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A selective, fluorescent probe for Hg^{2+} detection in aqueous solution

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Abstract

A novel fluorescent probe, 5-(2-benzothzaole)-2-thiophene boronic acid (**1**), for Hg^{2+} detection in aqueous solution was synthesized. (**1**) exhibited very strong fluorescence emission ($\phi = 0.92$) in tris–HCl (pH 7.42) buffer aqueous solution. It was found that the fluorescence emission of (**1**) was quenched significantly upon addition of Hg^{2+} in buffer aqueous solution, whereas no marked fluorescence quenching was detected with addition of other metal ions (Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Na^{+}, K^{+}) expect for Fe^{2+} and Fe^{3+}, for which a small fluorescence quenching was detected in same condition. Competition experiment showed that no obvious interference was observed in its fluorescence while (**1**) performed the titration with Hg^{2+} in the different mixtures of metal ions.

Keywords: Hg^{2+} detection; Fluorescent probe; Aqueous solution

1. Introduction

The development of sensitive and selective fluorescent sensor molecules is a fundamental goal in fluorometric metal ion analysis [1]. Besides the search for new fluoroionophores for alkali and alkaline-earth metal ions [2], much attention has been focused lately on the design of probes for heavy and transition metal ions [3–7]. Mercury contamination occurs through a variety of natural and anthropogenic sources [8,9], and it causes serious environmental and health problems became marine aquatic organisms convert inorganic mercury into neurotoxic methylmercury which bioaccumulates through the food chain [10]. Although a number of selective sensor for Hg^{2+} have been developed based on fluorogenic [11–15], redox [16,17], or chromogenic changes [18,19]. There is still a challenge to devise a practical Hg^{2+}-sensor that exhibits high selectivity, fast response and soluble in aqueous solution.

Herein, we present a novel probe, 5-(2′-benzothiazole)-2-thiopheneboronic acid (**1**) (Scheme 1), for Hg^{2+} detection. The advantages of this probe are based on the following aspects: (1) the probe is a novel, simple and stable, (2) the probe is highly sensitive and selective for Hg^{2+} detection, and (3) the probe can be used in aqueous solution.

2. Experimental

2.1. General methods

^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz with TMS as an internal reference and $CDCl_3$ as solvent. MS spectra were recorded with a Trio-2000 GC–MS spectrometer. UV absorption spectra and fluorescence spectra were carried out on an absorption spectrophotometer (Hitachi U-3010) and a fluorescence spectrophotometer (F-2500), respectively.

Synthesis: (1) 2-bromo-5-(2-benzothzaole) thiophene: treatment of 2-aminothiophenol (0.75 g, 6.0 mmol) and 2-bromo-5-thiophenecarboxaldehyde (0.95 g, 5.0 mmol) in DMSO (15 ml). The mixture was refluxed until no starting material was detected by TLC plate. The mixture was cooled to ambient temperature and poured into ice water (50 ml). The product was extracted with DCM, and the combined organic phase was dried with anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by flash column chromatography with petroleum/ethyl acetate (6:1) as eluent to afford 2-bromo-5-(2-benzothzaole) thiophene in yield 82%. ^{1}H NMR (300 MHz, $CDCl_3$): 8.02 (d, 1H, $J = 8.0$ Hz), 7.86 (d, 1H, $J = 7.9$ Hz),

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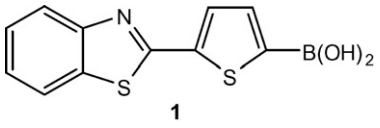

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Scheme 1. The molecular structure of probe (**1**).

