Mechanisms and Controlling Factors of Electron Transport through Geobacter sulfurreducens PilA Protein

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Abstract
It was demonstrated that the pilus of Geobacter sulfurreducens may be able to efficiently transfer electrons (act as a molecular conductor). Although experiments have been performed proving Geobacter sulfurreducens conductive properties, little quantitative estimation of the mechanisms and controlling factors of electron transfer have been performed including identification of transmission spectrum, density of states, and electron transfer paths. Two mechanisms of its conductivity have been proposed. In one, prosthetic groups associated with this protein are the main mediators of its electron transfer capabilities. In the other, the pilus itself can be an efficient conductor. We perform electronic structure and transport calculations, on PilA, a main protein of Geobacter sulfurreducens pilus, to estimate the conductance properties of this protein without prosthetic groups. Our results show that electron tunneling is not likely at low applied biases in part because strong transmission bands of fragments locate far from Fermi level, and because positively charged arginines and lysines in the middle of the protein form electrostatic traps, preventing efficient electron transfer. Application of high bias voltages potentially opens up the possibility for these traps to be filled out with electrons resulting in sequential electron transfer through the central region of the protein. In addition, phenylalanines and leucines in the protein form electron transfer loops that stabilize electrons, further aiding in sequential electron transfer through PilA at high applied voltages.

Objective
Identify the possibility of using Geobacter sulfurreducens PilA protein in biomolecular electronic devices:
• With molecular structure and electron transport calculations performed using high performance computing we take a step in identifying mechanisms of pil conductivity by looking at the possibilities of electron transport through specific regions of PilA, a major component of Geobacter sulfurreducens pilus.

Methods
PilA (PDB Accession 2M7G) has three fragments that are distinguishable by their amino acid compositions.

Fragment 1 = N-terminal fragment, Fragment 2 = Central fragment, Fragment 3 = C-terminal fragment

Results
Location of Transmission Bands Far from Fermi Indicate ET Not Likely at Low Voltages

Effective Potential Drops at Charged Amino Acids Indicate Formation of Electrostatic Traps

Fragments Exhibit Loops of Electron Cycling Which Aids in Sequential Transfer

Conclusions
• The lack of delocalization of frontier molecular orbitals, location of strong transmission bands far from Fermi level, weak electrode coupling, and formation electrostatic traps, indicates that at low biases, electron tunneling through PilA is unlikely.
• The tunneling through the peptide is possible after applying to the electrodes considerable bias voltages (over 6V) and only through the central peptide fragment.
• In this case, the charged amino acids, which form electrostatic traps in the middle of the peptide, act as a capacitor.
• Leucines and phenylalanines located in various parts of the peptide form ET loops with local forward and back electron cycling preventing electrons from direct coherent tunneling, but providing additional opportunity of sequential electron transfer through the peptide at high bias voltages.
• A possible application in electronic devices may be to manipulate the protein so electron transfer goes through only fragment 2.

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