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ORIGINAL PAPER

A Fluorescence Turn-on Sensor for Hg^{2+} with a Simple Receptor Available in Sulphide-Rich Environments

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Abstract Detection of Hg^{2+} in complex natural environmental conditions is extremely challenging, and no entirely successful methods currently exist. Here we report an easy-to-prepare fluorescent sensor **B3** with 2-aminophenol as Hg^{2+} receptor, which exhibits selective fluorescence enhancement toward Hg^{2+} over other metal ions. Especially, the fluorescence enhancement was unaffected by anions and cations existing in environment and organism. Moreover, **B3** can detect Hg^{2+} in sulphide-rich environments without cysteine, S^{2-} or EDTA altering the fluorescence intensity. Consequently, **B3** is capable of distinguishing between safe and toxic levels of Hg^{2+} in more complicated natural water systems with detection limit ≤2 ppb.

Keywords Fluorescent sensor · 2-aminophenol · Hg^{2+} · Sulphide-rich environments

Introduction

Hg^{2+}, a highly toxic heavy metal ion, seriously threatens many environmental and biological systems [1]. Today, mercury is present in daily life, such as in thermometers, batteries and electronic equipment [2–4]. The misuse of these products can lead to mercury leaks. Other sources such as volcanic emissions, combustion of fossil fuels, especially mining [5], also cause high concentrations of mercury in many environmental compartments [6] and a number of human health problems [2, 7]. These environmental and biological problems have prompted the development of methods for the detection and quantification of mercury, especially in situations where conventional techniques are not appropriate.

Recently, considerable efforts have been made to design Hg^{2+} fluorescent sensors with high sensitivity and selectivity, quick response time and easy signal detection. There are fluorescent probes based on different inorganic nanoparticles [8–13]. Main examples are organic molecules such as rhodamine or 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) based fluorescent turn-on sensors [14–23], a ratiometric fluorescent probe based on FRET [24, 25], a colorimetric sensor based on ruthenium complexes [26] and chemodosimeters based on mercury ion-promoted hydrolysis [27, 28]. Since most of these sensors tended to make use of the thiophilic property of mercury to design mercury ligands, they often contain sulphur atoms in their ligands. However, some mercapto containing biomolecules in organisms could form stable complexes with Hg^{2+} [29], and there has been little discussion of how to avoid interference from sulfide in organisms or from sulfur-rich environments, preventing them from being applicable in natural environmental conditions.

Therefore, we are still facing the challenge for the exploration of new fluorescent turn-on probes with new, simpler ligands applicable in environmental conditions. Due to properties such as a large molar extinction coefficient (ε), high fluorescence quantum yield (Φ) and insensitivity to solvent polarity and pH, BODIPY-based dyes have been used as efficient fluorescent sensors for different analytes [30–35] including our two Hg^{2+} fluorescent sensors **B1** [36] and **B2** [37]. Furthermore, 2-aminophenol has been proved to form a stable complex with Hg^{2+} in ethanol solution [38]. Therefore, herein we report a highly selective and sensitive fluorescence BODIPY-based turn-on sensor **B3** for Hg^{2+}, by introducing the very simple Hg^{2+} ligand, aminophenol, into BODIPY. In this molecule, $-NH_2$ is on the para-phenyl

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substitute, which can cause more efficient photo-induced electron transfer (PET) process from nitrogen to BODIPY. The compound is easy to be obtained by two steps via compound **2** and performs well in natural environmental conditions without sulphur element interference.