7.51–7.36 (m, 3H), 6.97 (d, 1H, $J = 4.0$). (2) 5-(2-benzothzaole)-2-thiophene boronic acid (**1**): to the solution of 2-bromo-5-(2-benzothzaole) thiophene (0.29 g, 1.0 mmol) in THF (30 ml) was added slowly *n*-BuLi (0.7 ml, 2.5 M in hexane) at −78 °C. The mixture was stirred for 1 h, and during this time the temperature of solution was raised to −45 °C. To the cooled above solution (−78 °C), $B(OCH_3)_3$ (0.23 g, 2.0 ml) was added and the mixture was stirred for 4 h (during this time the temperature of mixture was raised to ambient temperature), followed by quenched with HCl (5.0 ml, 1.0 M). The mixture was poured into ice water (50 ml) and extracted with DCM. The combined organic phase was dried with anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography with DCM/methanol (50:1) as eluent to afford target compound (**1**) in yield 80%. ^{1}H NMR (300 MHz, CD_3COCD_3): 8.06 (d, 1H, $J = 7.9$ Hz), 7.99 (d, 1H, $J = 8.0$ Hz), 7.80 (d, 1H, $J = 3.9$ Hz), 7.72 (d, 1H, $J = 3.7$ Hz), 7.64 (s, 2H), 7.53 (t, 1H), 7.43 (t, 1H). ^{13}C NMR (CD_3COCD_3): 205.6, 161.0, 153.9, 142.0, 136.5, 134.9, 129.7, 126.6, 125.5, 122.8, 121.9. HRMS (*m*/*z*) [M^+] calcd. for $C_{11}H_8BNO_2S_2$: 261.1322, found: 261.1328. Anal. Calcd. for $C_{11}H_8BNO_2S_2$: C, 50.60; H, 3.09; N, 5.36; S, 24.56. Found: C, 50.57, H, 3.06, N, 5.34, S, 24.58.

3. Results and discussion

The probe (**1**) exhibited different fluorescence emission with different pH value in tris–HCl buffer aqueous solution, and the largest fluorescence emission ($\phi_0 = 0.92$) in tris–HCl buffer aqueous solution was obtained when pH value is more than 7.42 (Fig. 1) by using fluorescein ($\phi = 0.90$) as the Ref. [20]. The maximum absorption and emission bands of (**1**) were at 343 nm ($\varepsilon = 2.5 \times 10^4$) and 415 nm in tris–HCl (pH 7.42) buffer aqueous solution, respectively (Fig. 2).

Addition of Hg^{2+} (0.01 M, in ethanol) to solution of (**1**) (1×10^{-5} M, tris–HCl buffer aqueous) produced a decrease in intensity of the 343 nm band in absorption spectra with a concomitant increase of a new one at 383 nm as shoulder (Fig. 3), which may be attributed to a complex of (**1**) with Hg^{2+}.

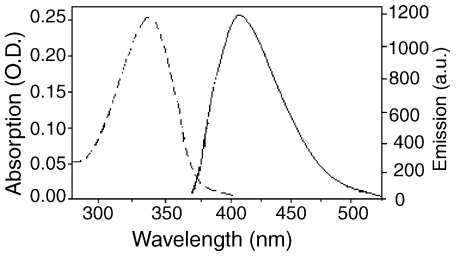


Fig. 2. Absorption (dashed line) and emission (solid line) spectra of (**1**) (1×10^{-5} M) in tris–HCl (0.01 M, pH 7.42) buffer aqueous solution.

A slight blue shift of absorption band (343 nm band) was detected with addition of Hg^{2+} to solution of (**1**). This may be due to the fact that complexation by a metal ion reduced the donor character of the sulfur atoms in thiophene rings. A 1:1 complex formation was determined from the absorption spectra changes of (**1**) (an isosbestic point appeared at 373 nm), where the absorption decreased linearly with addition of Hg^{2+} up to 1 equiv. and there it remained. The binding constant ($\log K = 3.48 \pm 0.02$) was estimated from the change in the spectral intensities by using the Excel program as reported [21].

To explore the site where Hg^{2+} coordinates to the ligand, the cation complexing property was analyzed by ^{1}H NMR (300 MHz). By comparing the ^{1}H NMR spectrum of the complexed cation with that of ligand found that all the signals arising form the aromatic protons shift downfield. Further investigation found that the largest chemical shift of signal was resulted from the proton ($\delta = 7.72$ ppm) in thiophene ring, which shifted by 0.25 ppm. Two other significant shifts of protons, one from the proton ($\delta = 7.81$ ppm) in thiophene ring and the other from the proton ($\delta = 8.02$ ppm) in benzene ring, were also observed by 0.13 and 0.11 ppm, respectively, chemical shift. Besides, the integral of signal at 7.64 ppm, which corresponds to the proton of OH group, decreased as well. All results suggested that the cation binding probably occurs at the N, S and O atoms, and the structure of complex was shown in Scheme 2.

