An Optical Fiber Chemical Sensor for Mercury Ions Based on a Porphyrin Dimer

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The synthesis of a novel fluoroionophore, 5-p-[(4-(10′,15′,20′-triphenyl-5′-porphinato) phenyloxyl]-1-butyloxyl]-phenyl-10,15,20-triphenylporphine (DTPP), and its application for preparation of a Hg(II)-sensitive optical fiber chemical sensor are described. The response of the sensor is based on the fluorescence quenching of DTPP by coordination with Hg(II). The porphyrin dimer-based sensor shows a linear response toward Hg(II) in the concentration range 5.2 \times 10^{-7} - 3.1 \times 10^{-4} \text{ mol L}^{-1}, with a working pH range from 2.4 to 8.0. The sensor shows excellent selectivity for Hg(II) over transition metal cations such as Cd(II), Co(II), Cu(II), Ni(II), Pb(II), Zn(II), and Fe(III). As a sensing agent, the porphyrin dimer shows obviously better fluorescence response characteristics toward Hg(II) compared to porphyrin monomer or metalloporphyrin. The effect of the composition of the sensor membrane was studied, and the experimental conditions were optimized. The sensor has been used for determination of Hg(II) in water samples.

Owing to the growing awareness of the toxicity of mercury even in low concentrations, searching for effective analytical methods in general, and optochemical sensors in particular, for a mercury assay has been the subject of current analytical research. Optochemical sensors can offer advantages in terms of size, cost, not requiring a reference element, and the fact that the analytical signal is free of the influence of an electromagnetic field and easy to transmit over a long distance. This type of mercury sensor according to reports so far, unfortunately, usually has interference problems caused by other heavy metal cations. To improve the analytical selectivity, it is essential to search carrier compounds that would react with mercury with sufficient high selectivity. Examples of recent advances along this line have been the synthesis of some new Hg(II) carriers including a boron dipyrromethene-type dye and macrocyclic ligand with 8-hydroxyquinoline moieties. Plaschke et al. reported a fluorometric method for Hg(II) assay with tetra(p-sulfonatophenyl)porphyrin and a sol-gel film optochemical sensor based on this compound, though the response characteristics of the sensor were not described in detail. The sulfonated sensing agent is a water-soluble porphyrin which might shorten the lifetime of the sensor. Inspired by the success of the work of Plaschke et al., we tried to synthesize a lipophilic porphyrin dimer, 5-p-[(4-(10′,15′,20′-triphenyl-5′-porphinato) phenyloxyl]-1-butyloxyl]-phenyl-10,15,20-triphenylporphine (DTPP) as a potential fluorionophore for mercury. This has really been an extension of the systematic study of porphyrin derivatives as carrier compounds in chemical sensor design undertaken in this laboratory. In this paper, a bifurcated optical fiber chemical sensor for Hg(II) based on lipophilic porphyrin dimer DTPP is reported. The sensor is based on the fact that Hg(II) can strongly quench the fluorescence of a DTPP-containing membrane. The use of twin porphyrin rings makes the sensor highly selective toward Hg(II) with respect to transition metal ions such as Cd(II), Co(III), Cu(II), Ni(II), Pb(II), Zn(II), and Fe(III). The sensor shows response toward Hg(II) with a linear concentration range of 5.2 \times 10^{-7} - 3.1 \times 10^{-4} \text{ mol L}^{-1}.

EXPERIMENTAL SECTION

Reagents. Twice-distilled water was used throughout all experiments. High molecular weight poly(vinyl chloride) (PVC), diisooctyl phthalate (DIOP), dibutyl sebacate (DBS), and dioctyl sebacate (DOS) were obtained from Shanghai Chemicals (Shanghai, China) and used as received. TPPh$_2$ was synthesized by Adler’s method $^{16}$ [tetraphenylporphinate]zinc (ZnTPP) was prepared according to documented procedures $^{17}$ and both were

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identified by elementary analysis and UV–visible and IR spectroscopy. Before being used, chloroform and benzaldehyde were subjected to simple distillation from K₂CO₃. Pyrrole was distilled at atmospheric pressure from CaH₂. Except when specified, other chemicals were of analytical reagent grade and used without further purification.