Experimental

Materials and Apparatus

All the chemicals and solvents were of analytical quality. The listed cations and anions were used in addition to Hg^{2+} to test the specificity: Na^+, K^+, Ca^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Mg^{2+}, Pb^{2+}, Ag^+, Cu^{2+}, Cr^{3+} and Zn^{2+}; NO_3^-, CH_3COO^-, SCN^-, ClO_4^-, CO_3^{2-}, $H_2PO_4^-$, Cl^-, and SO_4^{2-}, respectively. All the salts were then dissolved in distilled water. NMR spectra were recorded on a VARIAN INOVA-400 spectrometer with chemical shifts reported as ppm (in $CDCl_3$, TMS as internal standard). Mass spectral determinations were made on a HP1100LC/MSD mass spectrometer and a LC/Q-TOF MS spectrometer. Fluorescence measurements were performed on a VARIAN CARY Eclipse Fluorescence Spectrophotometer (Serial No. FL0812-M018) and the slit width was 5 nm for excitation and emission. Absorption spectra were measured on Lambda 35 UV/vis spectrophotometer. The pH measurements were recorded by PHS-SC instrument.

$$\Phi_{unk} = \Phi_{std} \frac{(I_{unk}/A_{unk})}{I_{std}/A_{std}} \left(\frac{n_{unk}}{n_{std}}\right)^2 \quad (1)$$

The fluorescence quantum yield was determined using optically matching solutions of rhodamine6G (Φ_f=0.94 in ethanol) as standard at an excitation wavelength of 500 nm, and the quantum yield is calculated using Eq. (1) [39] where Φ_{unk} and Φ_{std} are the radiative quantum yields of the sample and the standard, I_{unk} and I_{std} are the integrated emission intensities of the corrected spectra for the sample and the standard, A_{unk} and A_{std} are the absorbances of the sample and the standard at the excitation wavelength (500 nm in all cases), and n_{unk} and n_{std} are the indices of refraction of the sample and the standard solutions, respectively. Excitation and emission slit widths were modified to adjust the luminescent intensity in a suitable range. All the spectroscopic measurements were performed at least in triplicate and averaged.

Synthesis of Compound **2**

2,4-dimethylpyrrole (190 mg, 2 mmol) and 3-hydroxy-4-nitrobenzaldehyde (167 mg, 1 mmol) were dissolved in dry CH_2Cl_2 (150 mL) under nitrogen. One drop of trifluoroacetic acid (TFA) was added, and the solution was stirred for 5 h at room temperature. After the mixture was concentrated to 30 mL, a solution of 2,3-dichloro-5,6-dicyanoquinone (DDQ, 442 mg, 2 mmol) in 10 mL of CH_2Cl_2 was added and stirring was continued for 15 min, followed by the addition of triethylamine (2 mL) and BF_3•OEt_2 (4 mL). After stirring for another 45 min, the reaction mixture was washed with 50 mL water, extracted with dichloromethane (3×20 mL). The extract was dried over anhydrous magnesium sulfate and then concentrated under vacuum. The product was purified by flash column chromatography using petrol ether/ethyl acetate (5:1, v/v) as eluent, yielding compound **2** as red solid (88 mg, 23%). ^{1}H NMR (400 MHz, $CDCl_3$), δ:10.67(s, 1H), 8.26(d, 1H, *J*=8.0 Hz), 7.18(s, 1H), 6.98(d, 1H, *J*=8.0 Hz), 6.02(s, 2H), 2.56(s, 6H), 1.50(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 156.75, 155.42, 144.88, 142.48, 137.64, 133.65, 130.21, 126.07, 121.82, 120.37, 29.70, 14.67; TOF MS(ES): m/z calcd for 384.1331 (M-H^+), found: 384.1349.

Synthesis of Compound ***B3***

Compound **2** (100 mg, 0.26 mmol) was dissolved in 10 mL of methanol. H_2O (5 mL) and Fe (500 mg, 8.9 mmol) were added and the reaction mixture was heated to reflux. Hydrochloric acid in a methanol solution (2 mL, 0.6 mol L^{-1}) was added dropwise. The solution was refluxed for 3 h until complete consumption of the starting material (TLC monitoring). After cooling to room temperature, filtration and concentration at reduced pressure, the product was purified by flash column chromatography using petrol ether/ethyl acetate (4:1,v/v) as eluent, yielding **B3** as red solid (77 mg, 83%).^{1}H NMR(400 MHz, $CDCl_3$), δ: 6.91(d, 1H, *J*=8.0 Hz), 6.62(s, 1H), 6.56(d, 1H, *J*=8.0 Hz), 6.04(s, 2H), 2.48(s, 6H), 1.58(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 154.99, 144.36, 143.33, 142.09, 135.43, 131.86, 125.15, 120.94, 116.84, 114.57, 29.7, 14.57; TOF MS (ES): m/z calcd for 354.1589(M-H^+), found: 354.1592.

