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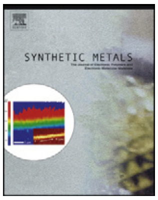

Electrochemical metal-ion sensors based on a novel manganese phthalocyanine complex

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ABSTRACT

In this paper, we investigated the electrochemical metal-ion sensor activity of a manganese phthalocyanine (MnPc). For this purpose, interactions of MnPc with various transition metal ions were examined in solution and in solid state. MnPc forms aggregates only with Ag^+ and Hg^{2+} ions selectively among various transition metal ions in solution, which indicates possible application of the complex as a metal sensor. For practical application, MnPc was immobilized in a polymeric cation exchange membrane, Nafion, on a glassy carbon electrode and used as an electrochemical receptor element. Sensor properties of MnPc were potentiometrically and amperometrically characterized as metal ion sensor with respect to reproducibility, repeatability, stability, linear concentration range, and sensitivity.

1. Introduction

Due to the potential impact of metal ions on human health and environment, sensitive methods of their detections are widely sought [1,2]. Laboratory techniques usually used for the determination of heavy metal ions, such as chromatography and mass-spectrometry, are rather cumbersome and expensive [3]. Electrochemical techniques provide an attractive means to analyze the content of a target sample due to the direct conversion of an event to an electronic signal [4]. Electrochemical determination of metal ions was usually performed by anodic stripping voltammetry (ASV) at mercury or solid electrodes [5]. Direct determination of metal ions by cyclic voltammetry (CV) using solid electrodes is limited because of a low signal-to-noise ratio. However, this limitation can be overcome by a modifying working electrode using some electrochemical recognition elements [5]. Tremendous recent attention has been concentrated to electrochemical molecular recognition in the sensor applications due to potential technological applications in the bioanalytical and environmental fields [6–10]. The aim of this field is the development of new receptors, capable to modify selectively their electrochemical responses upon interactions with the target species. For this purpose, enzymatic electrochemical is more suitable for rapid and simple measurements and for express analysis. The principle of determination of heavy metal ions is based on the inhibition effect of these toxic agents on the activity of certain enzymes. Many enzymes were examined on possibility of using for determination of heavy metal ions. Though good selectivity and high sensitivity can be obtained with enzymatic sensors, their inevitable drawbacks such as the chemical and thermal instabilities originated from the intrinsic nature of enzymes has turned recent efforts to defeat inefficient electron transfer of the enzymes and to direct the studies to the construction of enzyme-free electrodes. Redox mediators have found increasing attention aiming on the facilitate the electron-transfer mechanism between the active site of an enzyme and the electrode surface [11,12]. Use of mediators can cause interferences, since this configuration can facilitate the electron transfer of the parallel redox reaction in competition to the enzyme reaction [12]. Another major problem occurring with redox mediators is the leakage of the mediator from the surface of the electrode and hence the limited long-term stability of the electrodes [13]. Based on this context, there is considerable interest in the development of an electrochemical sensor without an enzyme and/or a redox mediator [14,15]. Following these considerations, considerable researches have been focused on transition metal complex-based catalysts as alternatives to enzyme sensors for high efficiency non-enzymatic and/or mediatorless electrocatalytic applications [14,15]. The aim of this field is the development of new molecular systems, capable to modify selectively their electrochemical responses upon interactions with the target species. These molecular systems should contain two components: (i) one electro-active group (antenna) behaves as mediator and (ii) binding sites specially designed for

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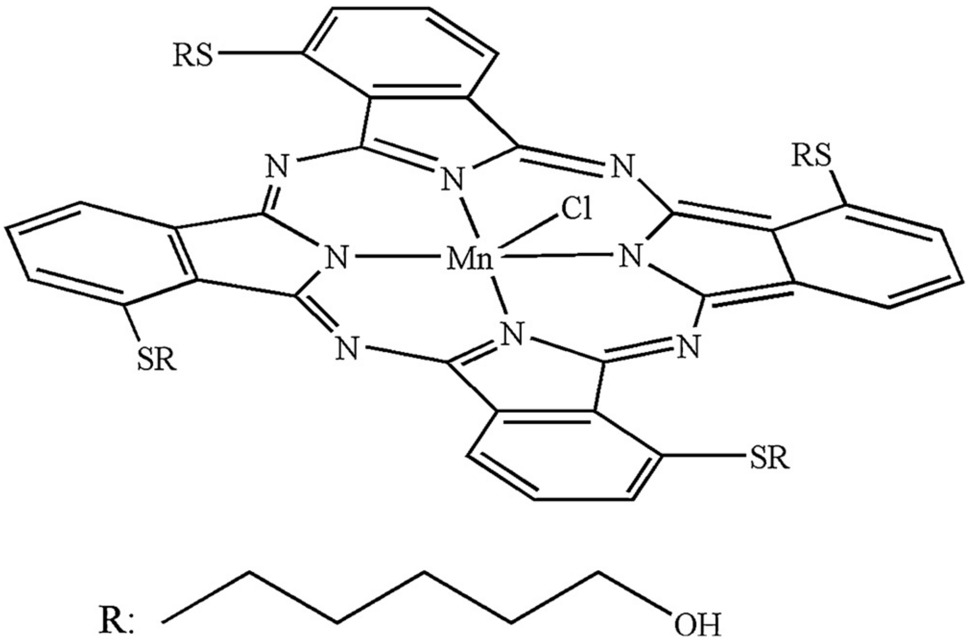