The investigation of fluorescence emission showed that ligand (**1**) exhibited strong fluorescence emission ($\phi_0 = 0.92$)

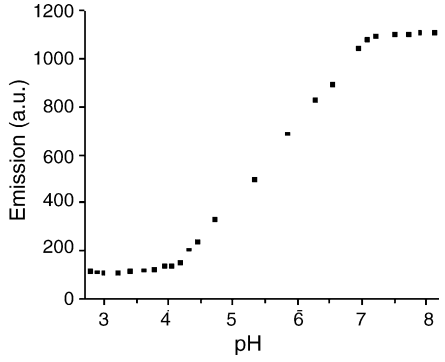


Fig. 1. Fluorescence intensity of (**1**) vs. pH (pH adjusted by 10% HCl or 10% NaOH) in aqueous water.

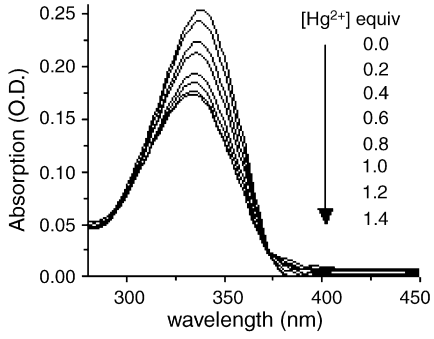
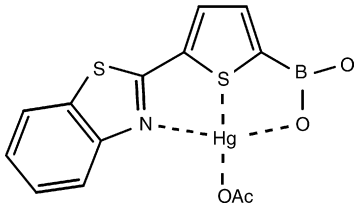


Fig. 3. Absorption changes of (**1**) (1×10^{-5} M) in tris–HCl (0.01 M, pH 7.42) buffer aqueous solution with addition of Hg^{2+}.



Scheme 2. Probably structure of ligand (**1**) complexed with Hg $(OAc)_2$.

in tris–HCl (pH 7.42) buffer aqueous solution, and maximum emission band at 415 nm (Fig. 2). Upon addition of Hg^{2+}, the intensity of the band at 415 nm was decreased significantly, and the emission spectra changes of ligand (**1**) with addition of amount of Hg^{2+} was presented in Fig. 4. It was found that the fluorescence quantum yield of mixture solution decreased from $\phi_0 = 0.92$ to $\phi = 0.015$ with addition of the amount of Hg^{2+} from 0 to 1.4 equiv., indicating that the fluorescence emission of ligand (**1**) was quenched largely by addition of Hg^{2+}. The reason why the fluorescence of ligand (**1**) was quenched with addition of Hg^{2+} may due to the following two aspects: one is probably because of ligand–metal–charge-transfer (LMCT), which is transition in which electronic charge is transferred from the ligand towards the coordinating metal. In this experiment, the electronic charge of ligand (**1**) (N, S and O-atoms) transferred to Hg^{2+} (d-orbital) and the electronic charge of ligand (**1**) was redistributed in an excited state, which resulted in the fluorescence quench of ligand (**1**). Another is probably because of boron acid. As shown in Fig. 1, the fluorescence emission of ligand (**1**) is very small in the solution of small pH value (pH 4), with increase of pH value, the fluorescence emission of ligand (**1**) is increased significantly till the pH value of solution is more than 7.4. The results above indicated that the existed oxygen anion in boron acid group may be in favor of fluorescence emission. Upon addition Hg^{2+} to buffer solution of ligand (**1**), one of oxygen anion transferred its negative charge to metal ion, which resulted in the decrease of fluorescence emission of ligand (**1**).

