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ORIGINAL PAPER

# Highly Selective and Sensitive Chemosensor for $Hg^{2+}$ Based on the Naphthalimide Fluorophore

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**Abstract** A new OFF-ON fluorescent chemosensor (H1) composed of a naphthalimide fluorophore and a 6-[(quinolin-8-yloxy)methyl]pyridin-2-ylmethanamine receptor has been synthesized and characterized by infra-red, $^{1}H$ NMR, $^{13}C$ NMR and mass spectrometry. The developed chemosensor H1 exhibited good turn-on and reversible responses toward $Hg^{2+}$, with excellent selectivity and sensitivity, in a neutral buffered aqueous solution. Other common metal ions did not interfere with the fluorescence-enhancement response to $Hg^{2+}$. Furthermore, the chemosensor H1, at a concentration of 10 μM, showed a rapid and linear response toward $Hg^{2+}$ in the concentration range 0–10 μM. On addition of 10 μM $Hg^{2+}$, the fluorescence intensity of H1 was enhanced about 4-fold. The detection limit was calculated to be 63 nM. The association constant was $1.11 \times 10^5$ $M^{-1}$. The fluorescence quantum yield and lifetime of H1/$Hg^{2+}$ were 0.42 and 3.83 ns, respectively.

**Keywords** Mercury ion · Fluorescent chemosensor · Photoinduced electron transfer · Turn-on · Reversible

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## Introduction

Mercury is a highly toxic and hazardous pollutant with recognized accumulative and persistent characteristics in the environment and biota [1]. Excessive exposure of the vital organs and tissues to mercury will lead to the dysfunction of the brain, kidney, and stomach, and to central nervous system defects [2, 3]. Given these environmental and toxicological concerns, there is a considerable interest in the development of new detection methods for $Hg^{2+}$ in the environment and in biological samples [4]. Current techniques for $Hg^{2+}$ screening usually require expensive and sophisticated instrumentation. However, fluorescent chemosensors detect $Hg^{2+}$, at relatively low cost, high selectivity, sensitivity, and simplicity. The design of fluorescent chemosensors is mainly based on intramolecular charge transfer [5, 6], through bond energy transfer [7], fluorescence resonance energy transfer [8–10], and photoinduced electron transfer (PET). Currently, PET is an active field in supramolecular chemistry because of the 'fluorophore-spacer-receptor' format [11]. A number of $Hg^{2+}$-selective based PET fluorescent chemosensors have therefore been reported in recent years [12–16].

Although many chemosensors for $Hg^{2+}$ are successful, there are some factors, such as water insolubility, fluorescence quenching by many heavy- and transition-metal ions, interference by protons, cross-sensitivity toward other metal ions, and nonreversible responses, which limit their application in biological and environmental systems [14]. Thus, to overcome these disadvantages and further broaden their application, there is a great need for the development of improved simple chemosensors capable of detecting $Hg^{2+}$.

Among many fluorophores, naphthalimide has been widely used as a signaling handle for the design of functional supramolecules [17] because of its advantageous

optical characteristics, such as a large stokes shift, high fluorescence quantum yield, modest excitation and emission wavelengths, high photostability, and a high absorption coefficient [18–22]. We previously reported an $Hg^{2+}$-selective fluorescent chemosensor, which was composed of two aminonaphthalimide fluorophores and a 2,6-bis(aminomethyl)- pyridine receptor [13] and could be used for the real-time detection of $Hg^{2+}$ inside a single living cell [23]. However, other metal ions, such as $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$, and $Ag^{+}$, also caused slight fluorescence enhancement.

Based on our previous works, in this study, we report a novel PET fluorescent chemosensor, H1, which is composed of a naphthalimide fluorophore and a 6-[(quinolin-8-yloxy)methyl]pyridine-2-ylmethanamine receptor. This fluorescence chemosensor for $Hg^{2+}$ has effectively solved the problem of interferences from other transition-metal ions. In addition, it shows reversible and fast responses toward $Hg^{2+}$ in a neutral buffered aqueous solution.