Fig. 1. Structure of α-substituted tetrakis(6-hydroxyhexylthiol)phthalocyaninato manganese (III) chloride (MnPc).

the specific guest, which is an artificial enzyme behaves as enzyme. Metallophthalocyanines (MPcs) are unique molecular materials carrying both binding sites like the enzymes and attractive functional antennas due to their excellent electrochemical properties, which can be adjusted by suitable metal center and substituents. It is known that the substituents of MPcs carrying O, N and S atoms behave as binding sites and form stable complexes with transition metal ions [16–23]. In our previous papers, we synthesized various MPcs and investigated the electrochemical, electrocatalytic, electrochromic, and metal sensing properties of these complexes [24–32]. In these papers, it has been demonstrated that substituent-functionalized MPcs were used as optical metal sensor in solution for heavy transition metal ions [30–32]. In our previous papers, MPc bearing crown ether substituents were investigated as an electrochemical metal sensor for the alkali metal ions in solution. In these papers, it was well documented that the reaction of alkali metal ions with the crown ether of the MPcs caused dimerization of the complex, which altered the electron transfer properties of the MPc complexes [33–35]. Thus in this work for the first time, we investigate the electrochemical sensor activities of the novel α-substituted tetrakis(6-hydroxyhexylthiol)phthalocyaninato manganese (III) chloride (MnPc, Fig. 1) in the solution and solid state for Ag^+ and Hg^{2+} ion sensing. MnPc was synthesized by our research group [36]. Electrochemical metal sensor activity of MnPc coated on a GCE was investigated with cyclic and square wave voltammetry and double potential step chronoamperometry techniques.

2. Experimental

2.1. Reagents and instrumentation

All chemicals were analytical reagent grade. 25% alcoholic solution of Nafion®, dimethyl sulfoxide (DMSO), tetrabuthylammoniumperchlorate (TBAP), $CuSO_4$, $Ni(CH_3COO)_2$, $Co(CH_3COO)_2$, $Pb(NO_3)_2$, $AgNO_3$, $Hg(NO_3)_2$, and $LiClO_4$ were bought from Sigma–Aldrich, Germany. MnPc (α-substituted tetrakis(6-hydroxyhexylthiol)phthalocyaninato manganese (III) chloride (Fig. 1)) was synthesized as reported earlier [36]. All sensor applications were performed in aqueous solution containing 0.10 mol dm^{-3} $LiClO_4$ as supporting electrolyte. Ultrapure water obtained from a Millipore water purification system (≥18 MΩ, Milli-Q, Millipore) was used in all runs.

The cyclic voltammetry (CV), square wave voltammetry (SWV) and double potential step chronoamperometry (DPSCA) measurements were carried out with Gamry Reference 600 potentiostat/galvanostat controlled by an external PC and utilizing a three-electrode configuration at 25 °C. The working electrode was bare and modified glassy carbon electrode with a surface area of 0.071 cm^2. A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. UV/vis absorption spectra were measured with an OceanOptics QE65000 diode array spectrophotometer.

2.2. Preparation of composite electrodes

Prior to modification, the GCE was polished on a polishing cloth with diamond slurry and rinsed thoroughly with ultra pure water, followed by sonicating in ethanol and ultra pure water successively. Then the electrode was allowed to dry at room temperature. Cast film technique was carried out for the preparation of composite electrodes as follows. First of all, MnPc was coated on a bare GCE and this electrode is abbreviated as GCE/MnPc. To prepare GCE/MnPc electrode, a 10.0 μl of 1.0×10^{-3} mol dm^{-3} MnPc dissolved in DMSO was cast on a bare GCE (effective area of 0.071 cm^2) by solvent evaporation under vacuum. Then MnPc was incorporated in Nafion on a bare GCE and this electrode is abbreviated as GCE/Nf/MnPc. To prepare GCE/Nf/MnPc electrode, firstly, a 10.0 μl of a mixture of 5.0 μl 5.0 wt.% alcoholic Nafion solution and 5.0 μl 1.0×10^{-3} mol dm^{-3} MnPc DMSO solution was cast on a GCE by solvent evaporation under vacuum. Then the modified electrode was dried at room temperature, washed with distilled water, and finally dried under vacuum and keep in 0.1 mol dm^{-3} $LiClO_4$ aqueous solution.

2.3. Sensor property of the composite electrodes

First of all, the experiments to find out the possible interaction of MnPc with transition metal ions, CV and SWV of MnPc in DMSO/TBAP electrolyte system was carried out without metal