**Synthesis of DTPP.** [(5-HP)TPPH₂] and [(5-BrBP)TPPH₂] were prepared and purified by methods reported by Yan et al.¹⁸ In 80 mL of DMF, 0.54 g of (5-BrBP)TPPH₂ and 0.90 g of (5-HP)TPPH₂ were dissolved to form a reaction mixture which was stirred at 65°C for 10 h. After addition of 80 mL of chloroform, the organic phase was separated and washed with water for several times, then 5 g of silica was added, and the solvent was evaporated. The residue retained on silica was transferred in a silica chromatographic column and eluted first with a mixture of eluant chloroform/petroleum ether (2:1) to remove unreacted (5-BrBP)TPPH₂ and then with chloroform to speed up its elution. The main band containing the product was collected. After the solvent was removed by rotary evaporation, 0.58 g (55.9%) of DTPP was obtained: UV–visible (CH₃Cl) λmax 419.5, 515.5, 551.5, 592, 645 nm; ¹H NMR (CDCl₃) (ppm) 8.8–8.9 (16H, pyrrole), 8.1–8.2 (16H, benzene), 7.7–7.8 (18H, benzene), 7.2–7.4 (4H, benzene), 4.4–4.5 (4H, CH₂O), 2.2–2.4 (4H, CH₂), −2.7 (4H, NH). Anal. Calcd for C₉₂H₆₆N₈O₂: C, 84.02; H, 5.02. Found: C, 84.83; H, 5.04; N, 8.46.

The reaction scheme is shown in Figure 1.

**Apparatus.** All fluorescence measurements were carried out on a Hitachi M-850 fluorescence spectrometer with excitation and emission slits set at 15 and 20 nm, respectively. A homemade poly(tetrafluoroethylene) flow cell (shown in Figure 2) and a bifurcated optical fiber (30+30 quartz fibers, diameter 6 mm and length 1 m) were used for the Hg(II)-sensing measurements. The excitation light was carried to the cell through one arm of the bifurcated optical fiber and the emission light collected through the other. A quartz glass plate (diameter 10 mm) covered with sensing membrane was fixed on the top of the flow chamber by the mounting screw nut with the membrane in contact with the sample solution. The sample solution was driven through the flow cell by a peristaltic pump (Guokang Instruments, Zhejiang, China) at a flow rate of 2.0 mL min⁻¹.

**RESULTS AND DISCUSSION**

**(Fluorescence Quenching of Optode by Hg(II).** Figure 3 shows the fluorescence spectra of the DTPP-based optode membrane exposed to a solution containing different concentrations of Hg(II), which are recorded at λex = 421.5 nm, λem = 620–740 nm. Owing to the conjugated double bond system and the high mobility of its π-electrons, DTPP exhibits fluorescence emission of Q(0–0) at 651.5 nm and Q(0–1) at 716.5 nm when excited by 421.5-nm radiation. From Figure 3, one can see that the fluorescence intensities of the optode membrane decrease with

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increase of the concentration of Hg(II), which constitutes the basis for the determination of Hg(II) with the optical fiber sensor proposed in this paper.

**Principle of Operation.** While in contact with the DTPP-based optode, Hg(II) in aqueous sample solution was extracted into the membrane phase and interacted with DTPP. Suppose a complexation equilibrium between Hg(II) (B) in the aqueous sample solution and DTPP (A) in the organic membrane phase is established with formation of a complex with a complexing ratio of \( m : n \), one has

\[
mb \text{ (aq)} = K \text{ m} \text{ (org)}
\]

\[
mb \text{ (org)} + nA \text{ (org)} \rightleftharpoons A_nB_m \text{ (org)}
\]

i.e. \( mb \text{ (aq)} + nA \text{ (org)} \rightleftharpoons A_nB_m \text{ (org)} \) (1)