Results and Discussions

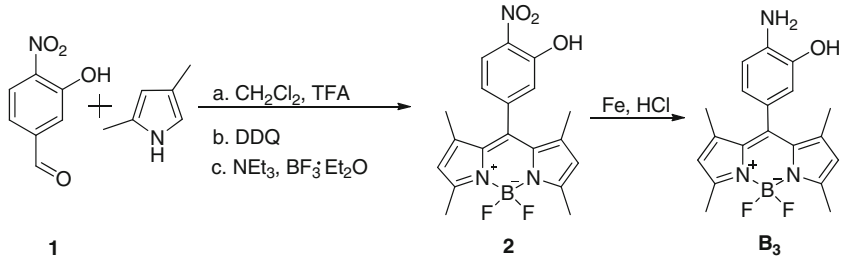
Synthese of **B3**

Scheme 1 outlines the synthetic route to **B3**. It was prepared in two steps. The TFA catalyzed condensation reaction of 3-hydroxy-4-nitrobenzaldehyde with 2,4-dimethylpyrrole gave compound **2**, which was reduced to give the target product **B3** [40]. Both compounds were confirmed by TOF-MS and NMR.

Fluorescence Detection of Hg^{2+} in Ethanol-Water Solution

The fluorescence and absorption studies were conducted in ethanol/HEPES buffer (20 mM HEPES, 100 mM $NaNO_3$, 1:1(v/v), pH=7.2). As expected, in the absence of Hg^{2+}, **B3** exhibited a very weak and characteristic BODIPY-like

Scheme 1 Synthetic procedures for **B3**



absorption at 495 nm with a corresponding emission maximum at 513 nm. The fluorescence quantum yield = 0.3%, indicative of efficient photo-induced electron transfer (PET) quenching from the receptor to BODIPY fluorophore [41].

