



An optical sensor for mercury ion based on the fluorescence quenching of tetra(*p*-dimethylaminophenyl)porphyrin

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ABSTRACT

An optical sensor for mercury ion (Hg^{2+}), based on quenching the fluorescence of the sensing reagent porphyrin immobilized in plasticized poly(vinyl chloride) (PVC) membrane, has been developed. The responses to mercury ion were compared for the sensors modified with three porphyrin compounds including 5,10,15,20-tetraphenylporphyrin (TPP), tetra(*p*-dimethylaminophenyl)porphyrin (TDMAPP) and tetra(*N*-phenylpyrazole) porphyrin (TPPP). Among them, TDMAPP showed the most remarkable response to Hg^{2+} . The drastic decrease of the TDMAPP fluorescence intensity was attributed to the formation of a complex between TDMAPP and Hg^{2+} , which has been utilized as the fabrication basis of a Hg^{2+} -sensitive fluorescence sensor. The analytical performance characteristics of the TDMAPP modified sensor was investigated. The response mechanism, especially involving the response difference of three porphyrin compounds, was discussed in detail. The sensor can be applied to the quantification of Hg^{2+} with a linear range covering from $4.0 \times 10^{-8} \text{ mol L}^{-1}$ to $4.0 \times 10^{-6} \text{ mol L}^{-1}$. The limit of detection was $8.0 \times 10^{-9} \text{ mol L}^{-1}$. The sensor exhibited excellent reproducibility, reversibility and selectivity. Also, the TDMAPP-based sensor was successfully used for the determination of Hg^{2+} in environmental water samples.

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1. Introduction

Chemical sensor technology can provide low-cost devices that can be tuned to a wide field of application by coating mass-sensitive or optical transducers with a chemically sensitive layer [1]. The detection of molecular species by fluorescent sensing is of current interest [2]. Optical sensor based on fluorescent probe can be designed according to two guiding principles: (i) the absorption and emission features of the fluorophore are directly affected by the close interaction with the analyte, and/or (ii) the transformation of the photophysical properties resulted from the conformational changes of the sensor that are susceptible to the interaction with the analyte. In fact, much research work has been performed to develop fluorescent sensors for the detection of transition and heavy metal ions [3–6], which offer distinct advantages in terms of sensitivity, selectivity and response time. Also, the theoretical basis of such optical membranes based on plasticized PVC has been well established [7–9]. The porphyrins are a class of naturally occurring macrocyclic compounds, which play a very important role in the metabolism of living organisms. They have been extensively studied due to their biological importance as well as analytical applications

[10]. Particular attention has been given to porphyrins as highly sensitive chromogenic reagents for spectrophotometric determination of several metal ions [11].

Heavy metals, one of the most hazardous classes of pollutants in water sources due to their nonbiodegradability, have caused widespread water endangerment, contamination of fish, and serious health problems [12]. Mercury is one of the most well known toxic metals. Its toxicity is attributed to its harmful effects on the central nervous system disturbing haemin synthesis as well as causing neuropsychiatric disorders [13]. The cases in Minamata Bay in Japan in 1953 [14] were particularly disastrous. Mercury is usually present at low concentrations in environmental samples as inorganic, free or complexed with inorganic and organic ligands or as organomercury compounds. Therefore, determination of trace amounts of mercury in environmental samples is of great interest due to increasing public concern about environmental pollution and their high toxicity and accumulative and persistent character in the environment and living organisms. In recent years, several fluorescent sensors have been developed for the determination of Hg^{2+} [15–17]. Shamsipur et al. [18] have prepared a Hg^{2+} fluorescence sensor by incorporating 1-(dansylamidopropyl)-1-aza-4,10-dithia-7-oxacyclododecane as a neutral Hg^{2+} -selective fluoroionophore in the plasticized PVC membrane containing potassium tetrakis(*p*-chlorophenyl) borate as a lipophilic anionic additive. At a pH 3.3, the proposed sensor displayed a calibration curve over a wide

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concentration range of 1.0×10^{-4} – 5.0×10^{-12} mol L $^{-1}$. He et al. [19] have developed a fluorescent sensor for Hg $^{2+}$ using 5,10,15-tris(pentafluorophenyl)corrole as fluorophore. The sensor showed a linear response towards Hg $^{2+}$ in the concentration range from 1.2×10^{-7} mol L $^{-1}$ to 1.0×10^{-4} mol L $^{-1}$. In a word, the response mechanisms of Hg $^{2+}$ fluorescent sensors reported were all based on the strong fluorescence quenching of fluorescent material by Hg $^{2+}$ ion. Moreover, these works all involved a very complex synthesis of fluorescent materials. As far as we know, some other analytical methods have been developed for the determination of mercury, such as electrochemical method [20–26], atomic absorption spectrometry [27–30] or cold-vapour inductively coupled plasma atomic emission [31], chromatographic determination [32–34], inductively coupled plasma-mass spectrometric analysis [35,36] or electrospray ionization mass spectrometry [37], room temperature phosphorimetry [38]. Although these methods are accurate, most require a tedious sample pre-treatment, sophisticated performance and/or expensive equipment. Therefore, a simple, fast, selective and sensitive analytical method is needed to determine mercury.

