



## Full Length Article

# Electrocatalytic behaviour of surface confined pentanethio cobalt (II) binuclear phthalocyanines towards the oxidation of 4-chlorophenol



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## ABSTRACT

Cobalt binuclear phthalocyanine (CoBiPc) bearing pentanethio substituents at the peripheral positions were synthesized. The immobilization of the synthesized cobalt phthalocyanines on gold electrode was achieved using self-assembled monolayer method (SAM). X-ray photoelectron spectroscopy (XPS) and Kelvin Probe (KP) techniques were used to characterise the formation of monomeric and binuclear phthalocyanine SAMs on the gold surface. The phthalocyanine SAMs on gold electrodes were investigated for electrocatalytic oxidation of 4-chlorophenol. The electrocatalytic properties of tetra- and octa-pentanethio substituted cobalt binuclear phthalocyanine (CoBiPc) are compared with their tetra- and octa-pentanethio substituted phthalocyanine (CoPc). The SAMs modified gold electrode surfaces showed a peak current enhancement and stability and reduction in electrocatalytic potentials compared to the bare or unmodified electrodes towards the detection of the 4-chlorophenol. The SAMs of cobalt binuclear phthalocyanines exhibited more enhanced electrocatalytic properties in terms of stability, detection peak current and reduction of the electrocatalytic over potential.

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## 1. Introduction

Metallophthalocyanines (MPcs) have received considerable attention due to their application versatility which includes electrocatalysis [1], photodynamic therapy [2], non-linear optics [3] and solar cells [4]. MPcs require their immobilization onto electrode surfaces for their use as electrocatalysts [5]. MPcs bearing sulphur groups form closely packed self-assembled monolayers (SAMs) on gold electrodes [6–10]. The SAMs modified surfaces have proved useful in chemical sensing, bioelectric devices and surface protection properties from corrosion and wettability [11]. The orientation of SAMs on the surface is controlled by the axial ligand on the central metal and substituents on the Pc ring, respectively [12]. MPcs bearing long chain alkylthio substituents have proved to form stable SAMs compared to the aromatic thio substituents [13]. SAMs of cobalt phthalocyanines (CoPcs) with alkylthio on peripheral positions have been well researched [14]. This study reports the use of SAMs of cobalt binuclear phthalocyanine complexes bearing pentanethio substituents on the peripheral positions for electrocatalysis of 4-chlorophenol. According to our knowledge this will be for the first time that these interesting molecules are reported as

SAMs for 4-chlorophenol electrocatalysis. Cyclic voltammetry and X-ray photoelectron spectroscopy (XPS) methods have been used to investigate the SAMs formation, kinetics and electrocatalytic behaviour towards the oxidation of 4-chlorophenol.

Chlorophenols are class of aromatic organic compounds substituted with hydroxyl or alcohol and one or more chlorine functional groups. The number chlorine substituents and their positions in relation to the alcohol functional group yield highly toxic organic substances [15,16]. These environmental toxic compounds are produced as effluents by several industrial and agricultural companies thus leading to an accumulation and contamination in the ecosystem and the food chain, respectively [17–19]. The chlorophenols have been classified as toxic organic contaminants or pollutants [20,21]. Therefore, their detection, quantification and remediation is of paramount importance for complete elimination in the food chain and ecosystem. This study investigates their detection and quantification using metallophthalocyanines (MPcs) modified electrodes as electrocatalysts.

## 2. Experimental

### 2.1. Materials

Chloroform, Methanol, tetrahydrofuran (THF), hexane, sulfuric acid and *N,N'*-dimethylformamide (DMF) were obtained

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