
Electrochemical approaches for molecular electronics

Emmanuel Maisonhaute*^{†1}

¹Laboratoire Interfaces et Systèmes Electrochimiques (LISE) – Université Pierre et Marie Curie (UPMC) - Paris VI, CNRS : UMR8235 – 4 Place Jussieu, 75005 Paris, France

Abstract

The talk will include two different parts representing some of our activities in the domain of molecular nanoobjects. First, electronic communication inside molecular systems is very complex since nuclear motions affect electronic levels and thus the final efficiency of the device. In this field electrochemistry has proven to be relevant to estimate the rate of electron transfer from a redox center towards an electrode. For practical applications, there is a need for a fast signal transduction. However, this raises the difficulty of finding a method with an adapted temporal resolution. We rely on ultrafast voltammetry for this purpose, and several examples of kinetic rates determination will be depicted. A first category will be molecular wires adsorbed onto electrodes. Here, a single electron is transferred per molecule. Larger systems such as dendrimers bear a multiplicity of redox centers, some of them being too far from the electrode to allow a direct communication. However a redox reaction can still occur by successive electron hopping between neighboring entities. On these large systems, we could access to the intramolecular dynamics of the redox entities.

On the other hand, complementary information can be obtained by performing conductance measurements relying on the the Scanning Tunneling Microscopy Break Junction method. Here a steady state value (the resistance of the molecule) is obtained, but at the single molecule level. It was observed that kinetically fast systems indeed display larger conductances. Electronic coupling factors for both experimental approaches were therefore evaluated based on superexchange mechanism theory. This suggests that coupling is surprisingly on the same order of magnitude or even larger in conductance measurements whereas electron transfer occurs on larger distances than in transient electrochemistry. It is thus very different to have a steady state flux of electrons through a single molecule than to localize a single electron per redox center in a large collection of molecules. Furthermore, in electrochemical conditions, the conductance changes with the electrode potential (at constant bias), mimicking a single molecule field effect transistor for which the gate electrode is the reference electrode.

*Speaker

[†]Corresponding author: emmanuel.maisonhaute@upmc.fr