

Electropolymerizable iron (III) and cobalt (II) dicyanophenoxy tetraphenylporphyrin complexes: Potential electrocatalysts

Kenneth I. Ozoemena*, Zhixin Zhao, Tebello Nyokong

Chemistry Department, Rhodes University, Grahamstown 6140, South Africa

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Abstract

Solution and solid phase electrochemical features of 5-[4-(3,4-dicyanophenoxy)phenyl],10,15,20-triphenylporphyrin complexes of iron(III) (FeCNOTPP(Cl)) and cobalt(II) (CoCNOTPP) have been described. These novel asymmetric dicyanophenoxy-derivatised cobalt and iron porphyrin complexes were electropolymerised onto glassy carbon electrodes, which in aqueous solutions, gave surface concentrations (ca. 10^{-10} mol cm⁻²) typical of monolayer coverages. The films also exhibited excellent stability and electrocatalysis towards the direct detection of important analytes as nitrite, nitric oxide, and hydrogen peroxide in aqueous solutions.

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Because of their utility as excellent biomimetic models for naturally occurring hemes, iron and cobalt porphyrin complexes have been widely used in electrochemical and electron transfer studies [1–11]. Several authors [5–7] have reported the potential applications of polymer films of metalloporphyrins (MPs) and their derivatives, especially on glassy carbon electrode (GCE), as new electrode materials for chemical and biological sensors. Iron and cobalt porphyrin based polymer films have intensely been reported because of their excellent electrocatalytic activities [5–11].

Electrochemical approach to film formation on electrodes is more preferable to such techniques as “dip-dry/drop-dry” methods, which are largely not reproducible and the thickness of the modifier on the electrode cannot be accurately controlled. The use of MP complexes bearing the cyano group (for example, the dicyanophenoxy or oxo-phthalonitrile, as reported in this paper) to form polymer films onto electrode surfaces is not known. In this work, we describe the first example of asymmetric dicyanophenoxy (or oxo-phthalonitrile) porphyrin complexes of iron

(III) and cobalt (II) (Fig. 1) electropolymerised onto GCE. Furthermore, we report a preliminary investigation on the feasibility of these novel film electrodes in interacting with important biomolecules, nitrite, nitric oxide, and hydrogen peroxide in aqueous solution.

The cobalt (II) 5-[4-(3,4-dicyanophenoxy)phenyl],10,15,20-triphenylporphyrin (herein abbreviated as CoCNOTPP) was synthesised as recently reported by our group [12] from 5-[4-(3,4-dicyanophenoxy)phenyl],10,15,20-triphenylporphyrin (H₂CNOTPP) ligand and cobalt acetate salt. Here, the iron (III) chloro-derivative (FeCNOTPP) was synthesised using a procedure similar to that for CoCNOTPP complex [12]. Briefly, a 100 mg (0.312 mmol) of H₂CNOTPP ligand, synthesised as before [12], was mixed with ferrous chloride tetrahydrate (FeCl₂ · 4 H₂O) (53 mg, 0.264 mmol) and dissolved in a mixture of dimethylformamide (DMF, 10 ml) and CH₂Cl₂ (10 ml) and refluxed for 6 h under a N₂ atmosphere with stirring in a 100-ml flask equipped with a condenser. After cooling to room temperature, the mixture was washed with 100 ml water three times to remove DMF. Column chromatography on silica gel with CH₂Cl₂ as eluent gave three bands. The first red band was the unreacted ligand (H₂CNOTPP). The second red band was the

* Corresponding author. Tel.: +27 46 603 8801; fax: +27 46 622 5109.
E-mail address: k.ozoemena@ru.ac.za (K.I. Ozoemena).