

Self-assembly of porphyrin molecules at electrified interfaces

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The self-assembly of organic molecules on solid surfaces is a promising strategy to obtain ultrathin films of designed functionality. In particular, porphyrins are a class of molecules with a wide range of potential applications. In this lecture we present a comparative study on the adsorption and self-assembly of Tetra(N-methyl-4-pyridyl)-porphyrin (TMPyP) and Tetra(4-trimethylammoniohenyl) molecules (TTMAPP) in cationic form from aqueous solution. The resultant structures on anion-modified (chloride, iodide) Cu(100), Cu(111), Au(100) and Au(111) single crystal electrode surfaces as well as structural transitions as a function of the electrochemical potential have been studied in situ, i.e. in solution, by cyclic voltametry (CV) and scanning tunneling microscopy (STM) as well as by ex situ X-ray photoelectron spectroscopy (XPS). In all cases the molecular cations spontaneously form well ordered monolayers, as exemplified in Fig.1, whose structure depends on the nature and symmetry of the metal substrate, the preadsorbed anion species as well as on the applied electrode potential. The resultant structures, imaged with submolecular resolution by in situ STM, are clearly correlated with the redox state of the molecules as indicated by CV and verified by XPS. As an example Fig.1 shows one of several possible phases of TTMAPP on an iodide modified Au(100) electrode surface.

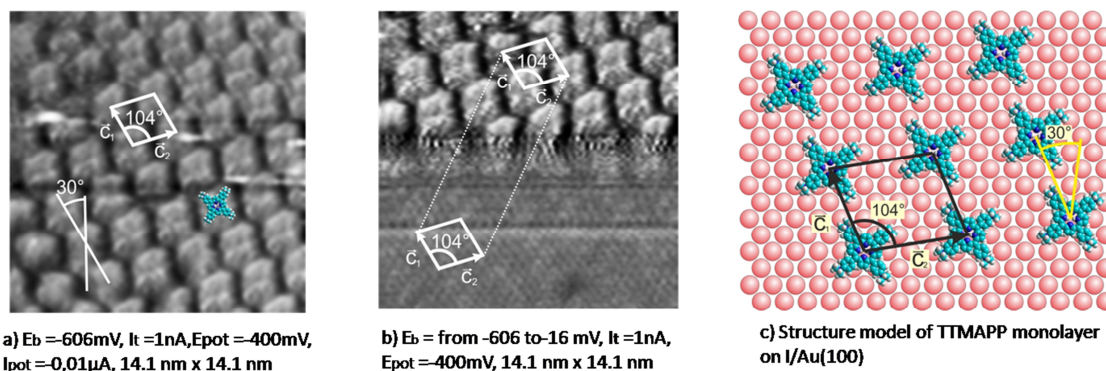


Fig. 1 Tetra(4-trimethylammoniohenyl) cations (TTMAPP) adsorbed on an iodide precovered Au(100) electrode; a) TTMAPP monolayer, b) partial tip-induced removal of the molecular overlayer enables structural correlation between the organic over- and the iodide underlayer, leading to the structure model given in c).