The selectivity of probe (**1**) was explored by monitoring the fluorescent emission of (**1**) (1×10^{-5} M) with other metal ions (0.01 M, ethanol) in tris–HCl buffer aqueous solution. As shown in Fig. 5, a large decrease of the fluorescence emission of (**1**) ($\phi_0/\phi = 16.3$) was obtained with addition of Hg^{2+}, but no

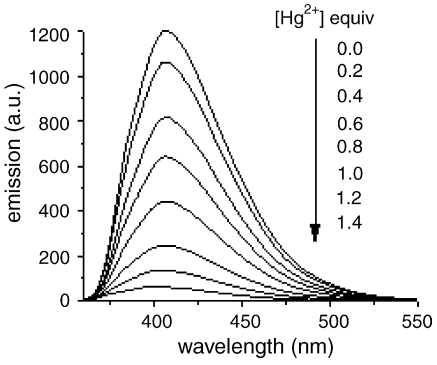


Fig. 4. Fluorescence changes of (**1**) (1×10^{-5} M) in tris–HCl (0.01 M, pH 7.42) buffer aqueous solution with addition of Hg^{2+}.

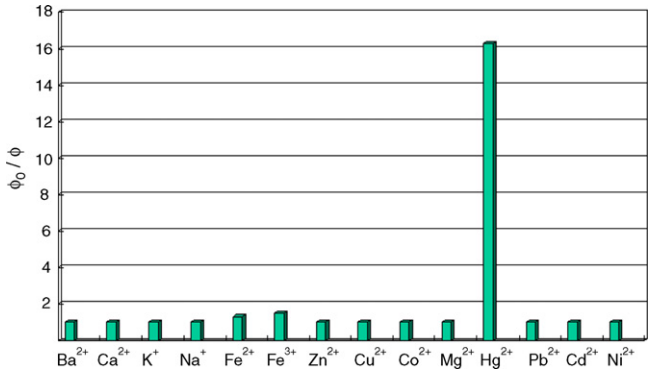


Fig. 5. Fluorescence changes of (**1**) (1×10^{-5} M) in tris–HCl (0.01 M, pH 7.42) buffer aqueous solution with metal ions.

decrease of fluorescent emission was detected ($\phi_0/\phi = 1$) with addition of other metal ions Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Na^{+}, and K^{+}, respectively, in the same condition except for Fe^{2+} and Fe^{3+}. For which a slight fluorescence quench was observed (Fe^{2+}: $\phi_0/\phi = 1.3$, Fe^{3+}: $\phi_0/\phi = 1.5$) in the same condition. It indicated that (**1**) was a highly selective fluorescent sensor for Hg^{2+} detection in tris–HCl buffer aqueous solution.

To further investigate the selectivity of probe (**1**), the competition experiments were conducted in which (**1**) (1×10^{-5}, tris–HCl buffer aqueous solution) was exposed to a solution of Hg^{2+} in the presence of Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Na^{+}, and K^{+} (5×10^{-5}M), as well as the mixture of the metal ions, respectively. It showed that, no significant changes in fluorescence intensity of (**1**) was found by comparison with that without the other metal ions besides Hg^{2+}. Moreover, no obvious interference was observed in fluorescence emission while performing the titrations with Hg^{2+} in the different mixtures of metal ions.

The sensitivity and stability of the probe (**1**) were also investigated. It was found that the concentration of Hg^{2+} could be detected at least down to 1×10^{-6} M when (**1**) was employed at 1×10^{-6} M in tris–HCl buffer aqueous solution. It was also found that (**1**) was stable in tris–HCl (pH 7.42) buffer aqueous solution at ambient temperature, and no significant change in absorption or emission was detected after solution of (**1**) was kept at ambient temperature for several months. Besides, (**1**) also performed sensitivity and selectivity for Hg^{2+} detection in pure water solution.

4. Conclusion

In summary, a novel, simple fluorescent probe for Hg^{2+} detection has been designed and synthesized, and it displays high selectivity and sensitivity for Hg^{2+} recognition in neutral buffer aqueous solution.

Acknowledgement

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