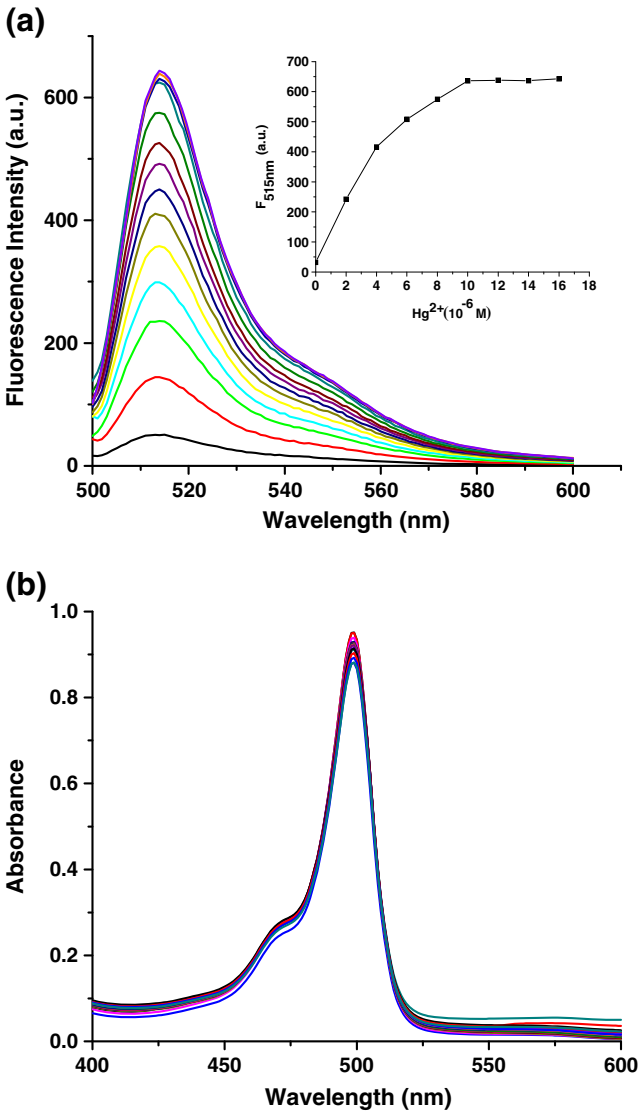


Fig. 1 Emission **a** and absorption **b** of **B3** (10 μM) to different concentrations of Hg^{2+} (0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 20 μM, the given concentrations correspond to the curves drawn from bottom to top of the images) with excitation at 495 nm in ethanol/HEPES buffer (20 mM HEPES, 100 mM $NaNO_3$, 1:1, v/v, pH 7.2). Inset **a**: saturation titration of **B3** (10 μM) with Hg^{2+}

Upon addition of Hg^{2+}, the fluorescence intensity increased by over 20-fold (Fig. 1a) without any shift in absorption spectrum (Fig. 1b). The saturation titration for **B3** (inset graph in Fig. 1a) reveals a 1:1 stoichiometry for the **B3**-Hg^{2+} complex [42]. The dissociation constant, $K_d = (7.78 \pm 0.4) \times 10^{-6}$ M, was obtained by plotting the fluorescence intensity (F/F_0) against [Hg^{2+}] [43].

The nitrate salts of Hg^{2+}, Na^+, K^+, Ca^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Mg^{2+}, Pb^{2+}, Ag^+, Cu^{2+}, Cr^{3+} and Zn^{2+} ions were used to evaluate the selectivity of metal ion binding properties of **B3** (Fig. 2). As expected, **B3** exhibited excellent fluorescence selectivity towards Hg^{2+} over all other alkali and alkaline earth metal ions, transition and heavy metal ions, although a slight fluorescence enhancement occurred with Ag^+. The competition experiments were conducted in the presence of Hg^{2+} mixed with metal ions at 50 μM mentioned above (Fig. 3a). The fluorescence emission profiles were unaffected by other metal ions except for a slight quenching by Ag^+ and Cu^{2+}.

The effect of anions must be considered when evaluating the response of fluorescent metal ion sensors. Lippard's group has proposed that formation of an Hg-Cl bond or

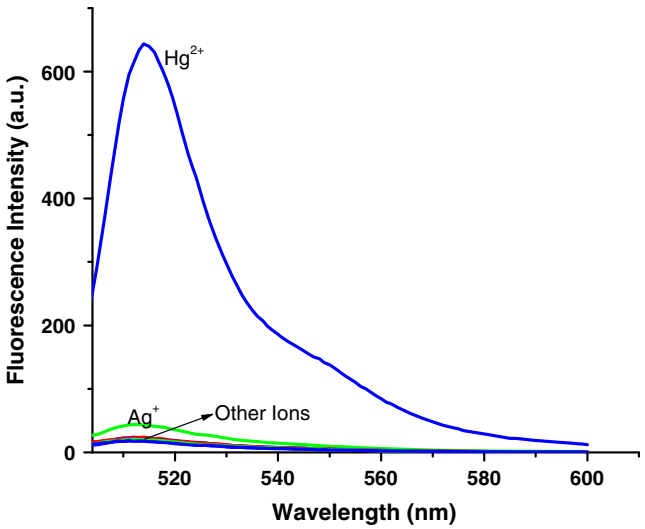


Fig. 2 Fluorescence spectra of **B3** (10 μM) in the presence of different metal ions (50 μM) in ethanol/HEPES buffer (20 mM HEPES, 100 mM $NaNO_3$, 1:1, v/v, pH 7.2) solution. Excitation: 495 nm. Other ions: Na^+, K^+, Ca^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Mg^{2+}, Pb^{2+}, Cu^{2+}, Cr^{3+} and Zn^{2+}

