

Full Paper

Self-Assembled Monolayers of Cobalt and Iron Phthalocyanine Complexes on Gold Electrodes: Comparative Surface Electrochemistry and Electrocatalytic Interaction with Thiols and Thiocyanate

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Abstract

The self-assembling of the octa(hydroxyethylthio)-metallophthalocyanine {MOHETPc (M = Co and Fe)} complexes and their similar analogues, octabutylthiometallophthalocyanine {MOBTPc (M = Co and Fe)} complexes on gold electrodes are investigated. Comparative surface voltammetric insights into their distinct self-assembling properties with respect to the passivation of Faradaic processes and surface coverages, including their solution electrochemistry, suggest different orientations and non-cleavage of their C–S bonds. In the pH 2–9 range, the reversible $[M^{(III)}Pc(-2)]^+ / [M^{(II)}Pc(-2)]$ redox couples show potential shifts close to $-59 \text{ mV} / \text{pH}$. The gold electrodes modified with the SAMs of these species show electrocatalytic activity towards the oxidation of thiols (L-cysteine, homocysteine and penicillamine) and thiocyanate in acidic media with detection limits in the region of 10^{-7} – $10^{-6} \text{ mol dm}^{-3}$. These monolayers are stable and easily reproducible.

Keywords: Voltammetry; Cobalt phthalocyanine, Iron phthalocyanine, Self-assembled monolayer, Thiols, Thiocyanate

1. Introduction

Metallophthalocyanine (MPc) complexes containing iron or cobalt metal centers are useful electrocatalysts [1–3]. Alkanethiol-substituted MPc complexes are of great importance because of the possibility of immobilizing them on gold electrodes as stable self-assembled monolayer (SAM) films for potential applications in electronic, photovoltaic and chemical sensing devices [4–6]. It has previously been established that octabutylthiometallophthalocyanine (MOBTPc) complexes of cobalt(II), CoOBTPc {Fig. 1 (1a)} [7, 8] and iron(II), FeOBTPc {Fig. 1 (2a)} [9] form stable, electroactive SAMs on gold electrodes. As part of our program in the search for novel thiol-derivatised MPc complexes and probing their electrocatalytic behavior as SAMs, the immobilization of octa(hydroxyethylthio)-phthalocyanine complexes of cobalt(II), CoOHETPc {Fig. 1 (1b)} and iron(II), FeOHETPc {Fig. 1 (2b)} on gold electrode by simple self-assembling technique is for the first time described. Voltammetry is the most convenient and sensitive technique for probing the structural properties of surface-confined species such as SAM on gold surface [10–13], and this technique is employed in this study to interrogate the integrity of the SAMs of complexes 1b and 2b on gold electrode in comparison with those of their similar analogues, 1a and 2a. This article provides an electrochemical insight into the orientations and structural properties of these complexes on spontaneous adsorption to gold

surface. It is known [14–16] that thioether-derivatised species (as in this study) form monolayers at gold surfaces with their C–S bonds intact. Indeed, it is easily observable from Figure 1 that there could be no SAM formation of the MPcs (1a, 1b, 2a or 2b) if the phthalocyanine ring-sulfur (Pc–S) bond cleavage occurs. It is also reasonable to assume that if their binding to gold involves the cleavage of the R groups, then their SAMs should show similar voltammetric behavior if subjected to similar experimental conditions.

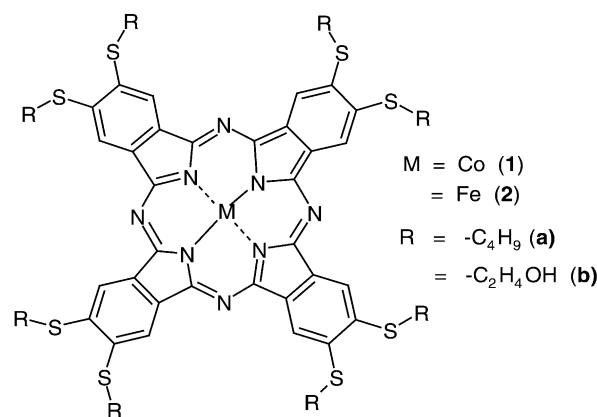


Fig. 1. Molecular structure of octathio-substituted metallophthalocyanine.