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Covalent attachment of cobalt (II) tetra-(3-carboxyphenoxy) phthalocyanine onto pre-grafted gold electrode for the determination of catecholamine neurotransmitters

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A B S T R A C T

The fabrication of electroactive thin films onto gold electrode surfaces yields very interesting surfaces with excellent electrocatalytic activity. Cobalt (II) tetra-(3-carboxyphenoxy) phthalocyanine (CoTCPhOPc) was successfully synthesized and fully characterized using FT-IR spectroscopy, ultraviolet-visible (UV–Vis) spectroscopy, magnetic circular dichroism (MCD) spectroscopy, elemental analysis, and mass spectrometry. The CoTCPhOPc was immobilized onto phenylethylamine (PEA) pre-grafted gold electrode surface, Au-PEA, using amide coupling reaction to obtain Au-PEA-CoTCPhOPc. This yielded pH sensitive thin films due to the terminal carboxylic acid groups. The Au-PEA-CoTCPhOPc electrode was shown to possess pH-selective properties towards negatively charged $[Fe(CN)_6]^{-3/-4}$ and positively charged $[Ru(NH_3)_6]^{2+/3+}$. Au-PEA-CoTCPhOPc electrode surface enabled the detection of catecholamines (dopamine, epinephrine, norepinephrine) and the screening off of ascorbic acid by means of pH functional groups. Excellent electrocatalytic oxidation with the limit of detection (LoD) determined using 3σ was found to be 1.32 (0.95), 3.08 and 2.11 (1.78) µM for electrooxidation and electroreduction (in brackets) of dopamine, epinephrine and norepinephrine; respectively. The limit of quantification (LoQ) was determined using 10σ and found to be 4.41 (3.12), 10.3 and 7.02 (5.93) µM electrooxidation and electroreduction (in brackets) for dopamine, epinephrine and norepinephrine; respectively. The Au-PEA-CoTCPhOPc thin monolayer film was shown to screen off ascorbic acid as no electrocatalytic oxidation was observed for up to 100 µM concentration.

1. Introduction

Various methods have been developed for the detection of biological molecules and electrochemical sensors show excellent advantages due to them being inexpensive, simple, sensitive and offer quick response time [1–3]. Additionally, they can be incorporated into robust, portable and miniaturized devices for targeted clinical and diagnostic applications [4]. Electrochemical sensor design involves modifying electrode surfaces with materials that impart specific and sensitive properties. Metallophthalocyanines (MPcs) are materials that can be immobilized onto conducting surfaces for the fabrication of electrochemical sensors [5,6]. Phthalocyanines are two-dimensional 18 π-electron aromatic porphyrin synthetic analogues consisting of four isoindole subunits linked together through nitrogen atoms. They can exist as metal free phthalocyanines [7,8] and metal containing phthalocyanines [8,9]. The incorporation of metal phthalocyanines in electrochemical sensors is due to their excellent electrocatalytic properties, driven by metal ions ability to gain (reduction) and loose (oxidation) electrons [2,9]. In addition, MPc complexes can be tailor-made for specific applications by changing the central metal ion and/or incorporating functional groups on the peripheral [10–12] and non-peripheral [13,14] positions of macrocycle ring. In this work, we investigated the synthesis of CoTCPhOPc and the covalent attachment onto pre-grafted gold surface with phenylethylamine (Au-PEA). The modified gold electrode surface yielded a pH sensitive thin monolayer films that can detect catecholamine neurotransmitters (dopamine, epinephrine and norepinephrine).

Within a biological system thousands of communications occur and these are done by neurotransmitters (chemical messengers) which pass messages from one neuron to the other or to cells [1]. Their analytical detection and monitoring is pivotal for the diagnosis of neural disorders [15,16]. Electrochemical sensors can be used for the detection of neurotransmitters [3,4,17–21]. However, electrochemical sensors suffers from a strong ascorbic acid

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