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β-Carboline-functionalized dithioacetal as Hg^{2+}-selective fluorescence probe in water

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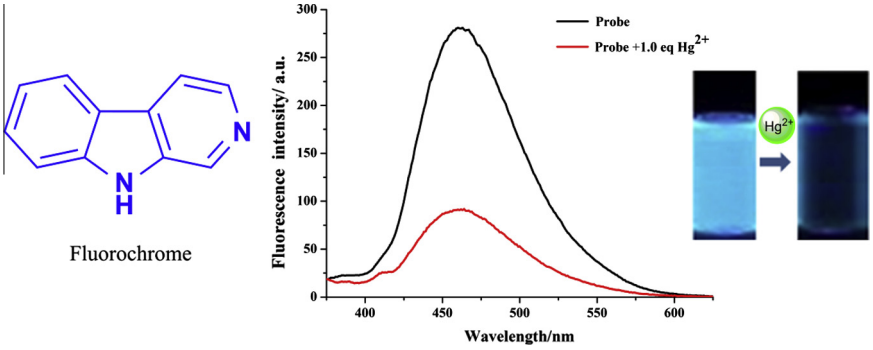
HIGHLIGHTS

- A water-soluble fluorescence probe has been designed and synthesized.
- The probe was highly effective for the detection and discrimination of Hg^{2+}.
- β-Carboline as a fluorophore is significant for the design of novel probes.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel sensing system based on the β-carboline core has been designed and synthesized for Hg^{2+} detection in water. We have demonstrated that a straight forward methodology can provide rapid, sensitive and selective recognition (cross-contamination experiments) for Hg^{2+} over a wide pH range. The vivid fluorescence change from blue to colorless can be clearly discriminated by the naked eye. Furthermore, there is a good negative correlation between the fluorescent intensity and the concentration of Hg^{2+} in the range 1.0×10^{-6} M–7.0×10^{-6} M. β-Carboline as a fluorophore synthesized via this route also provides a new strategy for the design of novel fluorescence probes and fluorochromes.

Introduction

Today, with increasingly rapid industrialization in many parts of the world, more and more heavy metal ions are being discharged into ecosystem. Bioaccumulation through the food chain has become a serious threat to human life and health. Chronic exposure to high levels of these heavy metal ions can lead to a series of diseases [1–3]. The mercury ion Hg^{2+}, one of the more severe environmental pollutants, is very harmful to the human body [4]. When absorbed, Hg^{2+} damages the brain, kidneys, and endocrine system [5]. Therefore, the rapid and selective detection of Hg^{2+} is very important. Atomic fluorescence spectrometry [6,7], cold vapor atomic fluorescence spectrometry [8], and gas or liquid chromatography [9,10] are usually used to quantitatively analyze Hg^{2+} content. However, all of these methods have complicated procedures, high costs, or low mobility. Significant efforts have been devoted to discovering effective fluorescence probes for Hg^{2+}, owing to the fluorescent probe method to detect analytes,

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is of outstanding sensitivity, neither invasive nor damaging, and has a short response time [11–19]. In recent years, many excellent sensors have been developed for the detection of Hg^{2+} [20–27]. However, most usually require complicated syntheses, expensive instruments and are insoluble in aqueous solutions [28,29]. The design and synthesis of new fluorescent probes that display a sensitive response to Hg^{2+} in water remain important goals.

β-Carboline, with the common tricyclic pyrido[3,4-b]indole ring structure, has been widely used in the study of antitumor drugs [30–33]. It also has another merit, that of being a good luminophor, which derives from its aromatic planar configuration; however, this property has been largely ignored. To the best of our knowledge, the study of β-carboline derivatives as luminous molecules has not yet been reported. Recently, dithioacetal as an Hg^{2+}-recognizing group has been developed, and exhibited high sensitivity and selectivity for Hg^{2+} [25]. However, the analyses were conducted only in organic solutions. Herein, we have designed a water-soluble chemosensor for Hg^{2+} by incorporating a β-carboline fragment with a dithioacetal that contains a hydrophilic carboxylic group. This compound exhibited a rapid and sensitive response to Hg^{2+} in aqueous solution, accompanied by a distinct color and fluorescence change.

