

# Electrochemistry *Within* Molecules using Ultrafast Cyclic Voltammetry

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The basic principles allowing undistorted cyclic voltammetry up to  $2.5 \text{ MV.s}^{-1}$  to be performed at ultramicroelectrodes are recalled. Access to this range of ultrahigh scan rates allows nanosecond-time scale to be explored voltammetrically which offers obvious kinetic advantages by widening the mechanistic scope of voltammetry so that it encompasses now more than nine orders of magnitude.

In this paper, we are interested in discussing a remarkable — but less promoted — advantage of ultrafast voltammetry. Indeed, scan rates in the megavolts-*per*-second range allow the creation of diffusion layers with a maximal extension of a few nanometers, *viz.*, which are comparable to the size of chemical and biological molecules. In other words, this allows the *in-situ* and *direct* monitoring of redox communication *within* molecules which are attached to an ultramicroelectrode surface.

The experimental validity and the interest of this concept are presented on the basis of two typical examples. One deals with the rate of redox commutation within a self-assembled monolayer of organometallic molecules bearing a redox terminal group,  $[\text{Os}(\text{bpy})_2\text{Cl}(\text{py-B})]^+$  adsorbed onto a platinum surface through the pyridyl moiety of their ligated bridge ( $-\text{B} = -(\text{CH}_2)_2\text{-py}$ ). The second application concerns the monitoring of the time-progression of electron-hopping diffusion through electron exchange between 64  $\text{Ru}^{\text{II/III}}(\text{tpy})_2$  redox groups distributed on a fourth generation PAMAM dendrimer molecule adsorbed onto an ultramicroelectrode. Besides the measurement of the rate of communication between adjacent ruthenium centers within one dendrimer, the method is extremely informative about the topology of the spatial arrangement of the 64 redox centers, so that it can be used as a molecular microtome with a resolution better than that of STM.

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