## Experimental Section

### Apparatus and Reagents

Fluorescence steady state spectra and fluorescence lifetime were obtained on a Hitachi F-4500 (Tokyo, Japan) and Edinburgh instruments FLS920 (Livingston, UK), respectively. UV–vis absorption spectra were measured on a Puxi TU-1901 (Beijing, China) spectrophotometer. All pH measurements were made with a Sartorius basic pH-meter PB-10 (Göttingen, Germany). $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AV-400 spectrometer with chemical shifts recorded as ppm (in $CDCl_3$, TMS as internal standard). Infra-red spectral data were measured with Nicolet Avatar-370. Mass spectral analyses were carried out on an Agilent 6310 ESI-Ion Trop Mass spectrometer (Santa Clara, CA, USA).

A stock solution of 50 mM $Hg^{2+}$ was prepared in double-distilled water. A 0.1M HEPES buffer solution (pH 7.2) was used. Double-distilled water was used throughout the experiments. All chemicals were purchased from commercial suppliers and used without further purification. N-butyl-4-butylamino- 1,8-naphthalimide ($\Phi_s$=0.81) in absolute ethanol was used as a quantum yield standard [21]. The fluorescence quantum yield ($\Phi_{fl}$) was calculated using the relative method according to the equation:

$$\Phi_{fl} = \Phi_s \times (F/F_s) \times (A_s/A) \times (n/n_s)^2$$

Where $\Phi_s$ is the reported quantum yield of the standard, $F$ and $F_s$ are the area of sample and standard solutions under the emission spectra, $A$ and $A_s$ are the absorbance of sample and standard solutions at the excitation wavelength (390 nm), respectively; $n_s$ and $n$ are refractive indexes of ethanol and methanol–water (1:9, *v*/*v*) solution, respectively.

### General Procedure for H1 Synthesis

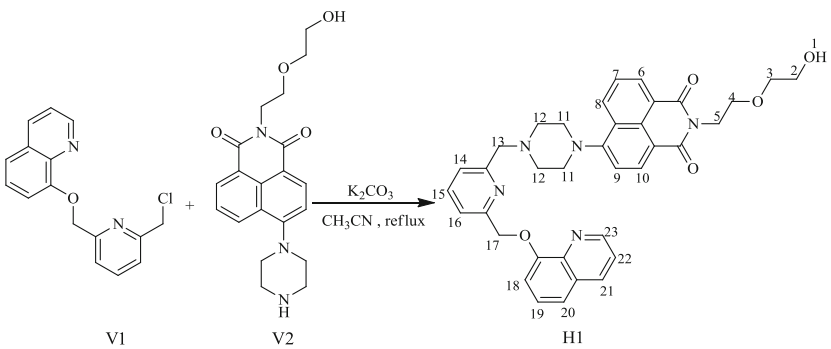
The chemosensor (H1) was synthesized from 2-chloromethyl-6-[(quinolin-8-yloxy)methyl]pyridine (V1) and 4-(piperazin-1-yl)-*N*-[(2-(2-hydroxyl)ethoxy)ethyl]-1,8-naphthalimide (V2) [24], as follows (Scheme 1).

V1 (0.15 g, 0.52 mmol) and V2 (0.22 g, 0.60 mmol), in the presence of $K_2CO_3$ (0.11 g, 0.80 mmol) were dissolved in 15.0 mL of dry acetonitrile. The reaction mixture was stirred under a nitrogen atmosphere and heated under reflux for 5 h. After removal of the solvent, the residue was purified by silica column chromatography with $CHCl_3$/methanol to afford H1 as 0.28 g (yield: 87 %) of a yellow oil. The structure of H1 was characterized by infra-red, $^1$H NMR, $^{13}$C NMR and electrospray ionization mass spectrometry (ESI-MS).

*IR (KBr)* $\nu$ 3353.4, 2926.0, 2854.8, 1687.7, 1649.3, 1572.6, 1539.7, 1506.8, 1457.5, 1375.3, 1315.1, 1232.9, 1189.0, 1117.8, 1084.9, 1052.1, 997.3, 821.9, 783.6, 750.9, 668.5 $cm^{-1}$.

