

# Comparative electrochemistry and electrocatalytic activities of cobalt, iron and manganese phthalocyanine complexes axially co-ordinated to mercaptopyrindine self-assembled monolayer at gold electrodes

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## Abstract

Comparative surface electrochemistry and electrocatalytic properties of solid ultrathin monolayer films of metallophthalocyanine (MPc) complexes of cobalt (CoPc), iron (FePc) and manganese (MnPc) self-immobilised, via axial ligation reaction, onto preformed 4-mercaptopyrindine self-assembled monolayers (SAMs) on gold electrodes have been described. Surface electrochemical parameters of the modified electrodes showed that these MPc-SAMs are densely packed with flat orientations. The electrochemical, electrocatalytic and stability properties of these MPc complexes follow this order: FePc > MnPc > CoPc. This finding is remarkable as it suggests that the success of using this method of self-assembling of MPc onto gold electrode is largely dependent on the bond distance between the pyridine linker and the central metal of the MPc; the shorter the distance, the faster the co-ordination and the better the electrocatalytic properties towards L-cysteine and thiocyanate. Thus, the superiority of FePc-based SAM over those of the MnPc and CoPc, has been proposed to be the result of the more favorable axial co-ordination properties of FePc with pyridine (i.e. shorter Fe–N(pyridine) bond length).

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## 1. Introduction

Metallophthalocyanine (MPc) complexes have attracted a lot of research interest because of their physico-chemical properties that could be harnessed for the fabrication of technologically important devices, such as electrochemical sensors, molecular electronics and photovoltaic devices [1,2]. These possible applications require the use of MPc complexes in their ultrathin solid films. The established strategies for obtaining ultrathin monolayer films of MPc complexes and related macrocycles on electrode surfaces include the Langmuir-Blodgett [3–7] spin-coating [7] and self-assembly [7–11]. The advantageous properties of the SAM technique, notably high order and stability [12–14], have led to the

growing interest in the fabrication of self-assembled MPc monolayers (MPc-SAMs) on gold. Transition metal (notably Fe, Co and Mn) phthalocyanine complexes are excellent electrocatalysts that are useful for the fabrication of MPc-SAM based electrochemical sensors.

Two major strategies for the fabrication MPc-SAMs are known. The first strategy involves the use of metallophthalocyanine complexes that are peripherally or non-peripherally substituted with sulfur-containing molecules. These thiol-derivatised MPc complexes can bond to the gold substrates via their thiol arm(s) [7–11]. The second and more recent strategy is by axial ligation of the MPc to a self-assembled monolayer of an N-donor molecule (such as 4-mercaptopyrindine) onto the gold surface [15,16]. A significant advantage of this second strategy is that it avoids the synthesis of thiol-derivatised MPc complexes. Mercatopyridine molecules adsorbed onto gold surfaces as SAM exhibit suitable molecular orientation for axial ligation with MPc

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