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# Characterization of manganese tetraarylthiosubstituted phthalocyanines self assembled monolayers

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ABSTRACT

Manganese tetraarylthiosubstituted phthalocyanines (complexes **1**–**5**) have been deposited on Au electrode surfaces through the self assembled monolayer (SAM) technique. SAM characteristics reported in this work are: ion barrier factor (~1); interfacial capacitance (303–539 $\mu F\,cm^{-2}$) and surface coverage ($1.06 \times 10^{-10}$–$2.80 \times 10^{-10}$ mol $cm^{-2}$). Atomic force microscopy was employed in characterizing a SAM. SAMs of complexes **1**–**5** were employed to detect L-cysteine (with limit of detection ranging from $2.83 \times 10^{-7}$ to $3.14 \times 10^{-7}$ M at potentials of 0.68–0.75 V *vs.* Ag|AgCl) and nitrite (limit of detection ranging from $1.78 \times 10^{-7}$ to $3.02 \times 10^{-7}$ M at potentials of 0.69–0.76 V *vs.* Ag|AgCl).



## 1. Introduction

Metallophthalocyanines (MPcs) are molecules that exhibit a series of electrochemical processes and may hence be used as versatile electron relays. Immobilization of metallophthalocyanines onto electrodes may create sensor interfaces that mediate electron transfer between the electrode and analyte resulting in possible sensor applications [1–3]. MPcs can be immobilized onto electrodes by the formation of self assembled monolayers (SAMs). SAMs of thiol derivatized MPcs form by self-organization on gold via their sulfur functionalities [4–7] resulting in versatile thin films. Alkyl or arylthio MPcs are known to form SAMs without cleavage of the aryl or alkyl group [7].

This work characterizes the SAMs of manganese phthalocyanine complexes (Fig. 1): **1** = 1,(4)-tetra-(2-mercaptopyridine) phthalocyaninato manganese (III); **2** = quaternized 1,(4)-tetra-(2-mercaptopyridine)phthalocyaninato manganese (III); **3** = 2,(3)-tetra-(2-mercaptopyridine)phthalocyaninato manganese (III); **4** = quaternized 2,(3)-tetra-(2-mercaptopyridine)phthalocyaninato manganese (III); **5** = 2,(3)-(tetraphenylthiophthalocyaninato) manganese (III). The synthesis of these complexes have recently been reported by our group [8,9].

Cysteine is vital in various biological processes [10] therefore its detection and analysis are of interest. Electrochemical detection of L-cysteine on unmodified electrodes has been limited by factors such as high overpotentials and low detection limits [11–13]. Modified electrodes, including those modified using SAMs, have been found to enhance the electrochemical oxidation of L-cysteine [14–16].

Nitrite is used in food industry. The detection of nitrite is important since excess nitrite is carcinogenic [17–20]. Even though nitrite detection on MPc modified electrodes is known [21,22], the challenge of lowering overpotentials remains. The Mn in MnPc complexes has variable oxidation states ($Mn^{II}$–$Mn^{IV}$) allowing for a wide range of analytes to be detected, hence the use of these complexes in this work.

## 2. Experimental

### 2.1. Materials

Complexes **1**–**5** have recently been reported by our group [8,9]. Acetone was provided by Protea Chemicals and distilled before

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