*$^1$H NMR ($CDCl_3$, 400 MHz)* $\delta$ *(*$10^{-6}$)* 2.58 (br, 1-H, 1H), 2.89 (br, 12-H, 4H), 3.35 (br, 11-H, 4H), 3.67-3.69 (m, 2-H, 3-H, 4H), 3.84 (t, 4-H, $J$ = 5.4 Hz, 2H), 3.87 (s, 13-H, 2H), 4.44 (t, 5-H, $J$ = 5.4 Hz, 2H), 5.58 (s, 17-H, 2H), 7.08 (dd, 18-H, $J_1$ = 2.0 Hz, $J_2$ = 6.8 Hz, 1H), 7.22 (d, 9-H, $J$ = 8.0 Hz, 1H), 7.36-7.43 (m, 14-H, 19-H, 20-H, 3H), 7.46 (dd, 22-H, $J_1$ = 4.0 Hz, $J_2$ = 8.4 Hz, 1H), 7.58 (d, 16-H, $J$ = 7.6 Hz, 1H), 7.69 (t, 7-H, 15-H, $J$ = 7.4 Hz, 2H), 8.15 (dd,

**Scheme 1** Synthesis of H1



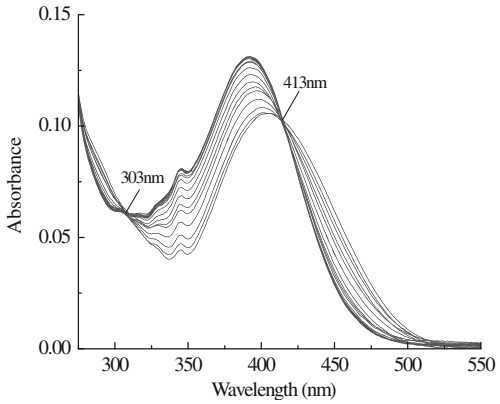



**Fig. 1** The absorption responses of H1 (10 μM) upon addition of $Hg^{2+}$ in HEPES buffered aqueous solution (methanol/water = 1:9, *v/v*, pH 7.2)

21-H, $J_1$ = 1.6 Hz, $J_2$ = 8.4 Hz, 1H), 8.43 (d, 8-H, $J$ = 8.4 Hz, 1H), 8.52 (d, 6-H, $J$ = 8.4 Hz, 1H), 8.59 (d, 10-H, $J$ = 7.2 Hz, 1H), 9.00 (dd, 23-H, $J_1$ = 1.6 Hz, $J_2$ = 4.4 Hz, 1H).

*$^{13}C$ NMR ($CDCl_3$, 100 MHz) δ (*$10^{-6}$)* 39.59, 53.29, 53.68, 62.12, 64.67, 68.79, 71.81, 72.45, 110.00, 115.18, 116.64, 120.25, 120.38, 121.99, 122.46, 123.29, 125.89, 126.38, 126.82, 129.79, 130.24, 130.84, 131.60, 133.12, 136.20, 137.69, 140.64, 149.74, 154.34, 156.48, 157.08, 157.91, 164.60, 165.09.

*ESI MS m/z* $[M+H]^+$ Calcd. 618.27, Found 618.0.

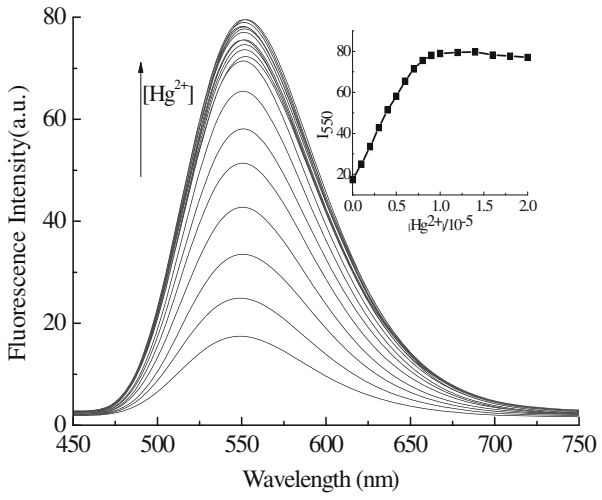



**Fig. 2** The fluorescence responses of H1 (10 μM) upon addition of $Hg^{2+}$ in HEPES buffered aqueous solution (methanol/water = 1:9, *v/v*, pH 7.2). Excitation wavelength was set at 390 nm with excitation and emission slit at 1.0/5.0 nm