Here \( K \), \( \beta \), and \( K \) are the distribution coefficient, the apparent complex formation constant of \( A_nB_m \), and the over-all equilibrium constant of the reaction, respectively. According to the modified Stern–Volmer equation, the relationships for the change of fluorescence intensities, the concentration of Hg(II) \([B]_{\text{aq}}\) in aqueous solution and the total concentration of DTPP \([A]_{\text{org}}\) in the membrane phase can be expressed as follows:

\[
\frac{F_0 - F}{F} = K[A]_{\text{org}}^{-1}[B]_{\text{aq}}^{n}
\]

Assuming \( \Delta F = F_0 - F \), one can obtain

\[
\log \left( \frac{\Delta F}{F} \right) = \log K + (n - 1) \log [A]_{\text{org}} + m \log [B]_{\text{aq}}
\]

(2)

Here \( F_0 \) and \( F \) denote the fluorescence intensities of the optode

Figure 3. Fluorescence emission spectra of optode membrane in the presence of different concentration of Hg\(^{2+}\): (1) 0, (2) 8.5 x 10\(^{-6}\), (3) 1.9 x 10\(^{-5}\), (4) 6.5 x 10\(^{-5}\), and (5) 1.3 x 10\(^{-4}\) mol-L\(^{-1}\) (\( \lambda_{\text{ex}} = 421.5 \) nm).

Figure 4. Plot of log(\(\Delta F/F\)) as a function of the log[Hg\(^{2+}\)] (obtained with optode 1).

membrane in absence and presence of Hg(II), respectively. It is obvious from eq 2 that \( m \) is the slope of the plot of log(\(\Delta F/F\)) versus log\([B]_{\text{aq}}\) (shown in Figure 4), which was calculated to be 1.

The relative fluorescence intensity \( \alpha \) is defined as the ratio of free \( A \), \([A]_f\), to the total amount of \( A \), \([A]_t\), in the membrane phase. It can be experimentally determined by measuring the fluorescence intensity of the optode:

\[
\frac{[A]_f}{[A]_t} = \frac{F - F_0}{F_b - F_0}
\]

Here \( F_b \) is the fluorescence intensity of the optode in the blank buffer solution and \( F_0 \) represents the fluorescence intensity of the same membrane when DTPP is completely complexed with Hg(II). \( F \) is the fluorescence intensity of the optode actually measured when in contact with Hg(II) solutions of a given concentration. The relationship between the \( \alpha \) and Hg(II) concentration \([B]_{\text{aq}}\) can be represented as

\[
\frac{\alpha^n}{1 - \alpha} = \frac{1}{nK[A]_{\text{org}}^{-1}[B]_{\text{aq}}^{m}}
\]

(4)

The response of the optode for different concentrations of Hg(II) is shown in Figure 5. Three curves are calculated using eq 4 with different ratios of Hg(II): DTPP, TPPH\(_2\), and ZnTPP with DOS as plasticizer to study the effect of sensing materials. The results are shown in Table 1.

**Optimization of Membrane Compositions.** Several optode membranes were prepared using different porphyrins including DTPP, TPPH\(_2\), and ZnTPP with DOS as plasticizer to study the effect of sensing materials. The results are shown in Table 1.

From Table 1 one can see that the optode based on DTPP shows obviously better response characteristics than that of TPPH\(_2\) in terms of working concentration range, while the optode based on ZnTPP shows no responses toward Hg(II). The effect

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of the structure of the porphyrins to the optode response is obvious. From the aforementioned discussion one can see that the fluorescence response of porphyrin derivatives toward Hg(II) is associated with the coordination between them. In a molecule of DTPP there are two porphyrin rings which provide two spots for coordination with Hg(II), while TPPH₂ has only one ring. ZnTPP has a central coordinating metal Zn that hinders the coordination of the Hg(II), which results in its inert response toward Hg(II).

Optodes with different plasticizers, i.e., DIOP, DBS, and DOS, were also prepared using DTPP as the sensing membrane component. The optode with DOS as the plasticizer gave the best response for Hg(II).

In the experiments, one also finds that, with the addition of lipophilic ion, sodium tetraphenylborate (NaTPB), the response characteristics of the optode membrane are improved. The results are shown in Table 2.

