Mercaptooxazole–phenazine based blue fluorescent sensor for the ultra-sensitive detection of mercury(II) ions in aqueous solution†

Hai-Li Zhang, Wen-Ting Li, Wen-Juan Qu, Tai-Bao Wei, Qi Lin, You-Ming Zhang and Hong Yao

Herein, a mercury(II) ion fluorescent sensor (Z-3) with high sensitivity and immediate response is designed and synthesized. The sensor uses the phenazine group as a luminophore and sulfhydryl as a recognition moiety. The sensor is easily synthesized and it exhibits a remarkable blue shift with Hg$^{2+}$. Correspondingly, its fluorescence color changes from yellow to blue. In addition, the low naked eye detection limit ($10^{-6}$) of the sensor allows the identification of concentration limits. Moreover, the sensor could detect mercury(II) ions over a wide pH range (from 2 to 8), which indicates that the detection can be carried out in aqueous systems. In addition, test strips are fabricated, which could act as a convenient pathway for the recognition of Hg$^{2+}$.

Among the reported sensors, phenazine and its derivatives have been widely employed in the design of fluorescent sensors due to their stable optical properties, easy synthesis, cheap raw materials and large conjugate systems. Although they act as an important skeleton in fluorescence sensors used to identify amino acids, citrate and other ions, we designed and synthesized a phenazine derivative Z-3 (Scheme 1), which could rapidly select Hg$^{2+}$ in aqueous solutions. Based on its deprotonation mechanism, the fluorescent sensor could detect Hg$^{2+}$ with blue fluorescence in a wide pH range (from 2–8). It also exhibits high selectivity ($2.14 \times 10^{-9}$ M) and other common metal ions have nearly no influence on its sensing behavior. Moreover, its naked eye minimum detection limits are $10^{-7}$ and $10^{-4}$ for solution and test strips, respectively, which greatly improve the practicality of this sensor. Moreover, the test strips also can act as a reliable means for the detection of Hg$^{2+}$ in real-time.

Fluorescence spectra were measured with different metal ions in DMSO/H$_2$O (v/v, 3 : 2, buffered with HEPES, pH = 7.20). As shown in Fig. 1a, the addition of Hg$^{2+}$ induced a distinct blue shift in the fluorescence emission bands, which is consistent with the above results.
fluorescence enhancement with an obvious blue-shift (from 544 to 496 nm). Moreover, the fluorescence color of the solutions changed from yellow to blue under illumination with a 365 nm UV lamp (Fig. 1b). We speculated that the sensor complexed with Hg²⁺, which resulted in the fluorescence colour change. All these facts indicate that the sensor could be used for the selective identification of Hg²⁺ among other cations.

The most important aspect of selective recognition is that the target analyte is detected over other possible interfering metal ions, and thus a competition experiment was carried out. In Fig. 2a and b, in the presence of other metal ions, such as Fe³⁺, Ag⁺, Ca²⁺, Cu²⁺, Co²⁺, Ni²⁺, Cd²⁺, Pb²⁺, Zn²⁺, Cr³⁺ and Mg²⁺, there was no evident fluorescence emission peak shift and color change. Therefore, it is clear that the interference of other ions is negligible during the detection of Hg²⁺. These results further suggest that Z-3 has a strong ability to complex with Hg²⁺ over other metal ions and could be used as a sensor for Hg²⁺ over a wide range of cations.

We also performed a fluorescence titration to verify the recognition behavior sensitivity (Fig. 3). In the fluorescence spectrum, upon the addition of Hg²⁺ to Z-3, the emission peak gradually blue shifted from 544 nm to 496 nm with a fluorescence color change from yellow to blue. The detection of Z-3 for Hg²⁺ calculated on the basis of 3σ/m for the fluorescence spectra (Fig. S3†) is 2.14 × 10⁻⁹ M, which is lower than the EPA guideline of 10 nM. This result also shows that Z-3 has higher sensitivity for Hg²⁺ compared with other reported Hg²⁺ sensors (Table 1).

In order to improve the actual operating performance of the detection behavior, we studied the pH scope of Z-3 + Hg²⁺ and fabricated comparison test strips. As shown in Fig. 4, Z-3 with Hg²⁺ exhibits strong fluorescence intensity in the pH range of 2–8, while the fluorescence intensity increases obviously at pH > 8, which may result from the fact that too high pH will result in a reaction between Hg²⁺ and -OH to form the corresponding metal hydroxides. This fact indicates that the sensor could be used in a wide pH range from 2 to 8 for the detection of Hg²⁺.
The peak at 14.41 ppm is ascribed to the NH proton in the 1H NMR spectrum. Moreover, we also observed a peak at 2675 cm⁻¹, which is consistent with the sensor (Z-3 + Hg²⁺) complex at various pH values in DMSO/H₂O (v/v, 3 : 2; buffered with HEPES, pH = 7.20) solution.

