



Synthesis, electrochemical characterization of tetra- and octa-substituted dodecyl-mercapto tin phthalocyanines in solution and as self-assembled monolayers

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ABSTRACT

Non-peripherally (α) tetra- (**9**) and octa- (**7**) substituted dodecyl-mercapto tin(IV) phthalocyanines were synthesized and their electrochemical behavior studied. Cyclic voltammetry and spectroelectrochemistry show ring-based reductions for **7** and **9**, the former shows two ring oxidations, while the latter shows only one ring-based oxidation. The adsorption kinetics of (**7**) and (**9**) on gold electrode were investigated by electrochemical impedance spectroscopy (EIS). The equilibrium constant (K) for the adsorption and the Gibbs free energy (ΔG_{ads}) of the SAMs were evaluated based on the Frumkin isotherm.

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1. Introduction

Phthalocyanines continuously find their usefulness in contemporary and emerging technologies such as, catalysis [1], photodynamic therapy (PDT) [2], non-linear optics [3], the security printing industry [4] and solar cells [5]. For use in electrocatalysis, phthalocyanines are employed to modify electrodes [6]. Various methods have been used to fabricate chemically modified electrodes, these include drop dry method [7], spin coating [8,9], vapour deposition [9,10], Langmuir–Blodgett [9] and self-assembled monolayer (SAM) technique [9–16]. SAMs are formed spontaneously on immersing a solid substrate into a solution containing the desired species with an appropriate functional group, in this case alkylthio substituted MPc complexes. The orientation of SAMs on gold is affected by factors such as the number and nature of substituents on the phthalocyanine ring, and axial ligation. SAMs of alkylthio derivatised MPcs (M mainly Co, Mn, Fe, Ni and Zn) containing peripheral and non-peripheral substituents

are relatively well researched [9,12–17]. However, the kinetics of SAM formation by MPc complexes has not received much attention. SAMs of SnPcs are not known. The central metal, ring substituents and axial ligands may influence the nature of SAMs formed. MPcs containing long chain substituents were found to give better SAMs compared to for example benzyl mercapto substituted SAMs [14]. Thus in this work we explore the SAM formation of $\text{Cl}_2\text{Sn(IV)Pc}$ octa or tetra-substituted with long chains on the non-peripheral positions (Scheme 1).

Various techniques have been used to study kinetics of alkanethiols adsorbed onto Au from liquid solution, such as electrochemical methods [18], atomic force microscopy (AFM) [19], quartz crystal microbalance (QCM) [20], surface plasmon resonance (SPR) [21] and electrochemical impedance spectroscopy (EIS) [22]. In this work, voltammetric, AFM and EIS methods are employed to investigate the formation and kinetics of SAMs of complexes **7** and **9** on Au.

The electrochemistry of SnPc complexes is not well known. These complexes have two oxidation states on the central metal and hence have the ability to be involved in electrocatalytic reactions. Sn(IV) porphyrin complexes have shown redox activity only on the ring [23], whereas Sn(II) porphyrins showed metal-based oxidation [24] via a formation a short-lived Sn(III) porphyrin species.

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