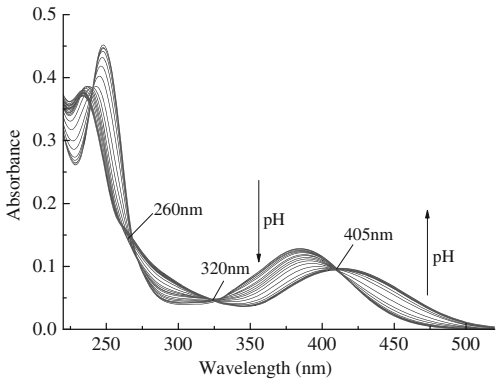



**Fig. 3** UV–vis absorption spectra of H1 (10 μM) upon influence of pH in aqueous solution (methanol/water = 1:9, *v/v*)

## Results and Discussion

### $Hg^{2+}$-Titration and Spectral Responses

The changes in UV–vis spectra of H1 with the gradual addition of $Hg^{2+}$ in a buffered aqueous solution (pH 7.2) were investigated (Fig. 1). The absorption band appeared at 405 nm ($\varepsilon$=1.1×$10^4$ $M^{-1}$·$cm^{-1}$) was observed in the absence of $Hg^{2+}$. When $Hg^{2+}$ (0–2 equiv) was added to a solution of H1 (10 μM) in methanol–water (1:9, *v/v*), the band centered at 405 nm progressively shifted to 390 nm ($\varepsilon$=1.3×$10^4$ $M^{-1}$·$cm^{-1}$), indicating that the electron-donating nitrogen atoms of the receptor, in the ground state, participated in H1/$Hg^{2+}$ complexation. The presence of two isosbestic points, at 303 nm and 413 nm, indicated the coexistence of free H1 and the H1/$Hg^{2+}$complex.

The changes in the emission spectrum of H1 (10 μM) and the intensity, monitored at 550 nm, with stepwise addition of $Hg^{2+}$ is showed in Fig. 2. At first, H1 has a weak fluorescent intensity ($\Phi_0$=0.13). The fluorescence intensity of H1 increased significantly upon gradual addition of $Hg^{2+}$. In contrast, this emission ($\Phi$=0.42) was saturated by ≥1 equiv of

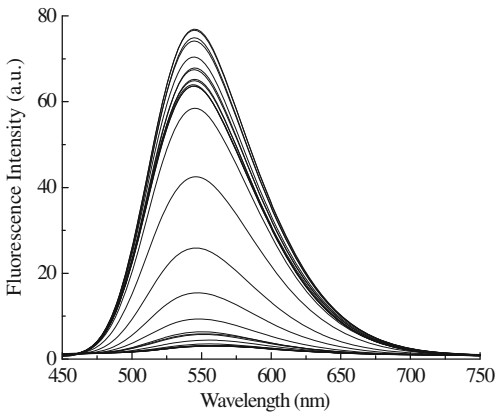



**Fig. 4** Fluorescence spectra of H1 (10 μM) upon influence of pH in aqueous solution (methanol/water = 1:9, *v/v*). Excitation wavelength was set at 390 nm with excitation and emission slit at 1.0/5.0 nm

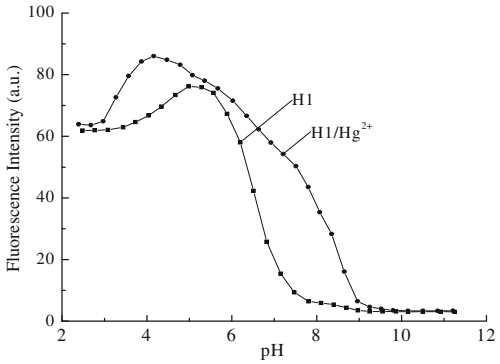



**Fig. 5** pH titration profiles of the H1 and H1/$Hg^{2+}$ complex in aqueous solution (methanol/water = 1:9, *v*/*v*). Excitation wavelength was set at 390 nm with excitation and emission slit at 1.0/5.0 nm

$Hg^{2+}$. Significantly, the intensity at 550 nm increased linearly with the $Hg^{2+}$ concentration, which indicated that H1 could potentially be used for the quantitative determination of $Hg^{2+}$. The linear equation was found to be y=4.3076 x+1.082 (linearly dependent coefficient: $R^2$=0.9914). The detection limit was calculated to be 63 nM (3σ/slope). This behavior is also diagnostic for a H1/$Hg^{2+}$formation of a complex with 1:1 stoichiometry. According to reported methods [25, 26], the associated constant was determined to be $1.11\times10^5$ $M^{-1}$.