From Table 2 one can see that the response concentration range of the optode membrane becomes wider and response time shorter as the amount of NaTPB in the optode membrane increases, which might be caused by the increasing hydrophilicity owing to the addition of NaTPB. This seems favorable for the Hg(II) approaching the solution/membrane interface and undergoing the reversible coordination/dissociation processes. However, the response concentration range of the optode membrane becomes narrower when the content of NaTPB is larger than 3%.

Data points experimentally obtained.

From Figure 5 one can see that, in a wide range of pH from 2.4 to 8.0, acidity does not affect the determination of Hg(II) with proposed optode. In other words, there is no need for strict control of the pH value of the sample solution for determination of Hg(II), which is chosen for further experiments.

**Effect of pH.** The fluorescence intensity versus pH plot for the DTPP optode shown in Figure 6 was obtained by adjusting the solution pH with hydrochloric acid and sodium hydroxide and fixing the Hg(II) concentration at 1.0 × 10⁻³ mol-L⁻¹. Considering the alkaline condition, a solution of a high concentration of Hg(II) might cause precipitation of HgO, so the experiment of the effect of pH on the response of the optode was carried out at a pH range from 0.3 to 8.0. It can be seen that, in the section of lower pH value, the fluorescence intensity of the optode decreased with decreasing pH value, which is similar to that obtained with TPPH₂ for determining surface-active species. This phenomenon might be caused by extraction of H⁺ from aqueous solution into the optode membrane at high acidity, which destroyed the conjugated double bond system of DTPP.

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Response Characteristics of the Optode. The response curve of the DTPP-based optode is shown in Figure 4. The linear response range covers from 5.2 × 10⁻⁷ to 3.1 × 10⁻⁴ mol-L⁻¹ Hg²⁺, which results in decreasing basic fluorescence intensity of the optode membrane. The experimental results show that the optode membrane composition consisting of 2% DTPP, 2% NaTPB, 64% DOS, and 32% PVC (w/w) could provide the best response for Hg(II), which is chosen for further experiments.

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experiments were carried out by fixing the concentration of Hg(II) in a pH 5.4 NaOAc–HOAc buffered solution. The response time for Hg(II) concentration of $5.0 \times 10^{-5}$ mol-L$^{-1}$ is 9 min; the renewal time for the optode is 4 min. The reproducibility and reversibility of the optode were studied by alternatively recording the fluorescence intensity for blank buffer solution and $5.0 \times 10^{-5}$ mol-L$^{-1}$ Hg(II). The relative standard deviations of the fluorescence intensities for the two solutions were found to be 0.8% and 1.1% respectively. The recorded results are shown in Figure 7. All these results indicate satisfactory reversibility and reproducibility of the optode. The short-time stability of the optode was tested by recording the fluorescence intensity of $5.0 \times 10^{-5}$ mol-L$^{-1}$ Hg(II) over a period of 12 h for 20 measurements. A relative standard deviation of the fluorescence reading of 1.2% was recorded. The fluorescence intensity of the optode decreased 7% after 100 measurements. The optode could be stored in wet conditions without substantial change of the fluorescence intensity for at least one month, which implies that the porphyrin dimer used is stable in a membrane in contact with water.

**Selectivity.** The interference for a number of common species of the fluorescence determination of Hg(II) was investigated. The experiments were carried out by fixing the concentration of Hg(II) at $1.0 \times 10^{-5}$ mol-L$^{-1}$ and then recording the change of the fluorescence intensity before and after adding the interference into the Hg(II) solution buffered with a NaOAc–HOAc solution (pH 5.4). The results presented in Table 3 reveal that the relative error of common interferences, such as transition, alkali, and alkaline earth metal cations, was less than $\pm 5\%$, which is considered as tolerated. The DTPP-based sensor exhibited excellent selectivity toward Hg(II) with respect to other coexisting interferences, which makes it feasible for practical applications.

