



Syntheses and electrochemical characterization of new water soluble octaarylthiosubstituted manganese phthalocyanines

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ABSTRACT

This paper reports on the synthesis and characterization of new manganese phthalocyanine (MnPc) complexes: 2,3-octakis-[(2-mercaptopyridine) phthalocyaninato] acetato manganese (III) (**1**) and its quaternized (hence water soluble) derivative, 2,3-octakis-[[*N*-methyl-2-mercaptopyridine) phthalocyaninato] acetato manganese (III)} sulphate (**2**). The complexes were used to form self assembled monolayers (SAMs). Voltammetry proved that both of the SAMs are well packed, strongly passivating and act as selective and efficient barriers to ion permeability. Furthermore, surface coverage studies confirmed that the MPC macrocycles adsorb onto the gold electrode as monolayers. Both MPC SAMs were successfully used as electrochemical sensors of nitrite.

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1. Introduction

Metallophthalocyanines (MPcs) are macrocyclic π -electron conjugated molecules which exhibit a series of electrochemical processes and can consequently be used as efficient electron mediators, for example, in electrocatalysis [1–6].

The presence of electron donating sulfur groups will result in the shift of the Q-band to longer wavelengths compared to unsubstituted MPc. Pc complexes containing Mn as a central metal, in particular, show a highly red-shifted Q-band [7]. The presence of sulfur will also make oxidation of these complexes favourable. Hence, in this work, we present the synthesis and electrochemistry of new sulphur substituted MnPc complexes (**1** and **2**, Scheme 1) and we compare their electrochemical behaviour with those of tetrasubstituted counterparts: manganese (III) 2,(3)-tetra-(2-mercaptopyridine) phthalocyanine (β -(OH)MnTMPyPc, **3 β**) and its quaternized derivative manganese (III) 2,(3)-tetra-*N*-methyl{(2-mercaptopyridine) phthalocyanine (β -(OH)Mn-Q-TMPyPc, **4 β**)}, Fig. 1. The syntheses and characterization of complexes **3** and **4** have been previously reported [8]. The water solubility of MnPc complexes is desirable despite the fact that the aggregation tendency in such a polar medium is very high. Hence, we present here the synthesis of a water soluble octa-substituted MnPc derivative (**2**).

MnPc complexes show interesting electrochemical behaviour with oxidation states of the central Mn ion ranging from Mn^I to Mn^{IV} [8–15]. The spectra of Mn^{II}Pc and Mn^{III}Pc complexes are now well known. For MnPc complexes tetra substituted with 2-mercaptopyridine at the peripheral positions (**3 β**) and then quaternized to give **4 β** , spectroelectrochemistry showed that the reduction of Mn^{II}Pc to Mn^IPc occurs only when the complex is in its quaternized form (**4 β**). The reduction (to Mn^IPc⁻²) of the quaternized form occurs at a lower potential than that of the unquaternized form (to Mn^{II}Pc⁻³), showing that metal (to Mn^IPc⁻²) versus ligand reduction (to Mn^{II}Pc⁻³) in Mn^{II}Pc complexes may depend on the nature of the ring substituents. This work explores the effect of increasing the number of substituents on the electrochemical behaviour of the mercaptopyridine substituted MnPc derivatives. Furthermore, arylthio derivatised MnPcs in this work are attached to gold electrodes to form self-assembled monolayers (SAMs). Alkyl or arylthio MPcs are known to form SAMs without cleavage of the aryl or alkyl group [16]. The SAMs are employed for the analyses of nitrite.

2. Experimental

2.1. Materials

Acetone was provided by Protea Chemicals and distilled before use. Dimethylformamide (DMF), methanol (MeOH), *n*-pentanol,

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