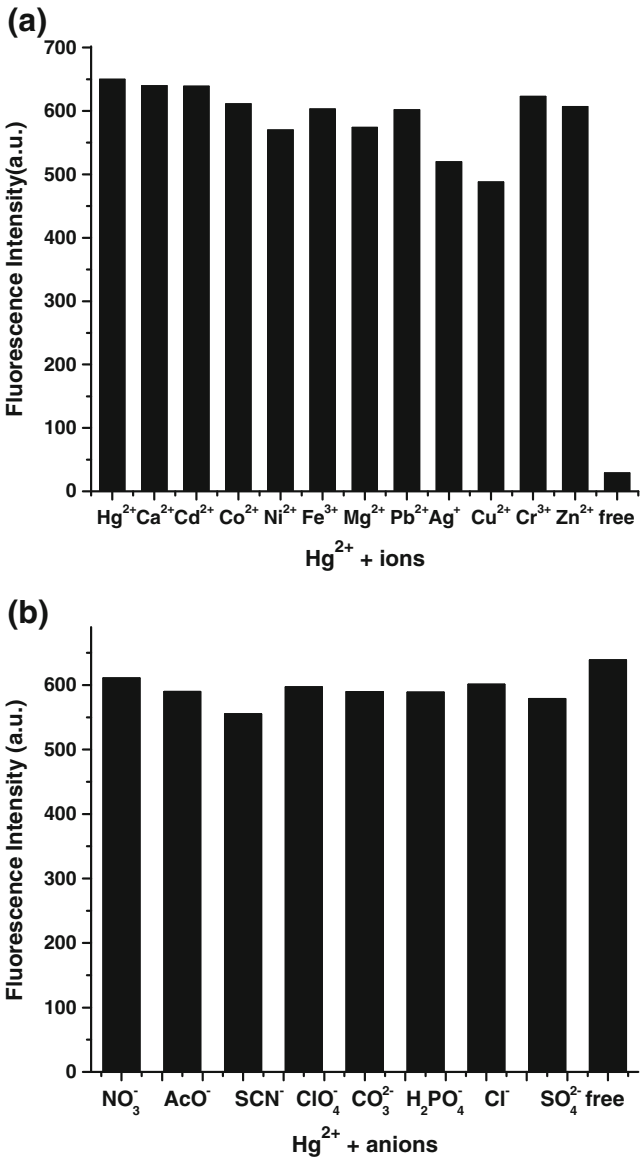


Fig. 3 **a** Fluorescence responses of **B3** (10 μM) to Hg^{2+} (50 μM) in the presence of selected metal ions (50 μM) in ethanol/HEPES buffer (20 mM HEPES, 100 mM $NaNO_3$, 1:1, v/v, pH 7.2) solution. **b** The fluorescence responses of **B3** (10 μM) containing 50 μM Hg^{2+} to the selected anions (50 μM) in ethanol/HEPES buffer (20 mM HEPES, 100 mM $NaNO_3$, 1:1, v/v, pH 7.2) solution. Excitation was provided at 495 nm and emission was integrated from 500 to 600 nm

strong ion-pairing will influence the fluorescence turn-on degree in these systems [44–46]. Lee [47] and our group [36] have also found that anions can control the fluorescence enhancement through formation of endo- or exo-metal complexes with Hg^{2+}. So we investigated the fluorescence response of **B3** toward Hg^{2+} in the presence of sodium salts of various anions such as NO_3^-, CH_3COO^-, SCN^-, ClO_4^-, CO_3^{2-}, $H_2PO_4^-$, Cl^-, and SO_4^{2-}. None of the anions gave rise to interference (Fig. 3b) which suggest that **B3** is applicable in complicated environmental samples.

