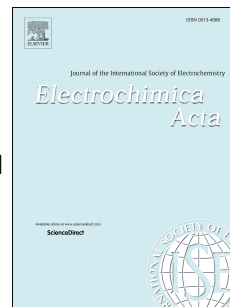


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Potential-induced phase transition of benzoxazole-2-thiol, naphthaleneoxazole-2-thiol and anthraceneoxazole-2-thiol monolayers on gold electrodes

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Title:**Potential-Induced Phase Transition of Benzoxazole-2-thiol, Naphthaleneoxazole-2-thiol and Anthraceneoxazole-2-thiol Monolayers on Gold Electrodes****Author names:**

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Abstract

In the present work we report the electrochemical characterization of self-assembled monolayers (SAMs) of N,O-heteroaromatic thiols, namely benzoxazole-2-thiol (**1**), naphthaleneoxazole-2-thiol (**2**) and anthraceneoxazole-2-thiol (**3**) on polycrystalline gold electrodes. SAMs were formed by immersion of pre-treated gold electrodes into ethanolic solutions of the title compounds. The modified electrodes exhibited a decrease of electroactivity, as found by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), in comparison to bare electrodes according to the length of the aromatic π -system. In addition, reductive desorption experiments confirmed that of the three compounds, **3** formed the most stable SAMs in agreement with EIS measurements which revealed better blocking properties against the redox couple in a test electrolyte indicating a charge transfer determined behaviour in the case of longer molecules. The charge transfer resistances revealed a trend towards higher resistances in the case of **3**. When performing EIS at various starting potentials and different electrolyte concentrations, it was found that at certain critical potentials (E_{crit}) a potential-induced structural change of the SAM occurred, with $E_{crit}(\mathbf{1}) > E_{crit}(\mathbf{2}) > E_{crit}(\mathbf{3})$. In the case of SAMs of **3** the nature of this alteration was investigated via scanning tunnelling microscopy and found to presumably be caused by an order-disorder-transition.

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