Experimental

All solvents and reagents were obtained from commercial sources without further purification. $HgCl_2$, $FeCl_3{\cdot}6H_2O$, $CuSO_4$, CH_3COOAg, $MgSO_4{\cdot}7H_2O$, $SrCl_2{\cdot}6H_2O$, $Ba(CH_3COO)_2$, $ZnSO_4{\cdot}7H_2O$, $Al(NO_3)_3{\cdot}7H_2O$, $(CH_3COO)_2Pb{\cdot}3H_2O$, $CdSO_4{\cdot}8H_2O$, and $FeSO_4{\cdot}8H_2O$ were purchased from the Aladdin Chemical Reagent Co. The silica gel and GF_{254} silica gel used in the analytical thin-layer chromatography (TLC) and preparative thin-layer chromatography (PTLC) were produced by the Qingdao Haiyang Chemical Co., Ltd, which we utilized during the experiment procedure. Electron ionisation mass spectroscopy (EI-MS) was undertaken with a Thermo Fisher spectrometry instrument. ^1H nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on a Bruker Avance 500 MHz spectrometer. ^{13}C NMR spectra were recorded at 25 °C on a Bruker Avance 125 MHz spectrometer. Tetramethylsilane (TMS) in $CDCl_3$ and dimethyl sulfoxide-d_6 (DMSO-d_6) were investigated as internal references for ^1H and ^{13}C NMR spectra, respectively. Ultraviolet (UV)–visible absorption spectra were determined on a Hitachi U-3310 spectrophotometer. The fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. High-performance liquid chromatography (HPLC) analysis were carried out with a Shimadzu LC-15C instrument.

*Synthesis of 9H-pyrido[3,4-b]indole (**2**) [34,35]*

L-tryptophan (5.00 g, 24.5 mmol) and distilled water (100 mL) were added to a 250 mL single-necked, round-bottomed flask equipped with a magnetic stirrer. Dilute sulfuric acid (0.1 M) was added drop wise to the solution until the L-tryptophan dissolved completely, and then formaldehyde (37%, 7.27 mL, 73.5 mmol) was added to the solution. After reacting for 6 h at room temperature (RT), the mixture was filtered, and the filter cake (a pale-yellow powder) was obtained. A mixture of the dry pale-yellow powder, SeO_2 (5.44 g, 49.0 mmol), and acetic acid (150 mL) were refluxed for 30 h, then the reaction mixture was cooled to RT to afford a red-brown oil, which was purified by flash column chromatography using petroleum ether/ethyl acetate (1:1, v/v) as the eluent to give 1.398 g (34%) of compound **2** as a pale-yellow solid. CAS: 244-63-3. Melting point: 199–200 °C. ^1H NMR (500 M Hz, DMSO-d_6) δ: 11.61 (s, 1H), 8.90 (s, 1H), 8.33 (d, J = 5 Hz, 1H), 8.09 (d, J = 5 Hz, 1H), 7.56 (m, 3H), 7.23 (m, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 143.07, 141.14, 137.42, 136.30, 129.22, 127.19, 122.17, 120.98, 119.04, 114.48, 111.00. EI-MS: m/z = 169.06 (calculated 168.07 for $C_{11}H_8N_2$).

*Synthesis of 4-(3-bromopropoxy)benzaldehyde(**4**) [36]*

A mixture of *p*-hydroxybenzaldehyde (610 mg, 5.0 mmol), 1,3-dibromopropane (1.00 mL, 10.0 mmol), K_2CO_3 (690 mg, 5.0 mmol), tetrabutylammonium hydrogen sulfate (34 mg, 0.1 mmol), and KI (83 mg, 0.5 mmol) in acetonitrile (20 mL) was refluxed for 8 h. The filtrate was collected and concentrated under reduced pressure to afford a residue, which was purified by column chromatography over silica gel eluting with petroleum ether/ethyl acetate (10:1, v/v; 6:1, v/v) to give 982 mg (81%) of compound **4** as a white solid. CAS Registry Number: 17954-81-3. ^1H NMR (500 MHz, $CDCl_3$) δ: 9.94 (s, 1H), 8.11 (d, J = 5 Hz, 1H) 7.89 (d, J = 5 Hz, 1H), 7.03 (d, J = 5 Hz, 2H), 4.25 (t, J = 5 Hz, 2H), 3.66 (t, J = 5 Hz, 2H), 2.37–2.42 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 190.80, 132.42, 132.45, 130.06, 114.87, 114.25, 121.81, 65.69, 32.16, 29.62. EI-MS: m/z = 241.98, 243.99 (calculated 243.10 for $C_{10}H_{11}BrO_2$).