In this paper, we tried to synthesize three lipophilic porphyrin compounds, 5,10,15,20-tetraphenylporphyrin (TPP), tetra(*p*-dimethylaminophenyl)porphyrin (TDMAPP) and tetra(*N*-phenylpyrazole) porphyrin (TPPP) and respectively used them as sensing reagents in a hydrophobic membrane of PVC matrix. As a macrocyclic compound, porphyrin exhibits strong fluorescence in visible region owing to the conjugated double bond system and the high mobility of its π -electron. After being immobilized in a plasticized PVC membrane, porphyrin can selectively extract Hg $^{2+}$ from aqueous sample solution into organic membrane phase and form a metalloporphyrin compound, which results in a decrease of porphyrin fluorescence. This has been utilized as the preparation basis of Hg $^{2+}$ -sensitive fluorescent sensor. The recognition abilities for mercury ion of three porphyrin compounds were compared. The recognition difference of three porphyrin compounds was discussed in detail. TDMAPP showed preferable analytical performance characteristics for Hg $^{2+}$ as compared to the two other porphyrin compounds. The analytical performance characteristics of the TDMAPP modified sensor was investigated. This sensor can be used for the determination of Hg $^{2+}$ with a linear range covering from 4.0×10^{-8} mol L $^{-1}$ to 4.0×10^{-6} mol L $^{-1}$ with a detection limit of 8.0×10^{-9} mol L $^{-1}$. It showed excellent reproducibility, reversibility and selectivity. Also, the response mechanism of the sensing membrane was discussed.

2. Experimental

2.1. Reagents

High molecular weight poly(vinyl chloride) (PVC) (MW ~300,000), di-iso-octyl sebacate (DOS), tetrahydrofuran (THF) and mercuric nitrate (Hg(NO $_3$) $_2$ ·H $_2$ O) were purchased from Shanghai Chemical Reagents (Shanghai, China). Three porphyrin compounds (Fig. 1), TPP [39], TDMAPP [40], TPPP [41] were synthesized according to the corresponding references and these products were verified by IR, MS, NMR and element analysis. All reagents were of analytical reagent grade. Doubly distilled water was used throughout.

2.2. Apparatus

All fluorescence measurements were performed with a Hitachi F-4500 fluorescence spectrometer. Excitation and emission slits were set at 5.0 nm and 10.0 nm respectively. All experiments were carried out at 20 °C. A homemade flow cell was used for the Hg $^{2+}$ -sensing measurements.

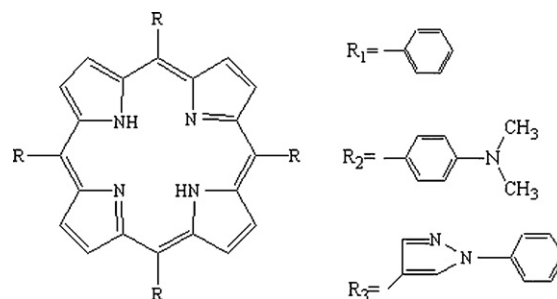


Fig. 1. The chemical structure of three porphyrin compounds: 1, TPP: R=R $_1$; 2, TDMAPP: R=R $_2$; 3, TPPP: R=R $_3$.

2.3. Membrane fabrication

A circular 35 mm diameter quartz slide was first treated in dichlorodimethylsilane (10% solution in toluene) overnight at room temperature to make the surface hydrophobic and was washed sequentially with toluene, acetone and distilled water. Then, the quartz slide was fixed on the end of an aluminum alloy rod and then rotated at a frequency of 600 rpm. The sensing membrane solution was prepared by dissolving a mixture of 80 mg of PVC, 160 mg of DOS in 2.0 mL 5.0×10^{-5} mol L $^{-1}$ TDMAPP (or TPP or TPPP) THF solution. With a syringe, 0.2 mL of the membrane solution was injected on the center of the quartz slide. After spinning for 5.0 s, a membrane of approximately 4.0 μ m thickness was then coated onto the quartz slide and dried in ambient air for 30 min prior to use [42].

2.4. Measurement procedure

The prepared PVC membrane was installed in a homemade flow cell with about 3.4 mL volume capacity. The cell was mounted into the fluorescence spectrometer in a fixed position to ensure the detection of fluorescence emission intensity without interference from the excitation light source [43]. The fluorescence intensity was measured at the maximal excitation wavelength of 438 nm and the maximal emission wavelength of 673 nm. The Hg $^{2+}$ solution was introduced into the flow cell by a peristaltic pump. After each measurement, the membrane was washed with 0.1 mol L $^{-1}$ HCl solution and then with the buffer solution until its fluorescence intensity reached the original blank value.

A standard stock solution of 2.0×10^{-5} mol L $^{-1}$ Hg $^{2+}$ was prepared. The working solutions were obtained by serial dilutions of this stock solution with 0.01 mol L $^{-1}$ phosphate buffer solution (pH 8.0).

3. Results and discussion

3.1. The fluorescence spectra of three porphyrin compounds and their responses to Hg $^{2+}$

The fluorescence spectra of three porphyrin compounds, as well as their responses to Hg $^{2+}$, are shown in Fig. 2. Owing to the conjugated double bond system and the high mobility of their π -electrons, three porphyrin compounds all exhibited strong fluorescence emission. Noticeable decreases of fluorescence intensities were observed in the presence of Hg $^{2+}$. It was noticed that the fluorescence intensity of TDMAPP was much stronger than those of TPP and TPPP. It seemed that the fluorescence quenching degree of TDMAPP was more remarkable than that of the two other porphyrin compounds. This can be explained by the fact that in comparison with TPP, the electron cloud density in porphyrin ring center of TDMAPP increased due to the introduction of electron-donating dimethylamino group into the phenyl group of TPP, which resulted

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