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

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ARTICLE INFO

Article history:

Received 24 November 2008

Received in revised form 14 January 2009

Accepted 16 January 2009

Available online 23 January 2009

Keywords:

Optical sensor

Porphyrin

Mercury ion

Fluorescence

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

Fig. 2. The fluorescence spectra of three porphyrin compounds and their Hg^{2+} complexes. a and a', b and b', c and c', respectively represent the fluorescence spectra of TDMAPP, TPP, TPPP in the absence and presence of Hg^{2+} . The concentration of Hg^{2+} was $4.0 \times 10^{-7} \text{ mol L}^{-1}$.

in the enhancement of complexation ability of TDMAPP with Hg^{2+} . While for TPPP, an electron-donating pyrazole group, was introduced in the position between phenyl group and porphyrin ring. The electron cloud density in pyrazole group was also distributed to the phenyl group except for porphyrin ring center of TPPP, which resulted in the thinner electron cloud density of porphyrin ring center of TPPP as compared to that of TDMAPP. So, the complexation ability with Hg^{2+} of TPPP was weaker than that of TDMAPP. As for TPP, the electron cloud density of porphyrin ring center was relatively the thinnest owing to the electron deficiency of coupled phenyl group. Accordingly, the complexation ability of TPP with Hg^{2+} was the weakest among the three porphyrin compounds.

For the fabrication of a sensor, sensitivity is the most important parameter. From the view of sensor sensitivity, the sensing membrane containing TDMAPP was chosen as an optimal optical sensor.

3.2. Effect of pH value

The effect of pH value on the fluorescence intensity of TDMAPP sensing membrane was examined (Fig. 3). The blank fluorescence intensity of the sensing membrane itself was found to be dependent

Fig. 3. The effect of pH value on the fluorescence intensity of sensing membrane.

Fig. 4. The fluorescence emission spectra of the sensing membrane exposed to the solution containing different concentrations of Hg^{2+} : 1, 0; 2, $4.0 \times 10^{-8} \text{ mol L}^{-1}$; 3, $6.0 \times 10^{-8} \text{ mol L}^{-1}$; 4, $8.0 \times 10^{-8} \text{ mol L}^{-1}$; 5, $1.0 \times 10^{-7} \text{ mol L}^{-1}$; 6, $2.0 \times 10^{-7} \text{ mol L}^{-1}$; 7, $4.0 \times 10^{-7} \text{ mol L}^{-1}$; 8, $6.0 \times 10^{-7} \text{ mol L}^{-1}$; 9, $8.0 \times 10^{-7} \text{ mol L}^{-1}$; 10, $1.0 \times 10^{-6} \text{ mol L}^{-1}$; 11, $2.0 \times 10^{-6} \text{ mol L}^{-1}$; 12, $4.0 \times 10^{-6} \text{ mol L}^{-1}$.

on the acidity of the soaking solution due to the existing of nitrogen atoms in TDMAPP molecule. It was found that the fluorescence intensity of sensing membrane enhanced with the increase of pH value till pH 8.0. No drastic changes of the fluorescence intensities were observed between 8.0 and 12.0. At high acidity, H^+ might be extracted into membrane phase and then complexed with the nitrogen atoms forming the protonated complex. Thus, the π -electron conjugated double bond system of TDMAPP would be destroyed, which resulted in the decrease of TDMAPP fluorescence intensity. In addition, at acidic condition, the coordination interaction between the protonated porphyrin and metal cation was very weak, and hence the fluorescence quenching efficiency would of course also decrease. Therefore, pH 8.0 phosphate buffer solution (0.01 mol L^{-1}) was selected as optimal experimental condition.

3.3. Response to Hg^{2+} of sensing membrane

Fig. 4 shows the fluorescence emission spectra of the TDMAPP sensing membrane exposed to the solutions containing different concentrations of Hg^{2+} . Noticeable decrease of fluorescence emission intensity appeared in the presence of Hg^{2+} , which was attributed to the formation of a complex between TDMAPP and Hg^{2+} . Also, the fluorescence intensities of sensing membrane were gradually decreased with increasing Hg^{2+} concentrations, which has been utilized as the quantitative basis of the Hg^{2+} sensor.

