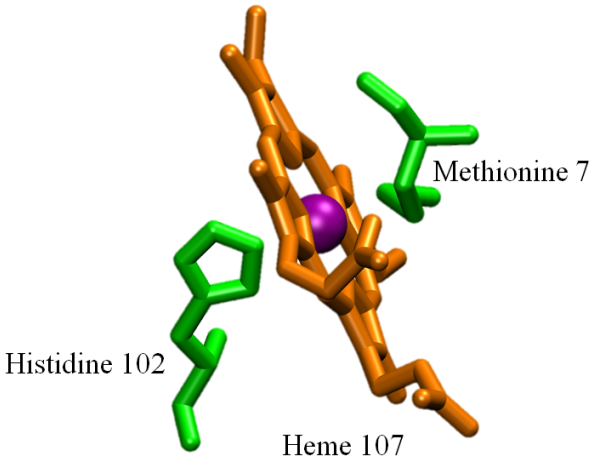

Fig. 2. Details of the redox-active heme site (Purple: Fe, Orange: Porphyrin ring, Green: Axial histidine and methionine)

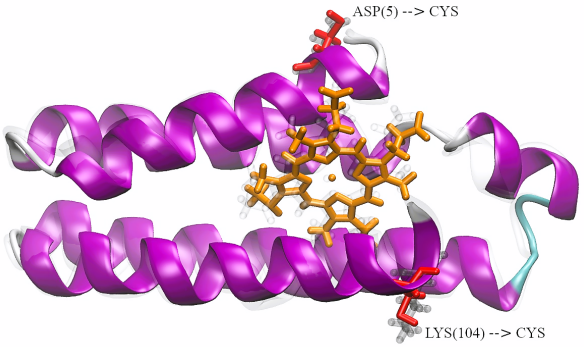

Fig. 3. Mutated (Asp5 to Cys and Lys104 to Cys) vs non-mutated (Native cytochrome b_{562}) (Ghost: Native, Color: Mutated)

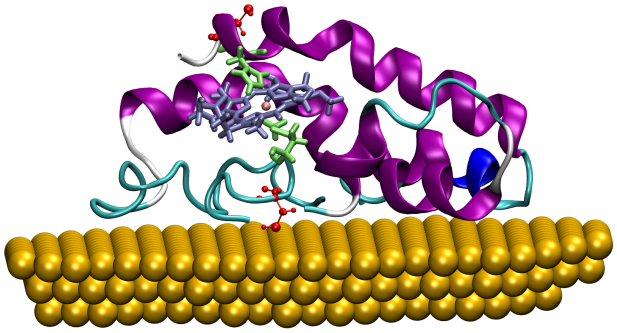

Fig. 4. Mutated cytochrome b562 adsorbed onto a gold surface