*Synthesis of 4-(3-(9H-pyrido[3,4-b]indol-9-yl)propoxy)benzaldehyde (**5**) [37]*

A mixture of compound **2** (336 mg, 2.0 mmol), NaH (144 mg, 6.0 mmol) and dry *N*,*N*-dimethylformamide (DMF, 20 mL) was stirred in an ice bath for 30 min, and then compound **4** (532 mg, 2.2 mmol) was added to the solution. After reacting for 24 h at RT and extraction with dichloromethane (DCM), the organic phase was dried over Na_2SO_4. The solvent was removed, and the residue was purified by PTLC using DCM/ethyl acetate/triethylamine (20:1.5:0.2, v/v/v) as the eluent, to give 541 mg (82%) of compound **5** as a yellow solid. Melting point: 107–108 °C. ^1H NMR (500 MHz, $CDCl_3$) δ: 9.90 (s, 1H), 8.94 (s, 1H), 8.49 (d, J = 5 Hz, 1H), 8.16 (d, J = 8 Hz, 1H), 7.98 (d, J = 5 Hz, 1H), 7.84 (d, J = 8.5 Hz, 2H), 7.48–7.54 (m, 2H), 7.30 (t, J = 5 Hz, 1H), 6.97 (d, J = 5 Hz, 2H), 4.67 (t, J = 5 Hz, 2H), 4.00 (t, J = 5 Hz, 2H), 2.43–2.48 (m, 2H). ^{13}CC NMR (125 MHz, $CDCl_3$) δ: 190.78, 163.39, 141.20, 139.20, 136.44, 132.05, 131.91, 130.25, 128.52, 121.98, 121.17, 119.88, 114.73, 114.63, 109.32, 64.70, 39.65, 28.66. EI-MS: m/z = 331.15 (calculated 330.14 for $C_{21}H_{18}N_2O_2$).

*Synthesis of 2-(((4-(3-(9H-pyrido[3,4-b]indol-9-yl)propoxy)phenyl) ((2-methoxy-2-oxoethyl)thio) methyl)thio) acetic acid(**6**) [38]*

Boron trifluoride diethyl etherate (380 μL, 3.0 mmol) was added to a DCM solution of **5** (660 mg, 2.0 mmol) and methyl thioglycolate (268 μL, 3.0 mmol). After stirring in an ice bath for 8 h, the reaction was quenched with water. Then, the suspension was concentrated under reduced pressure to afford a yellow oily residue. A mixture of the residue and aqueous NaOH solution (20 mL, 0.1 M) in methanol/tetrahydrofuran (THF) (1:1, v/v, 20 mL) was stirred at RT for 24 h. The solution was extracted with ethyl acetate, and then the pH of the aqueous phase was adjusted to 3–4 by the addition of aqueous HCl (0.1 M). The solution was cooled in a refrigerator, and a white floc precipitate appeared. Purified by PTLC using DCM/methanol/formic acid (15:1:0.15, v/v/v) as the eluent, 377 mg (37%) of compound **6** was obtained as a white solid. Melting point: 177–178 °C. ^1H NMR (500 MHz, DMSO-d_6) δ: 8.31–8.36 (m, 3H), 8.13 (s, 1H), 7.82 (s, 1H), 7.70 (s, 1H), 7.55 (s, 1H), 7.26 (s, 2H), 7.03 (s, 1H), 6.85 (s, 1H), 5.23 (s, 1H), 4.68 (s, 2H), 4.03 (s, 3H), 3.41–3.56 (m, 2H), 3.20–3.25 (m, 2H), 2.31 (d, 2H), 0.84 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 191.80, 170.50, 163.69, 141.15, 138.94, 136.52, 133.00, 132.24, 130.12, 129.23, 128.76, 127.75, 122.45, 119.98, 115.04, 114.81, 110.51, 65.58, 65.00, 52.54, 33.91,