3.4. Theoretical principle of sensing membrane determination

Suppose a complexation equilibrium between Hg^{2+} in the aqueous solution (aq) and TDMAPP in the plasticized PVC membrane phase (org) is established with formation of a complex with a complexing ratio of $m:n$, the overall equilibrium can be represented as follows [7–9]:

i.e.

Table 1The information of other published methods for the determination of Hg^{2+} .

Analytical methods	Linear range (mol L^{-1})	The limit of detection (mol L^{-1})
Electrochemical method	2.0×10^{-6} – 1.0×10^{-5}	4.0×10^{-7}
Atomic absorption or emission spectrometry	2.5×10^{-8} – 5.0×10^{-6}	2.0×10^{-8}
Chromatography	–	2.5×10^{-10}
Mass spectrometry	–	3.5×10^{-12}
Fluorimetry	5.0×10^{-12} – 1.0×10^{-4}	8.0×10^{-13}
Room temperature phosphorimetry	2.0×10^{-8} – 2.0×10^{-7}	2.3×10^{-9}

where A represents Hg^{2+} and B denotes TDMAPP. When the difference between the activity and concentration is neglected for simplification, the corresponding equilibrium constant K can be expressed by the law of mass action:

$$K = k_d \beta = \frac{[A_m B_n]_{(\text{org})}}{[A]^m_{(\text{aq})} [B]^n_{(\text{org})}} \quad (4)$$

where k_d is the distribution coefficient of Hg^{2+} between the organic and aqueous phases, β is complex formation constant respectively, and $[A_m B_n]$, $[A]$, $[B]$ are the concentrations of respective species.

When the concentrations of Hg^{2+} and TDMAPP in membrane are low, the observed fluorescence intensity of the membrane is a sum of several contributions.

$$F_0 = K_B C_{B(\text{org})} \quad (5)$$

$$F = K_A [A]_{(\text{org})} + K_B [B]_{(\text{org})} + K_{A_m B_n} [A_m B_n]_{(\text{org})} \quad (6)$$

where F_0 is the fluorescence intensity of the sensing membrane when applied to blank solution, F is the fluorescence intensity of the sensing membrane when applied to Hg^{2+} solution, $C_{B(\text{org})}$ is the total concentration of TDMAPP in the membrane, and the K_i values represent the individual proportion constants and include instrumental parameters as well as the quantum efficiency of the complex species.

To indicate the degree of association between TDMAPP and Hg^{2+} in the sensing membrane, a response parameter, α , needs to be introduced and defined as follows:

$$\alpha = \frac{C_{B(\text{org})} - [B]_{(\text{org})}}{C_{B(\text{org})}} = \frac{n[A_m B_n]_{(\text{org})}}{C_{B(\text{org})}} \quad (7)$$

It can be derived from Eq. (5) to Eq. (7) that:

$$\alpha = \frac{F - F_0}{F_1 - F_0} \quad (8)$$

where F_1 is the fluorescence intensity at membrane saturation.

Combining Eq. (4) and Eq. (7), one can obtain the following quantitative equation:

$$\frac{\alpha^n}{1 - \alpha} = \frac{1}{n K C_B^{n-1} [A]^m} \quad (9)$$

The relationship between α and $[A]$ as expressed by Eq. (9) is the basis of the quantitative determination of Hg^{2+} using this sensing membrane.

3.5. Response characteristics of the optical sensor

The reproducibility and reversibility of the optical sensor in the determination of Hg^{2+} were evaluated by repetitively exposing the sensing membrane to Hg^{2+} solution of different concentrations, 0.1 mol L^{-1} HCl solution and phosphate buffer solution (pH 8.0). The standard deviations of different sample solutions for three determinations were found to be 4.24 ($6.0 \times 10^{-8} \text{ mol L}^{-1}$), 3.78 ($4.0 \times 10^{-7} \text{ mol L}^{-1}$), and 4.02 ($2.0 \times 10^{-6} \text{ mol L}^{-1}$). The standard deviation of blank solution was 3.63 for 12 determinations. The optical sensor was regenerated with 0.1 mol L^{-1} HCl solution. The

Hg^{2+} complexed with TDMAPP could be eluted out of the sensing membrane quickly and completely, which demonstrated the excellent reproducibility and reversibility of the sensor.