## Effect of pH on Chemosensor Performance

The pH of the environment around the fluorescent chemosensor usually affects its performance because of protonation or deprotonation of the fluorophore [27]. The influence of pH on H1 was determined in methanol–water (1:9, *v*/*v*) solution. Figure 3 shows the UV–vis spectroscopic changes; there are three isosbestic points at 260 nm, 320 nm and 405 nm. The band centered at 385 nm progressively red shifted to 415 nm with increasing pH.

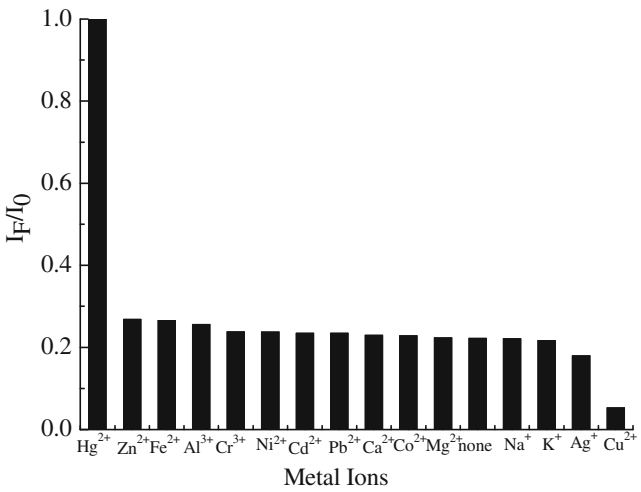



**Fig. 6** Fluorescence responses of H1 (10 μM) at 550 nm in HEPES buffered aqueous solution (methanol/water = 1:9, *v*/*v*, pH 7.2) after the addition of 50 μM of various metal ions. Excitation wavelength was set at 390 nm with excitation and emission slit at 1.0/5.0 nm

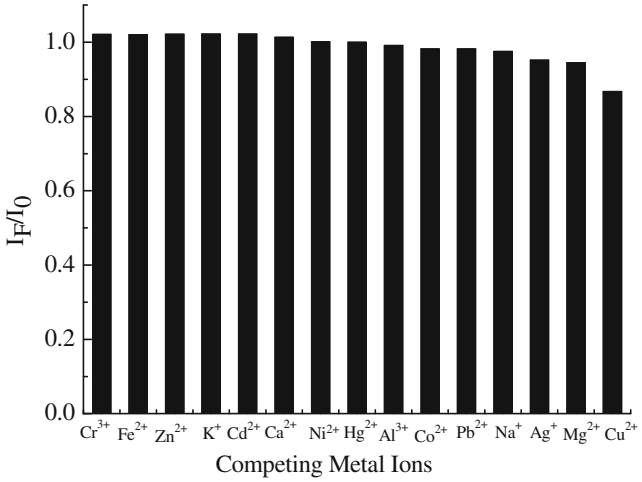



**Fig. 7** Fluorescence responses of H1 (10 μM) to $Hg^{2+}$ (50 μM) in the presence of other metal ions (50 μM) at 550 nm in HEPES buffered aqueous solution (methanol/water = 1:9, *v*/*v*, pH 7.2). Excitation wavelength was set at 390 nm with excitation and emission slit at 1.0/5.0 nm

The fluorescence responses of H1 (10 μM) in methanol/water solution (1:9, *v*/*v*) were adjusted with varying amounts of perchloric acid and NaOH (Fig. 4). The fluorescence intensity increased about 13-fold and the maximum emission wavelength blue-shifted from 560 nm to 545 nm with a pH decrease from 9.0 to 5.3. From pH 2.5 to 4.9, the fluorescence intensity of the H1 steadily increased (Fig. 5). H1 contains two main proton receptors, namely a piperazinyl group and a quinolinyl group. The receptors have sufficiently different p$K_a$ values (7.78 for N-benzoylpiperazine versus 4.60 for 8-methylquinoline as models) [28, 29] for them to be stepwise protonated. Gan et al. [30] have studied the luminescent properties and PET of naphthalimides with piperazine substituents; their studies suggested that the fluorescence intensity of the 4-amino-1,8-naphthalimide

