Chemical Modulation of Protein Electrode Interactions Enables Control of Frontier Orbital Alignment in Gold-Azurin-Gold Junctions

Authors: Jerry A. Fereiro[1], Gilad Porat[2], Tatyana Bendikov[4], Israel Pecht[3], Mudi Sheves[2] & David Cahen[*1]

Affiliations:

[1]Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel

[2]Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, Israel

[3]Department of Immunology, Weizmann Institute of Science, Rehovot, Israel

[4]Chemical Research Support Unit, Weizmann Institute of Science, Rehovot, Israel.

Abstract: Modulation of the electrode-protein coupling in a solid-state protein junction can have a major impact on the electronic transport (ETp) across the junction. We have established this by comparing four different Au-Azurin(Az) - Au junction types, at cryogenic temperature. Az is covalently bound in all junctions by Au-S bonding to lithographically prepared Au bottom electrode (Au-Az). Au nanowires, with covalently bound Mercapto-Propionic Acid (MPA), having a free carboxylic group at its other end, serve as the top electrode. In the presence of such a linker/spacer (Au-linker//Az-Au junctions), I-V plots show step like features, indicating resonant electron tunnelling through discrete energy levels. The MPA linker's carboxylic group was chemically modified using EDC/NHS to form covalent protein-linker bond (Au-protein-$(CH_2)_2$CO-NH -Au junction). This covalent protein-linker interaction switched the ETp mechanism from resonant to off-resonant tunneling. We also examined an intermediate situation where only a limited number of MPA molecules were reacted with EDC/NHS to form covalent bond with Az. Comparison of the IETS results obtained from such different configurations were used in order to elucidate the relative position of the Az energy levels with respect to electrodes Fermi level. The results presented here demonstrate the possibility of regulating energy level alignment in a two-terminal protein junction, by the latter chemical modification i.e. without a gate electrode.