For the sensing membrane in contact with a $6.0 \times 10^{-7} \text{ mol L}^{-1}$ Hg^{2+} solution, the fluorescence intensity at 673 nm was recorded over a period of 8 h. The fluorescence intensity was recorded with a 30 min interval, a standard deviation of 4.65 was obtained. After a series of 100 times measurements of Hg^{2+} solution, the fluorescence intensity value of the sensor did not change.

From Eq. (9), it can be seen that when the stoichiometric ratio of complex changes, the relative fluorescence intensity value α with the various concentration of Hg^{2+} exhibits different functional relationships. According to Eq. (9), the experimental data were fitted by altering the ratio of m to n and the equilibrium constant K . Fig. 5 shows the fitted curve for the determination of Hg^{2+} . The curve of the 1:1 complex ratio and $K = 2.5 \times 10^6 \text{ L mol}^{-1}$ was in agreement with the experimental data, which can serve as the calibration curve. A linear range for Hg^{2+} covered from $4.0 \times 10^{-8} \text{ mol L}^{-1}$ to $4.0 \times 10^{-6} \text{ mol L}^{-1}$. The limit of detection, defined according to 3σ concept, was $8.0 \times 10^{-9} \text{ mol L}^{-1}$. As a comparison, Table 1 gave the information of other published methods for the determination of Hg^{2+} .

3.6. Selectivity

Some common ions including alkali, alkaline earth and heavy metal ions were chosen for the study on selectivity of the Hg^{2+} sensor. A foreign species was considered not to interfere with measurement if a relative error caused by it was less than 5% in the determination of $2.0 \times 10^{-7} \text{ mol L}^{-1}$ Hg^{2+} . The results presented in

Fig. 5. Relative fluorescence intensity α as a function of $\log[\text{Hg}^{2+}]$. The curve fitting the experimental data were calculated from Eq. (9). 1, $m:n=3:1$ and $K=1.0 \times 10^{19}$; 2, $m:n=2:1$ and $K=5.0 \times 10^{12}$; 3, $m:n=1:1$ and $K=2.5 \times 10^6$; 4, $m:n=1:2$ and $K=2.5 \times 10^9$; 5, $m:n=1:3$ and $K=3.0 \times 10^{12}$.

Table 2Interference of different species to the fluorescent determination of Hg^{2+} with the prepared sensor.

Interferent	Concentration ^a (mol L^{-1})	Fluorescence intensity ($\Delta F = F_i - F_{i0}$) ^b	Relative error (%) ($(\Delta F/F_{i0}) \times 100$)
Na^+	1.0×10^{-1}	−2.1	−1.6
K^+	1.0×10^{-1}	−2.6	−1.9
Ca^{2+}	1.0×10^{-1}	2.3	1.7
Mg^{2+}	1.0×10^{-1}	−3.0	−2.2
Ba^{2+}	1.0×10^{-1}	2.8	2.1
Al^{3+}	1.0×10^{-1}	2.4	1.8
Zn^{2+}	1.0×10^{-5}	−3.4	−2.5
Fe^{2+}	1.0×10^{-5}	−3.5	−2.6
Fe^{3+}	1.0×10^{-5}	−3.2	−2.4
Ag^+	1.0×10^{-5}	4.3	3.2
Cd^{2+}	1.0×10^{-5}	−3.9	−2.9
Co^{2+}	1.0×10^{-5}	3.7	2.7
Ni^{2+}	1.0×10^{-5}	2.5	1.9
Pb^{2+}	1.0×10^{-5}	3.8	2.8
Cu^{2+}	1.0×10^{-5}	−4.1	−3.0

^a The concentration of Hg^{2+} was fixed at $2.0 \times 10^{-7} \text{ mol L}^{-1}$ (pH 8.0).^b F_i and F_{i0} are the fluorescence intensities of the sensing membrane contacting with $2.0 \times 10^{-7} \text{ mol L}^{-1} \text{ Hg}^{2+}$ solution with and without the addition of the interferent.**Table 3**Determination of Hg^{2+} in different water samples.