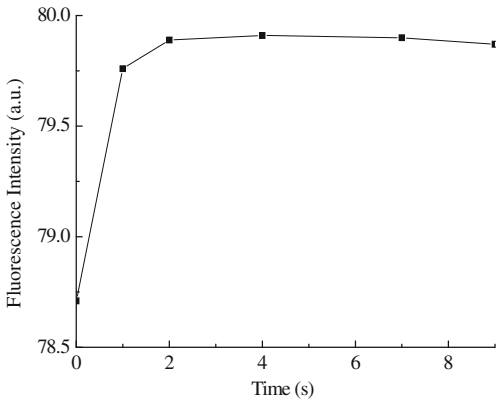



**Fig. 8** Time responses of H1 (10 μM) in the presence of $Hg^{2+}$ (50 μM) in HEPES buffered aqueous solution (methanol/water = 1:9, *v*/*v*, pH 7.2). Excitation wavelength was set at 390 nm with excitation and emission slits at1.0/5.0 nm

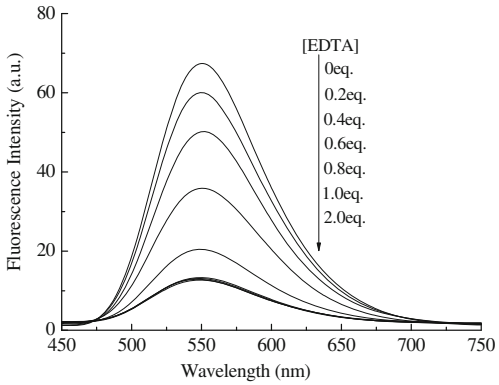



**Fig. 9** Fluorescence responses of H1/$Hg^{2+}$ upon addition of EDTA in HEPES buffered aqueous solution (methanol/water = 1:9, *v*/*v*, pH 7.2). Excitation wavelength was set at 390 nm with excitation and emission slits at 1.0/5.0 nm

fluorophore did not decrease under acid conditions. The quinoline moiety contains a pyridyl nitrogen group, which is able to act as a weak base under acidic conditions [31]. A PET quenching process from the fluorescent signaling unit to the quinolinium cation receptor is therefore responsible for the fluorescent properties of H1.

To study the applicability of H1, the effects of pH on the fluorescence response of H1/$Hg^{2+}$ were investigated. The experiments were carried out in the pH range 2.0–12.0, with the concentration of H1 fixed at 10 μM and that of $Hg^{2+}$ at 50 μM (Fig. 5). At pH values higher than 9.0, the fluorescence intensity of H1/$Hg^{2+}$ and that of H1 become closer to each other, probably because the formation of a hydroxo-complex of $Hg^{2+}$ is favored under these conditions [32]. From pH 9.0 to 4.0, the fluorescence intensity steadily increased, which

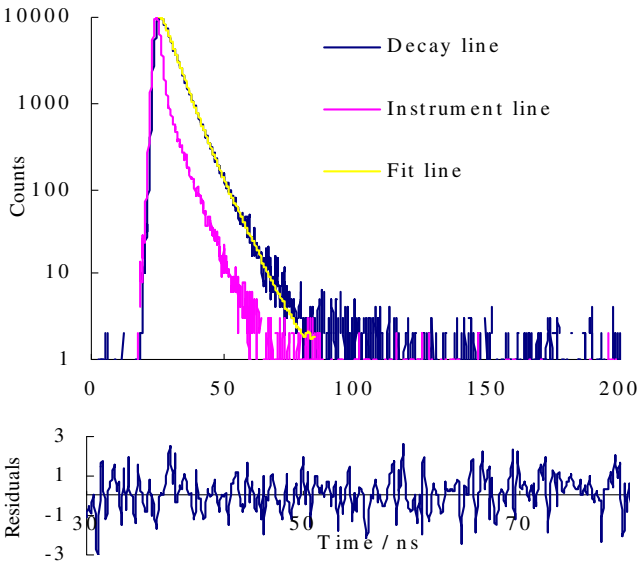



**Fig. 10** Fluorescence decay profile of H1 in HEPES buffered aqueous solution (methanol/water = 1:9, *v*/*v*, pH 7.2). Excitation and emission wavelength were set at 390/550 nm with excitation and emission slit at 13.0/13.0 nm

