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Self-Assembled Monolayers from Symmetrical Di-Thiols: Preparation, Characterization and Application for the Assembly of Electrochemically Active Films [†]

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Abstract: 1,3-dimercaptopropan-2-ol, a symmetrical di-thiol, has been synthesized and applied as a new type of anchor molecule to prepare a self-assembled monolayer (SAM) on a gold surface. The formed monolayers were studied by cyclic voltammetry, impedance spectroscopy, X-ray photoelectron spectroscopy, kinetic capacitance, and contact angle measurements. The SAM structure depends on the adsorption conditions. A short incubation time of the electrode at high concentration of this di-thiol leads to the predominating binding through one thiol group of the adsorbate to the gold surface, while a long incubation at low concentration leads to the predominating binding by both thiol groups. A comparative study of the desorption and replacement of SAMs indicates a strong stability increase when the SAM molecules bond gold surfaces by two bonds mainly. This monolayer was used to immobilize electrochemically active p-benzoquinone moiety. The surface concentration of p-benzoquinone obtained from cyclic voltammetry is $2.5 \pm 0.2 \times 10^{-10}$ mol cm⁻², which corresponds to the functionalization of $65 \pm 5\%$ of SAM molecules. The obtained highly stable SAM with redox-active terminal group can be applied for different tasks of chemical sensing and biosensing. As an example, an application of this system for electrocatalytical oxidation of dihydronicotinamide adenosine dinucleotide (NADH) was tested.

Keywords: self-assembled monolayer; immobilization fashion; X-ray photoelectron spectroscopy; p-benzoquinone; electron transfer; cyclic voltammetry; NADH sensor

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