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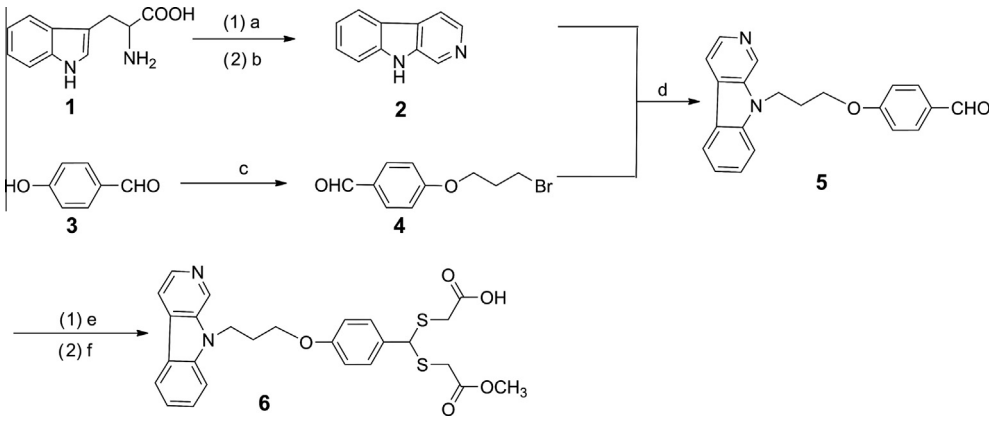

Scheme 1. Synthesis of compound **6**. (a) H_2O, HCHO, H_2SO_4, RT, 6 h; (b) SeO_2, CH_3COOH, reflux, 30 h (34% yield over two steps); (c) 1,3-dibromopropane, CH_3CN, K_2CO_3, KI, tetrabutylammonium hydrogen sulfate, reflux, 8 h, 81%; (d) NaH, DMF, 0 °C 30 min, RT, 24 h, 82%; (e) $HSCH_2COOCH_3$, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 0 °C, 8 h; (f) CH_3OH/THF (1/1, v/v), 0.1 M NaOH, RT, 24 h (37% yield over two steps).

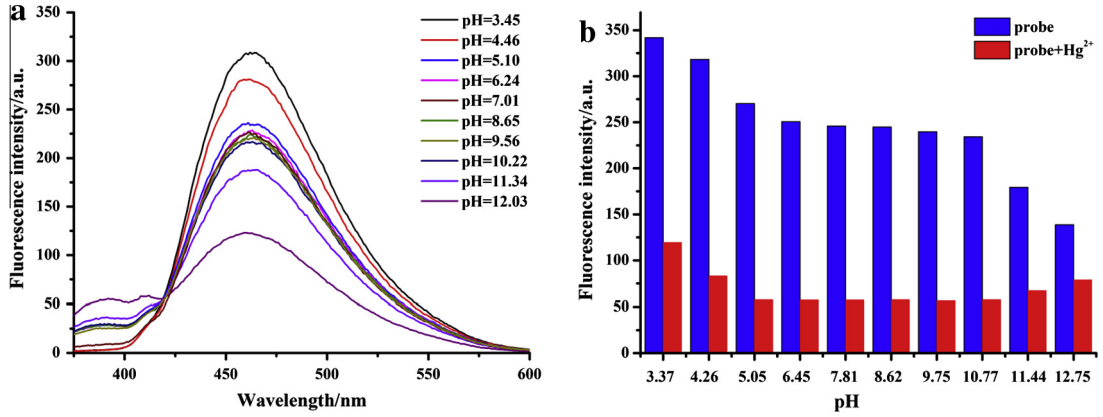

Fig. 1. (a) Fluorescent intensity curve of probe **6** (1.0×10^{-5} M) at different pH values (pH adjusted by HCl and NaOH solutions) at 293 K. (b) Fluorescent intensity curve of probe **6** (1.0×10^{-5} M) in the absence (blue) and presence (red) of Hg^{2+} (1.0×10^{-5} M) at different pH values (pH adjusted by HCl and NaOH solutions) at 293 K. The excitation wavelength was 360 nm, and the emission intensity was measured at 462 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