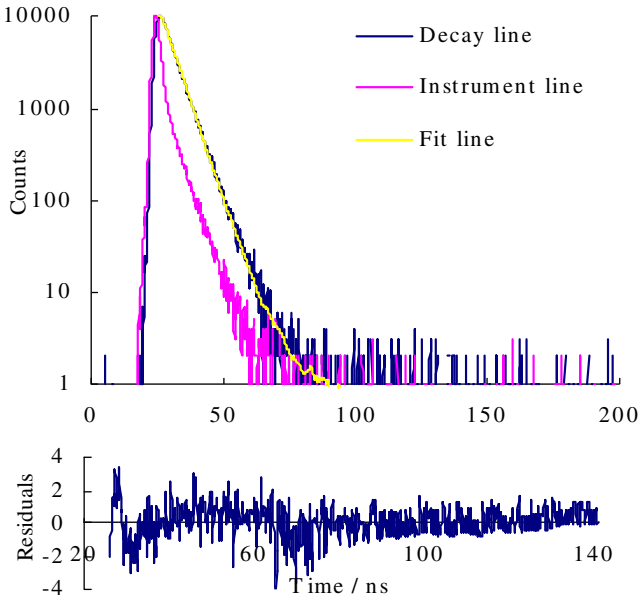



**Fig. 11** Fluorescence decay profile of H1/$Hg^{2+}$ in HEPES buffered aqueous solution (methanol/water = 1:9, *v*/*v*, pH 7.2). Excitation and emission wavelength were set at 390/550 nm with excitation and emission slit at 13.0/13.0 nm

indicated that H1 and $Hg^{2+}$ effectively formed a complex. However, when the pH decreased from 3.6 to 3.0, the fluorescence intensity decreased slightly; this might be attributable to the large number of protons transforming the quinolinyl group into a quinolinium cation [33, 34]. This behavior may not favor for the formation of H1/$Hg^{2+}$complexes. At pH< 3.0, the intensity returned to the original H1 value, indicating complete dissociation, and thus $Hg^{2+}$ no longer affected the fluorescence intensity of H1.

## Selectivity Studies

The selectivity of H1 for various metal ions was investigated. The selectivity of H1 for $Hg^{2+}$ over various other detected metal ions was high. Even chemically closely related metal ions (e.g., $Cd^{2+}$ and $Pb^{2+}$) did not quench or generate fluorescence (Fig. 6). H1 shows a very weak emission as a result of the efficient PET quenching of the excited state of the 4-amino-1,8-naphthalimide moiety by the lone pair of electrons on the nitrogen atom in piperazine. On adding $Hg^{2+}$, the fluorescence intensity of H1 increases 4-fold. The recognition process was shown to respond to $Hg^{2+}$

**Table 1** Fluorescence lifetimes of the chemosensor and its metal complex

| Compound | $\tau_1$(ns) | $\tau_2$(ns) | $\chi^2$ |
|---|---|---|---|
| H1 | 3.41 (86 %) | 7.12 (14 %) | 1.08 |
| H1-$Hg^{2+}$ | 3.83 (100 %) | – | 1.03 |

via inhibition of PET. This showed that H1 could discriminate $Hg^{2+}$ from other metal ions fluoroscopically.

Figure 7 shows the results of an experiment to explore further the use of H1 as an ion-selective fluorescent chemosensor for $Hg^{2+}$. The fluorescence changes in the chemosensor were highly specific for $Hg^{2+}$ in the presence of other abundant cellular metal ions (e.g., $Na^{+}$, $K^{+}$, $Mg^{2+}$, and $Ca^{2+}$), essential transition-metal ions in cells (e.g., $Zn^{2+}$, $Fe^{2+}$, $Co^{2+}$, and $Ni^{2+}$), and environmentally relevant heavy metal ions (e.g., $Ag^{+}$, $Pb^{2+}$, $Cr^{3+}$, and $Cd^{2+}$). Excess amounts of these metal ions were added to 50 μM $Hg^{2+}$ in a buffered methanol/water (1:9, *v*/*v*) solution and the fluorescence responses of the chemosensor were detected and then compared with that of a buffer aqueous solution containing only 50 μM $Hg^{2+}$. H1 showed almost unchanged responses to $Hg^{2+}$ before and after addition of other interfering metal ions. $Cu^{2+}$ had a low negative interference effect on this fluorescent assay for $Hg^{2+}$. These results indicate that H1 is highly selective and has great potential for biomedical and environmental applications.