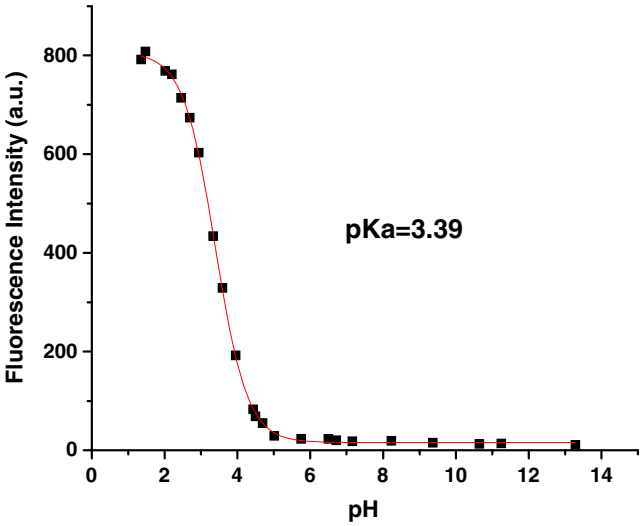


Fig. 4 Dependence of the fluorescence intensity of free **B3** on pH in ethanol/HEPES buffer (20 mM HEPES, 100 mM $NaNO_3$, 1:1, v/v, pH 7.2) solution. [**B3**]=10 μM, Excitation was provided at 495 nm and emission was integrated from 500 to 600 nm

It is known that the pH-insensitivity of fluorescence in near neutral and weakly acidic media is of importance for environmental and biological analyses. The common disadvantage of PET-based sensors is the interference of a proton, which also binds with the coordinate site, inhibits the PET process and enhances the fluorescence. In this case, the fluorescence intensity of free **B3** reached a steady minimal value when pH>5.0. The switching is reversible. This also demonstrates a typical PET fluorescence on/off effect. The resulting sigmoidal curve gives a p*K*a of **B3** is 3.39 (Fig. 4). This indicates that **B3** can work in near neutral and weakly acidic media, which is important for practical applications to environmental and biological analysis.

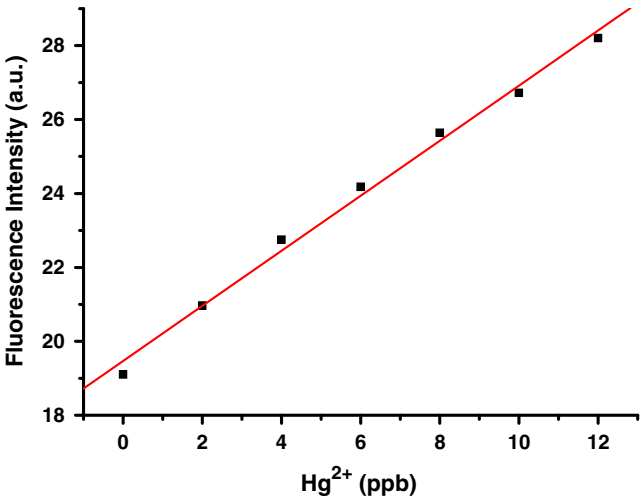


Fig. 5 The changes of fluorescence intensity of **B3** (5 μM) upon addition of Hg^{2+} (0–12 ppb) in ethanol/HEPES buffer (20 mM HEPES, 100 mM $NaNO_3$, 1:1, v/v, pH 7.2) solution