**Preliminary Analytical Application.** Recovery of spiked Hg$^{2+}$ in Xiang River and Industrial wastewaters was studied with the proposed optical fiber sensor. Xiang River and industrial wastewaters were simply filtered and showed that no Hg(II) was present. So they were spiked with standard mercury solutions and then analyzed with the proposed sensor. Results are shown in Table 4. One can see that the recovery study of spiked Hg$^{2+}$ determined by the DTPP-based optical fiber sensor shows satisfactory results. The present sensor seems useful for the determination of Hg(II) in real samples.

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**Table 3. Interference of Different Species to the Fluorescence Determination of Hg$^{2+}$ with the Proposed Optode**

<table>
<thead>
<tr>
<th>interference</th>
<th>concn$^a$ (mol-L$^{-1}$)</th>
<th>fluorescence ($\Delta F = F - F_0$)</th>
<th>relative error ($%$ ($\Delta F / F_0$) $\times 100$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$^+$</td>
<td>$1.0 \times 10^{-2}$</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>$1.0 \times 10^{-2}$</td>
<td>1.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>$1.0 \times 10^{-2}$</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>$1.0 \times 10^{-2}$</td>
<td>$-0.9$</td>
<td>1.5</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>$1.0 \times 10^{-2}$</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>2.1</td>
<td>3.4</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$-1.4$</td>
<td>-2.3</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$-0.6$</td>
<td>-1.0</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$-0.8$</td>
<td>-1.3</td>
</tr>
<tr>
<td>Be$^{2+}$</td>
<td>$1.0 \times 10^{-1}$</td>
<td>$-0.4$</td>
<td>-0.7</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>$1.0 \times 10^{-1}$</td>
<td>$-1.8$</td>
<td>-3.0</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>$1.0 \times 10^{-1}$</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>$1.0 \times 10^{-2}$</td>
<td>1.2</td>
<td>2.0</td>
</tr>
<tr>
<td>Na$^{+}$</td>
<td>$1.0 \times 10^{-1}$</td>
<td>$-0.8$</td>
<td>-1.3</td>
</tr>
<tr>
<td>K$^+$</td>
<td>$1.0 \times 10^{-1}$</td>
<td>$-0.5$</td>
<td>-0.8</td>
</tr>
</tbody>
</table>

$^a$ The concentration of Hg$^{2+}$ is fixed at $1.0 \times 10^{-5}$ mol-L$^{-1}$ (pH 5.4).

$^b$ $F$ and $F_0$ are the fluorescence intensities of the optode contacting with $1.0 \times 10^{-5}$ mol-L$^{-1}$ Hg$^{2+}$ solution with and without adding the interference ($F_0 = 60.8$).

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**Table 4. Recovery Study of Spiked Hg$^{2+}$ in Xiang River Water and Industrial Wastewaters**

<table>
<thead>
<tr>
<th>sample</th>
<th>Hg$^{2+}$ spiked (mol-L$^{-1}$)</th>
<th>Hg$^{2+}$ recovered (mol-L$^{-1}$)</th>
<th>recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xiang River water 1</td>
<td>$2.0 \times 10^{-6}$</td>
<td>$(2.08 \pm 0.11) \times 10^{-6}$</td>
<td>104.0</td>
</tr>
<tr>
<td>Xiang River water 2</td>
<td>$5.0 \times 10^{-6}$</td>
<td>$(4.72 \pm 0.26) \times 10^{-6}$</td>
<td>94.4</td>
</tr>
<tr>
<td>Xiang River water 3</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$(0.97 \pm 0.41) \times 10^{-5}$</td>
<td>97.0</td>
</tr>
<tr>
<td>industrial wastewater 1</td>
<td>$2.0 \times 10^{-6}$</td>
<td>$(2.21 \pm 0.13) \times 10^{-6}$</td>
<td>110.5</td>
</tr>
<tr>
<td>industrial wastewater 2</td>
<td>$5.0 \times 10^{-6}$</td>
<td>$(5.41 \pm 0.31) \times 10^{-6}$</td>
<td>108.2</td>
</tr>
<tr>
<td>industrial wastewater 3</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$(1.06 \pm 0.14) \times 10^{-5}$</td>
<td>106.0</td>
</tr>
</tbody>
</table>