### Response Time and $Hg^{2+}$ Binding Reversibility for H1

Besides high sensitivity and selectivity, achieving a short response time and a reversible response for the analyte of interest in a complex matrix is critical in chemosensor development [35]. We studied the response times and chemical reversibility of the binding of H1 with $Hg^{2+}$ in a buffered methanol/water (1:9, *v*/*v*) solution. The response time of the chemosensor to $Hg^{2+}$ was quick, and a stable reading could be obtained within approximately 2 min (see Fig. 8). In addition, because of the high stability of the EDTA-$Hg^{2+}$ complex (stability constant log $K_{EDTA\text{-}Hg}$=21.5) [36], it was expected that the addition of EDTA would liberate $Hg^{2+}$ from the metal-ligand complex, releasing free H1. As shown in Fig. 9, on addition of 2 equiv of EDTA (20 μM) to the $Hg^{2+}$ (10 μM) complex of H1 (10 μM) in buffered methanol/water (1:9, *v*/*v*) solution, a significant decrease in the fluorescence signal at 550 nm was observed. These results demonstrated that the $Hg^{2+}$ binding of H1 in buffered aqueous solution is chemically reversible. The chemosensor could therefore be used for real-time tracking of $Hg^{2+}$ in biological samples.

### Time-Resolved Fluorescence Studies

The exponential decay profiles of H1 and H1/$Hg^{2+}$ were investigated. Figure 10 and 11 show fitting of the decay traces by deconvolution, taking into account the instrument impulse [37]. The fluorescence lifetime data of H1 and H1/$Hg^{2+}$ in buffered methanol/water (1:9, *v*/*v*) solution are listed in Table 1. The goodness of fit was characterized by $\chi^2$ values of 1.08 and 1.03. In this study, direct excitation into the 4-amino-1,8-naphthalimide band ($\lambda_{ex}$=390 nm) and selective observation at 550 nm led, as expected, to very similar average lifetimes for the 1,8-naphthalimide fluorophore in H1 and in H1/$Hg^{2+}$.

For simplicity, the average lifetimes $\tau_{av}$, obtained using Eq. (1) ($\alpha_i$ is the weighted pre-exponential factor), were calculated [38].

$$\tau_{av} = \sum_{i=1}^{n} \alpha_i \tau_i \text{ with } \sum_{i=1}^{n} \alpha_i = 1 \quad (1)$$

For H1, $\tau_{av}$ is 3.93 ns [$\tau_1$ 3.41 ns (86 %), $\tau_2$ 7.12 ns (14 %)]; after formation of H1/$Hg^{2+}$ complex, the fluorescence lifetime ($\tau$) is 3.83 ns (100 %). To better understand the fluorescence lifetime, further work aimed at investigating the intramolecular interactions between 1,8-naphthalimide and quinoline is under way, as well as the development of materials for Hg-contamination treatment

## Conclusions

In summary, we designed and synthesized a novel fluorescent chemosensor based on the PET mechanism. The chemosensor exhibits reversible and fast responses toward $Hg^{2+}$ in a buffered aqueous solution. In addition, this fluorescence chemosensor for $Hg^{2+}$ has effectively solved the problem of interferences from other transition-metal ions. Furthermore, H1 is capable of quantitative detection of $Hg^{2+}$ via a turn-on fluorescent response, with a linear range 0–10 μM; the detection limit was calculated to be 63 nM. The fluorescence quantum yield and lifetime of H1/$Hg^{2+}$ were 0.42 and 3.83 ns, respectively. These selective and sensitive results may lead to the potential applications in managing environmental pollution and detecting biomedical samples.

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