Electron Transport Mechanisms in Cytochrome b_{562} Junctions

Gowtham Nirmal Jonnalagadda, Xiaojing Wu*, Lukas Hronek, and Zdenek Futera
Faculty of Science, University of South Bohemia, Branisovska 1760,
370 05 Ceske Budejovice, Czech Republic.
* Laboratoire de Chimie, ENS de Lyon 46, allée d'Italie, 69364 Lyon, France
e-mail: jonnag00@jcu.cz

INTRODUCTION

Cytochrome b_{562} (Cyt b_{562}) (Fig. 1) is a small redox-active heme protein that has served as a key model system for understanding biological electron transfer processes. Electron transport in such proteins plays a crucial role in various biochemical functions, including respiration and enzymatic catalysis. Investigating its transport properties in protein-metal junctions provides valuable insights into charge transfer mechanisms relevant to bioelectronic interfaces. Recent experimental studies have demonstrated the conductive properties of Cyt b_{562} on gold surfaces [1], but a deeper theoretical understanding of its charge transport mechanism is necessary. This study presents a comprehensive theoretical analysis of electron transport in Cyt b_{562} based junctions using a multiscale computational approach, examining both coherent and incoherent transport processes.

METHODOLOGY

To model electron transport, molecular dynamics (MD) simulations were employed to generate junction geometries under both vacuum-dried (Fig. 2) and solvated conditions (Fig. 3), where the protein was covalently bound to gold contacts in various configurations [2]. Charge transport was analyzed through two mechanisms: coherent tunneling, studied using the Landauer-Büttiker formalism within the Density Functional Theory (DFT) framework [3], and incoherent hopping, modeled using the semi-classical Marcus theory. [3], [4]

RESULTS

The study identified tunneling as the dominant charge transport mechanism, explaining experimental observations of Cyt b_{562} junctions. The tunneling exhibited an exponential but shallow distance dependence, highlighting the significance of structural orientations and protein-electrode contacts in determining conductance. While solvation effects had only a minor influence on electronic properties, primarily through adsorption arrangements, temperature dependence was crucial. The hopping mechanism showed a strong temperature dependence, whereas the tunneling currents remained nearly unaffected, reinforcing the role of coherent transport in these systems. [5]

FUNDING

The research is supported by Czech Science Foundation (GACR) Grant No. 20-02067Y.

REFERENCES

[1] M. Elliott, D.D. Jones *Approaches to Single-molecule Studies of Metalloprotein Electron Transfer Using Scanning Tunneling Probe-based Techniques.* Biochem. Soc. Trans. **46**, 9 (2018).

[2] Z. Futera *et al. Coherent Electron Transport across a 3 nm Bioelectronic Junction Made of Multi-heme Proteins.* J. Phys. Chem. Lett. **11**, 9766 (2020).

[3] Z. Futera, X. Wu, and J. Blumberger *Tunneling to Hopping Transition in Multiheme Cytochrome Bioelectronic Junctions.* J. Phys. Chem. Lett. **14**, 445 (2023).

[4] O.V. Kontkanen, D. Biriukov, Z. Futera *Reorganization Free Energy of Copper Protein in Solution, in Vacuum and on Metal Surfaces.* J. Chem. Phys. **156**, 175101 (2022).

[5] G.N. Jonnalagadda, X. Wu, L. Hronek, and Z. Futera *Structural, Solvent, and Temperature Effects on Protein Junction Conductance* J. Phys. Chem. Lett. **15**, 11608 (2024).

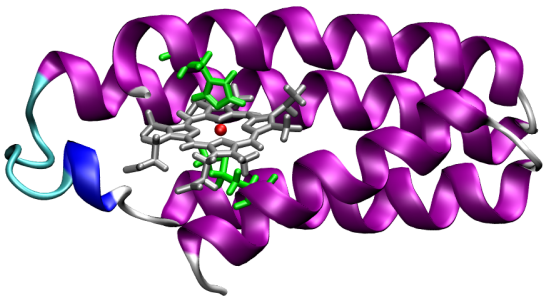

Fig. 1. Crystal structure of cytochrome b_{562} (PDB id 2BC5)

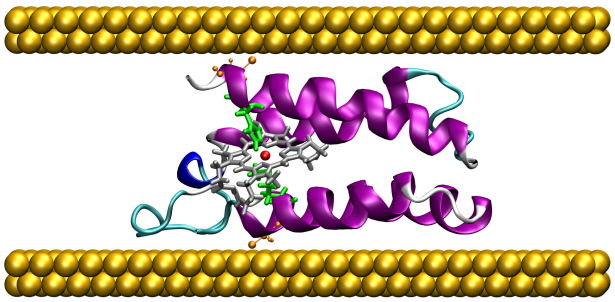

Fig. 2. Vacuum lying junction structure of Cyt b_{562}

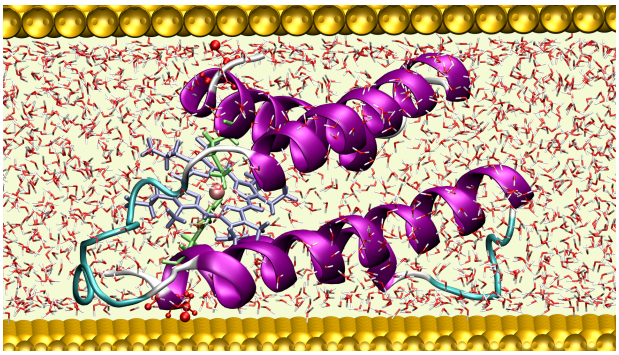

Fig. 3. Solvent lying junction structure of Cyt b_{562}

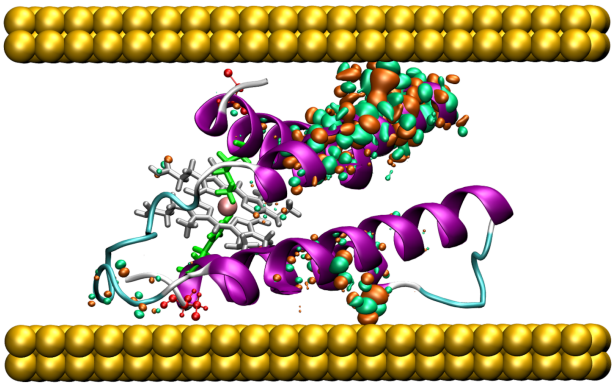

Fig. 4. Dominant conduction channel on the solvated lying structure of Cyt b_{562}