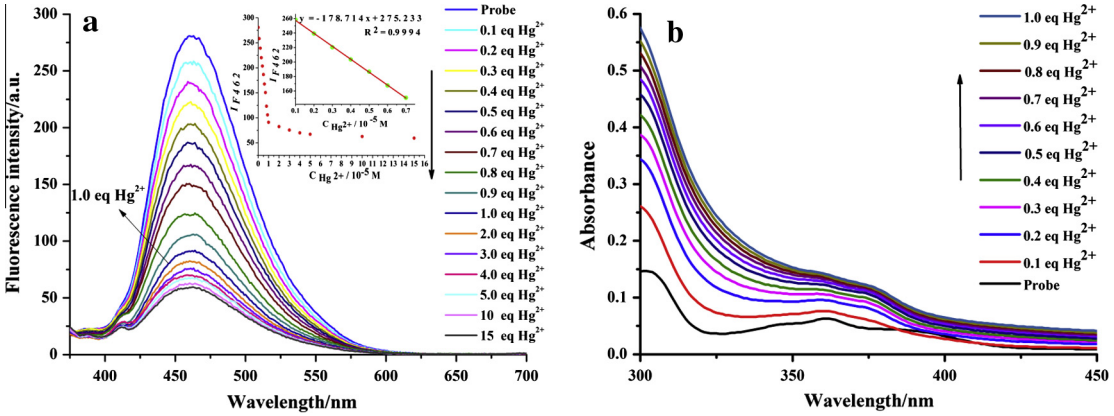

Fig. 2. (a) Fluorescence titration of compound **6** (1.0×10^{-5} M) with Hg^{2+} in a pH 6.8 PBS solution at 293 K. [Hg^{2+}] (1×10^{-5} M): 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 3, 4, 5, 10, and 15. The excitation wavelength was 360 nm. The emission intensity was measured at 462 nm. (b) Absorbance intensity titration of probe **6** (1.0×10^{-4} M) with Hg^{2+} in a pH 6.8 PBS solution at 293 K. [Hg^{2+}] (1×10^{-4} M): 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0.

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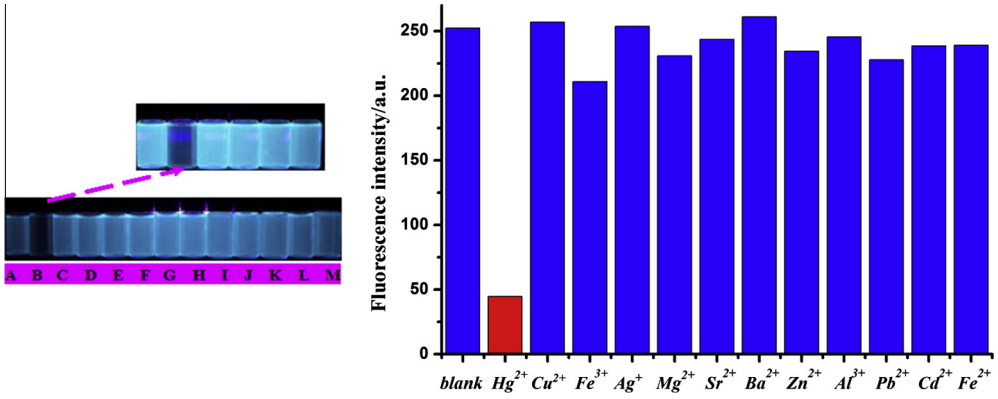

Fig. 3. Fluorescent intensity change of compound **6** (1.0×10^{-5} M) in a pH 6.8 PBS solution at 293 K in the presence of 10 equivalents of different metal ions. Inset: compound **6** in the presence of different metal ions. A: **6** (1.0×10^{-5} M). B–M: **6** + Hg^{2+}, Cu^{2+}, Fe^{3+}, Ag^{+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Al^{3+}, Pb^{2+}, Cd^{2+}, and Fe^{2+} (1.0×10^{-4} M).

29.47, 28.67, 28.47. EI-MS: m/z = 510.94 (calculated 510.63 for $C_{26}H_{26}N_2O_5S_2$).

Results and discussion

Synthesis

The synthetic approach to the title compound is outlined in Scheme 1. Compound **1** was used as the starting material to obtain *β*-carboline. After reacting with formaldehyde and selenium dioxide, respectively, compound **1** was cyclized and converted to *β*-carboline. In the presence of K_2CO_3 and KI, compound **3** was allowed to react with 1,3-dibromopropane, to produce compound **4**, which can combine with compound **2** to produce compound **5**. The title compound **6** can be obtained via reacting compound **5** with methyl thioglycolate with the help of a Lewis acid, $BF_3{\cdot}Et_2O$, and subsequent hydrolysis. The carboxylic group facilitated the good solubility of compound **6** in methanol and water. At the same time, an ester group was retained, to keep its stability in air.

