

Electron-Transfer Proteins for Biomolecular Electronic Devices

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Novel molecular materials are attracting the interest of researchers worldwide [1] as possible building blocks of advanced nanoscale devices. The great advantage of employing biological molecules to implement next-generation electronics is linked not only to the intrinsic molecular nano-scale, which allows to overcome the limitations of top-down nanostructure fabrication, but also to their self-assembling and recognition capabilities. These peculiarities guarantee, in principle, to realize arrays of identical devices with well-controlled transport characteristics. In this framework, we have recently advanced the proposal of using the blue copper protein Azurin to form the active layer of a nanoelectronic device [2]. Indeed, the physiological electron-transfer function of Azurin [3], together with its mechanical stability, make it a candidate of choice for such applications.

We show here that a biomolecular electron rectifier in the solid state can be implemented by interconnecting an Azurin monolayer immobilized on SiO₂ with two gold nanoelectrodes [2,4]. This rectifier exhibits discrete current steps in the positive wing of the I-V curve, which are ascribed to resonant tunnelling through the redox active center. This result represents a fundamental step for the realization of protein-based electronic devices, such as field-effect transistors or single-electron transistors.

We then focus on understanding how the devices work and the current flows between the electrodes through the protein medium. Our computational analysis concentrates on two separate issues that will be connected in future modelling. (i) *Activity of the Cu site*. To interpret the electron transfer process in terms of the quantum electronic structure, we performed plane wave pseudopotential ab-initio DFT calculations of the electron spectra and wavefunctions of the protein redox-active site, including the Cu ion and the five ligated amino acids, in the two stable charge states (Cu⁺¹ and Cu⁺²). (ii) *Azurin self-assembly*. To characterize the self-assembly and immobilization of the protein onto the device substrate in the region between the electrodes, we employed classical molecular mechanics techniques [4] to compute the electrostatic properties of the whole protein. The ab-initio quantum mechanical results show differences between the electron spectra of the oxidized and the reduced forms, and identify strong correlation effects when an electron is added (removed) at the Cu site. The results of the classical simulations allow us to account for the rectifying behaviour of the fabricated devices [2] in terms of the strong molecular electrostatic dipole.

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