**Bioelectrochemistry at the single-molecule level**

Professor Jens Ulstrup

Department of Chemistry, Technical University of Denmark, 2800 Kongens Lyngby, Denmark

The scanning probe microscopies, scanning tunnelling (STM) and atomic force microscopy (AFM) enable addressing molecules on solid surfaces with a degree of detail that even reaches the single molecule directly in aqueous chemical and biological media under electrochemical control (*in situ* STM and AFM). Redox molecules are of particular interest but pose greater theoretical and conceptual challenges than non-redox molecules. *In* *situ* STM and AFM of biomolecules such as (metallo) proteins and DNA-based molecules pose even greater single-molecule challenges but offer in return intriguing insight in the ways these molecules operate.

Single-molecule bioelectrochemistry (metalloproteins, DNA) requires well-defined (atomically planar) electrode surfaces modified by molecular monolayers (SAMs). Such surfaces have themselves been mapped to sub-molecular resolution and disclose an intriguing variety of local environments. ***Structural*** mapping of redox metalloproteins such as blue copper, heme, and iron-sulfur proteins as well as the metalloenzymes nitrite reductase and laccase were first in focus, now followed by single-molecule electron transport and enzyme ***function***. These efforts are presently being extended to DNA-based molecules. We shall overview some of these studies and note some observations, theoretical concepts, and some outstanding “puzzles”.

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