Fluorescence and UV study with Hg^{2+}

To evaluate the applicability of compound **6** as an Hg^{2+} fluorescence probe in different environments, its photophysical properties were studied in aqueous solution at various pH values. The results showed that the fluorescence intensity remained high at pH values between 5.05 and 10.77 in water (Fig. 1), which suggested that compound **6** could function over a wide range of pH for detection. Phosphate-buffered solution (PBS) at pH 6.8 was selected as the detecting environment because the pH of drinking water is about 6.8.

The titration reaction curve of **6** toward Hg^{2+} was investigated, and compound **6** was found to exhibit high sensitivity toward Hg^{2+}. As shown in Fig. 2a, on addition of Hg^{2+} to a PBS solution of compound **6**, a gradual decrease in the intensity of the 462 nm emission band was observed. The fluorescence intensity of compound **6** declined by 70% after the addition of 1.0 equivalent of Hg^{2+} to the PBS solution. The quantum yields before and after combining with Hg^{2+} had been determined, and their values are 0.289 and 0.066 (Table S1, in the Supporting Information), respectively.

Similar to the fluorescence spectra, the absorption spectra also showed a visible response toward Hg^{2+}. On addition of Hg^{2+} to the PBS solution of compound **6**, the absorbance intensity increased smoothly (Fig. 2b). The linear response range of compound **6** for Hg^{2+} was measured under optimal experimental conditions. As shown in Fig. 2a, the fluorescent intensity of compound **6** decreased with an increasing concentration of Hg^{2+}. Although a

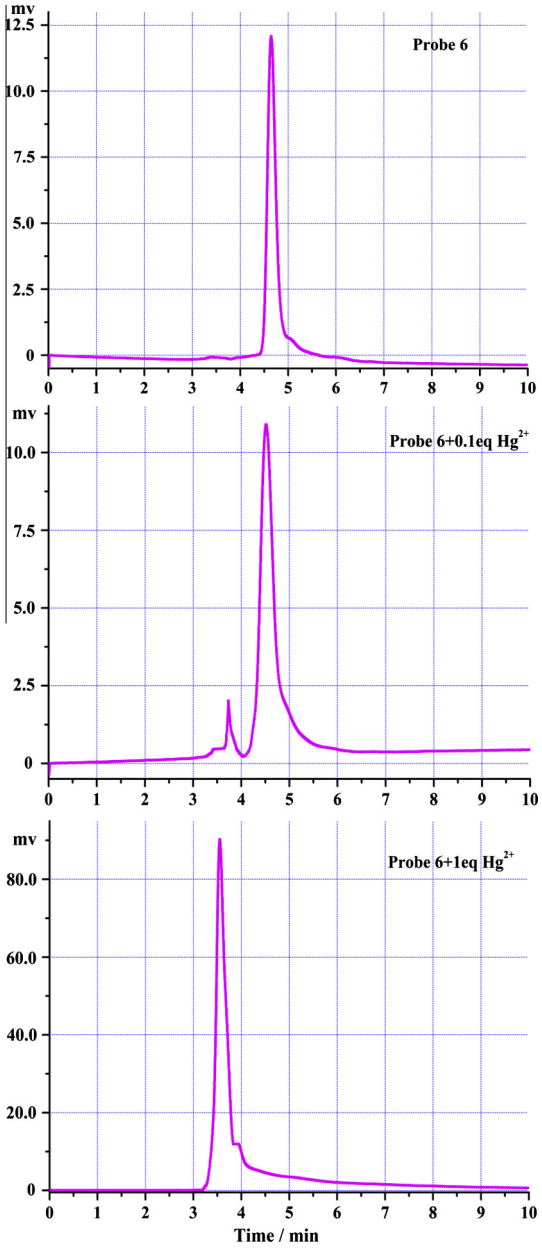

Fig. 4. Chromatographic conditions: C18 reversed-phase column, column temperature of 40 °C, detection wavelength of 360 nm, eluted with water:methanol (1:1) over 10 min at a flow rate of 0.5 mL/min.