Test strips were prepared by immersing filter paper into a DMSO solution of Z-3 (2 × 10⁻⁴ M) and then drying them in air. The test strips containing Z-3 were utilized to sense Hg²⁺. As shown in Fig. 5, with a decrease in the Hg²⁺ concentration, the test paper fluorescence color gradually becomes yellow. The minimum identification limit of the test strips is 10⁻⁴ M. Moreover, the test strips could act as a convenient method for the detection of Hg²⁺ in an aqueous solution. We also conducted the experiments with the minimum detection limit with respect to naked eyes. As shown in Fig. 6, when the concentration of Hg²⁺ is 10⁻⁸ M, the fluorescence color of the solution is consistent with the sensor (Z-3). We thought that the lowest detection limit of Hg²⁺ was 10⁻⁸ M.

In order to study the combination of mercury ions with Z-3, we first studied the isomerization of Z-3. As shown in Fig. S1, the peak at 14.41 ppm is ascribed to the NH proton in the 1H NMR spectrum. Moreover, we also observed a peak at 2675 cm⁻¹ in the IR spectrum (Fig. S2), which is the characteristic peak of –SH. Based on these facts, we believe that Z-3 has two tautomers of thioketone (–S) and thiols (–SH), and the structure of thione (–S) is the main form in solution. From the 1H NMR titration (Fig. 7), the peak at 14.41 ppm disappeared with the addition of Hg²⁺, which suggests that the complexation occurred after the –NH proton was fully deprotonated. Amazingly, the solution precipitated solid on the addition of 0.2 equivalents of mercury ions. We speculate that it may be from the perchlorate, and its molecular formula may be [Z-3 + Hg⁺]ClO₄⁻. In addition, we also carried out an IR experiment on the solid of Z-3 and Z-3 + Hg²⁺.

As shown in Fig. S3, the peak at 2675 cm⁻¹, which was recognized as the characteristic peak of –SH, disappeared upon the addition of Hg²⁺. All these results indicate that the mercury ions coordinated with the sulfur atom and nitrogen atom on the oxazole ring after the protonation of the sensor.

Moreover, in order to clarify the stoichiometric relationship between Hg²⁺ and Z-3, the Job plot was obtained. As shown in Fig. 8, the fluorescence intensity at 496 nm was plotted against molar fraction of Z-3 sensor. The maximum emission intensity was reached when the molar fraction was 0.4. This result manifests a 1 : 1 ratio for the Z-3 + Hg²⁺ complex.

Based on all these facts, we propose a reasonable mechanism for the detection of Hg²⁺ by the sensor in an aqueous solution (Fig. 9). We hypothesize that the thiocarbonyl and secondary amine nitrogen of the oxazole motif coordinate with Hg²⁺, and then the complex and perchloric acid form a salt and precipitate.

Table 1 A comparison of the detection limits for Hg²⁺

<table>
<thead>
<tr>
<th>Method</th>
<th>Analyte</th>
<th>Solvent</th>
<th>Detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. 39</td>
<td>Hg²⁺</td>
<td>1-Propanol-cyclohexane</td>
<td>1.7 × 10⁻⁸ M</td>
</tr>
<tr>
<td>Ref. 40</td>
<td>Hg²⁺</td>
<td>MeOH-H₂O</td>
<td>2.1 × 10⁻⁷ M</td>
</tr>
<tr>
<td>Ref. 41</td>
<td>Hg²⁺</td>
<td>THF-HEPES</td>
<td>8 × 10⁻⁷ M</td>
</tr>
<tr>
<td>Ref. 42</td>
<td>Hg²⁺</td>
<td>CH₃CN-H₂O</td>
<td>9 × 10⁻⁷ M</td>
</tr>
<tr>
<td>Our work</td>
<td>Hg²⁺</td>
<td>DMSO-HEPES</td>
<td>2.14 × 10⁻⁸ M</td>
</tr>
</tbody>
</table>

Fig. 6 Naked-eyes detection limit under UV lamp at 365 nm. From left to right, the concentration of Hg²⁺ is 10⁻¹ M, 10⁻² M, 10⁻³ M, 10⁻⁴ M, 10⁻⁶ M, 10⁻⁸ M, and 0 M.

Fig. 5 Photographs of test strips (the concentration of Hg²⁺ is 0 M, 10⁻¹ M, 10⁻² M, 10⁻³ M, 10⁻⁴ M, 10⁻⁶ M, both under an UV lamp at 365 nm).
In conclusion, we obtained a fluorescent sensor Z-3 via a simple method for the detection of Hg²⁺, which displays high selectivity and sensitivity in the recognition process. The sensor exhibits an obvious fluorescence colour change from yellow to blue, and its detection behaviour operates in a wide pH range. Moreover, its test strips and naked-eyes minimum detection limit greatly improve the practicality of Z-3. Hence, this study also implies that phenazine and its derivatives are potential candidates for the detection of ions.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