Sample	Hg^{2+} spiked (mol L^{-1})	Hg^{2+} founded (mol L^{-1}) (mean ^a ± S.D. ^b)	Recovery (%)
Xiang river			
1	6.0×10^{-8}	$(6.31 \pm 0.43) \times 10^{-8}$	105.2
2	4.0×10^{-7}	$(3.74 \pm 0.25) \times 10^{-7}$	93.5
3	2.0×10^{-6}	$(1.92 \pm 0.32) \times 10^{-6}$	96.0
Tap water			
1	8.0×10^{-8}	$(7.79 \pm 0.29) \times 10^{-8}$	97.4
2	4.0×10^{-7}	$(4.11 \pm 0.34) \times 10^{-7}$	102.8
3	1.0×10^{-6}	$(0.95 \pm 0.21) \times 10^{-6}$	95.1
Waste water			
1	5.0×10^{-8}	$(5.47 \pm 0.48) \times 10^{-8}$	109.4
2	4.0×10^{-7}	$(4.30 \pm 0.46) \times 10^{-7}$	107.5
3	3.0×10^{-6}	$(2.78 \pm 0.37) \times 10^{-6}$	92.7

^a Mean of three determinations.^b Standard deviation.

Table 2 revealed that most of the species tested caused no interference when existed in specified molar excesses.

3.7. The response mechanism of the sensing membrane

The sensing membrane described here belongs to the class of ionic-exchange system described previously [43]. The extraction of Hg^{2+} from the aqueous sample solution into membrane phase and its complexation by the lipophilic fluorescence indicator TDMAPP proceeded with the loss of two protons from the nitrogen atoms. This ionic-exchange process was determined by the electroneutrality in the organic membrane phase. TDMAPP immobilized in the PVC membrane acted not only as a selective host molecule for Hg^{2+} , but also as a fluorescence transducer. The sensing mechanism involved the extraction of Hg^{2+} from aqueous sample solution to organic membrane phase and the formation of a metalloporphyrin complex between TDMAPP and Hg^{2+} , which resulted in the fluorescence quenching of TDMAPP.

3.8. Preliminary analytical application

Recovery of spiked Hg^{2+} in different water samples was studied with the prepared optical sensor. Different water samples were simply filtered and the results showed that no Hg^{2+} existed. Thus, different concentrations of Hg^{2+} were respectively spiked in filtered water samples and then analyzed with the optical sensor. Results are shown in Table 3. One can see that the recovery study of spiked Hg^{2+} determined by the TDMAPP-based optical sensor exhibited satisfactory results.

4. Conclusions

Three porphyrin compounds were synthesized. Their fluorescence spectra and their response characteristics to Hg^{2+} were investigated. Among them, TDMAPP showed preferable fluorescence response to Hg^{2+} . Thereby, a sensitive, fast and simple optical sensor for the determination of Hg^{2+} has been developed based on the fluorescence quenching of TDMAPP. The quenching of TDMAPP fluorescence was fast and the degree of the quenching was proportional to Hg^{2+} concentration. The sensing membrane containing TDMAPP reversibly responded to Hg^{2+} and showed extremely high selectivity to Hg^{2+} in the presence of some alkali, alkaline earth and heavy metal ions. The limit of detection for Hg^{2+} was $8.0 \times 10^{-9} \text{ mol L}^{-1}$. This sensor has been used for the determination of Hg^{2+} in different water samples with satisfactory recovery.

Acknowledgements

This work was supported by “973” National Basic Research Program of China (No. 2007CB310500) and NSF (20775023, 20675028, 20775023) of China.

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