Dynamical characterization of the adsorption and Electron Transfer Processes of Cyt-*c* at SAM-Coated Electrodes

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Direct electrochemistry of redox proteins immobilized on electrodes represents an active field of research that allows determination of thermodynamic and kinetic parameters, as well as elucidation of mechanistic aspects of redox enzymes, and is also relevant for the development of biofuell cells and sensors, based on immobilized redox enzymes. The mostly used strategy for the immobilization of proteins on metal electrodes consists in coating the metal surface with self-assembled monolayers (SAMs) of □-functionalized alkanethiols, selected in order to achieve efficient immobilization trough electrostatic or hydrophobic interactions.

Using this strategy we measured the distance dependence of the electron transfer (ET) rates for Cytochrome-c (Cyt) and other proteins. Interestingly, a similar qualitative behaviour was observed for all cases. At long distances ET rate follows the expected exponential dependence, however, at short distances the rate becomes distance independent. The origin for this behaviour has been elusive and controversial. In a recent work by our group, we reported the first direct evidence that the rate limiting step for the reduction of Cyt adsorbed on short SAMs, could be protein reorientation (i.e dynamics), and that this process is likely to be controlled by the interfacial electric field.

Here we have extended these studies and complemented them with Molecular Dynamics simulations (MDS), in order to study the adsorption process, the dynamics of the Cyt/SAM complex, and the relation of the structural and dynamical properties with the ET transfer rate, estimated using the pathways algorithm. The combination of spectroscopic experiments and computer simulations provides an unprecedented detailed picture of the electrochemical reaction of Cyt at interfaces and opens new perspectives for bioelectrochemistry in general.