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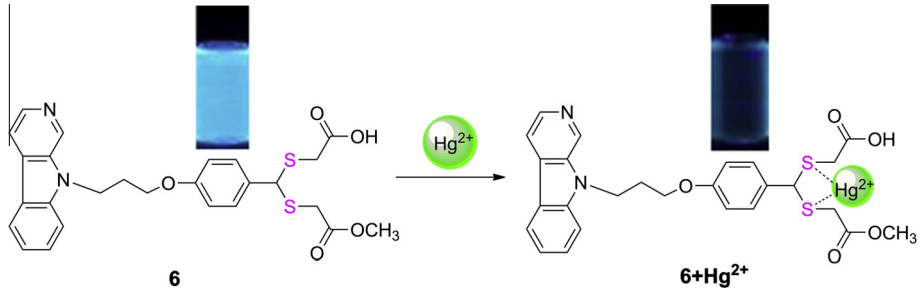

Fig. 5. Proposed sensing mechanism for complex (**6** + Hg^{2+}).

good Stern–Volmer relationship could not be obtained, there is a good negative correlation between the fluorescent intensity (y) and the concentration of Hg^{2+} ion in the range 1.0×10^{-6} M–7.0×10^{-6} M.

Fig. 3 illustrates the fluorescent intensity changes of compound **6** in the presence of Hg^{2+}, Cu^{2+}, Fe^{3+}, Ag^{+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Al^{3+}, Pb^{2+}, Cd^{2+} and Fe^{2+} in pH 6.8 PBS solution. Compound **6** exhibited a high selectivity toward Hg^{2+}, and only Hg^{2+} could quench the fluorescence of compound **6**. The vivid fluorescence changes from blue to colorless could be clearly discriminated by the naked eye. The fluorescence intensity of compound **6** changed very little in the presence of the other metal ions, because compound **6** can combine with Hg^{2+} ion to give complex whereas the other metal ions cannot. To gain more insight into the ion selectivity of compound **6** for Hg^{2+}, cross-contamination experiments were carried out in the presence of Hg^{2+} mixed with other metal ions, namely Cu^{2+}, Fe^{3+}, Ag^{+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Al^{3+}, Pb^{2+}, $Cd^{2+}$and Fe^{2+}. As illustrated in Fig. S1 (in the Supporting Information), it is evident that the selectivity of compound **6** towards Hg^{2+} is almost unaffected by the competing ions.

It is well known that reaction time is an important indicator when evaluating a probe: a fast-responding probe has more practical value. The reaction time of compound **6** towards Hg^{2+} in pH 6.8 PBS solution was investigated, and the results are shown in Fig. S2 (in the Supporting Information). From the reaction time curve, it can be seen that compound **6** has a rapid response, and reaches a relatively stable plateau less than 0.5 min after the addition of Hg^{2+}, which indicates that compound **6** can efficiently detect Hg^{2+}.

Mechanism studies

To make certain of the complexing mechanism of compound **6** with Hg^{2+}, a series of verified experiment were carried on. Compound **5**, in which β-carboline was only contained (not dithioacetal segment), was used to titrate the Hg^{2+}. The results indicated that the nitrogen atom of the β-carboline ring could not bind with Hg^{2+} (Fig. S3, in the Supporting Information). The absorbance intensity dropped a little, which might be caused by solvent effect after the addition of Hg^{2+}. The slight fluorescence enhancement might be due to the creation of an acidic environment caused by the hydrolysis of Hg^{2+}, which corresponds to the results of Fig. 1.

Fig. 4 depicts the course of probe **6** binding with Hg^{2+}, as tracked by HPLC. The signal of compound **6** completely disappeared when an equivalent amount of Hg^{2+} was added. Simultaneously, a new peak appeared, which meant a new compound produced. Based on the above results, the structure of a 1:1 complex of compound **6** and Hg^{2+} was proposed, as shown in Fig. 5. It is suggested that the complex **6**–Hg^{2+} utilizes the two sulfur atoms for complex formation to inhibit excited state intramolecular proton transfer (ESIPT) processing, leading to a dramatic fluorescence quenching. This is linked to a binding site via a bridge of three alkyl carbons (two CH_2 and one CH) to a dithioacetal, which results in the pendant arm being sufficiently flexible to lead to an interaction with Hg^{2+}.

Conclusions

In summary, we have developed a water-soluble fluorescence probe by incorporating a β-carboline fragment with a dithioacetal. This probe exhibits a rapid response and high selectivity and sensitivity to Hg^{2+} over other metal ions in water. Moreover, this probe can function over a wide pH range (from 5.05 to 10.77) for the detection of Hg^{2+} ion. Based on a complex reaction, Hg^{2+} can bind with this probe to form a complex, resulting in obvious fluorescence quenching. Significantly, β-carboline as a fluorophore has potential for the design of novel fluorescence probes.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.09.111.

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