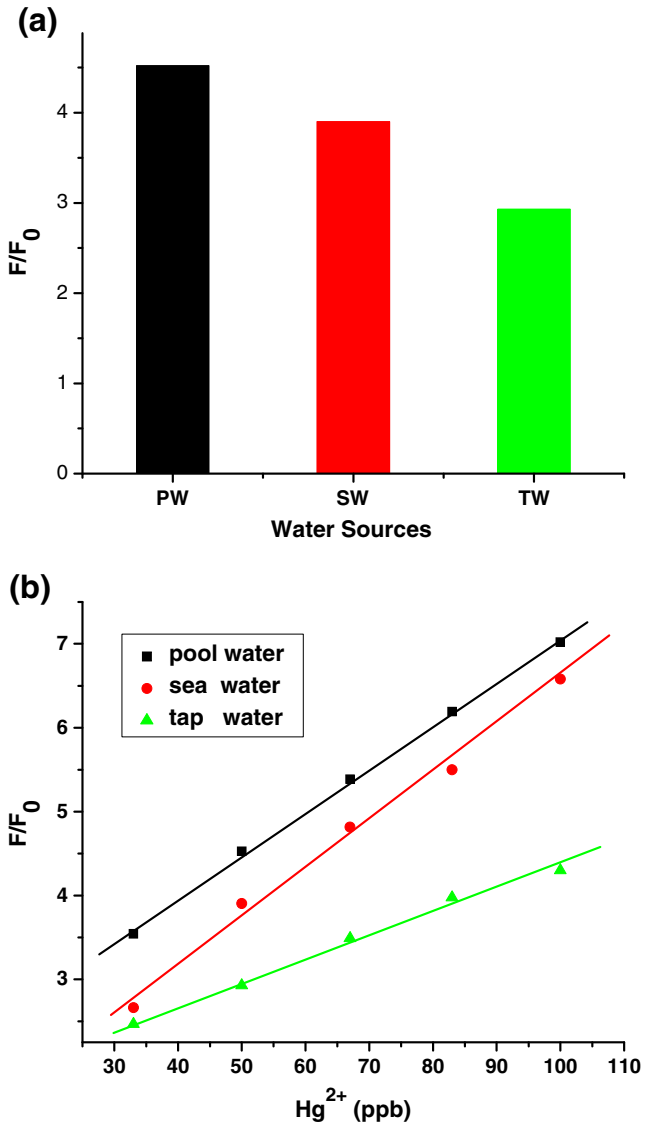


Fig. 6 **a** The linear fluorescence enhancement (F/F_0) of **B3** (10 μM) upon addition of Hg^{2+} to different natural water samples: pool water (PW, black circles), seawater (SW, red square), and tap water (TW, green triangles). The response (F) is normalized to the emission of the free **B3** (F_0). The samples were excited at 495 nm, and the emission intensities were recorded at 513 nm. **b** Fluorescence response of **B3** (10 μM) to Hg^{2+} (50 ppb) in different natural water samples

For a fluorescent molecular sensor to be practically applicable, the detection limit is important. As seen in Fig. 5, the fluorescence intensity of the **B3** solution was proportional to the amount of Hg^{2+} added in the range of ppb level (detection limit ≤2 ppb) indicating that **B3** can detect environmentally relevant concentrations of Hg^{2+}. **B3** is much more sensitive to Hg^{2+} than our previous sensors **B1** and **B2**.

Fluorescence Detection of Hg^{2+} in Natural Water Samples

A variety of natural and anthropogenic environmental contaminants pose serious problems for human health and ecology. Environmental application presents a unique set of challenges and requires detailed studies of sensor performance in the environmental samples [48]. Therefore, we next proceeded to test the sensor on natural water samples. All these studies were conducted on pure natural water without any organic solvent. We chose samples from three different sources: the seawater from Yellow Sea (Dalian, China), pool water and tap water. The Environmental Protection Agency (U.S. EPA) standard for the limit of inorganic Hg in industrial waste water is no more than 50 ppb [49]. As shown in Fig. 6a, about 3.9-fold (SW), 4.5-fold (PW), 2.9-fold (TW)enhancement of fluorescence intensity were displayed when 50 ppb of Hg^{2+} was added in water with **B3,** respectively. Furthermore, F/F_0 in natural water samples are linearly proportional to the amount of Hg^{2+} (Fig. 6b). The result shows that **B3** is capable of distinguishing between the safe and toxic levels of Hg^{2+} in more complicated natural water systems.

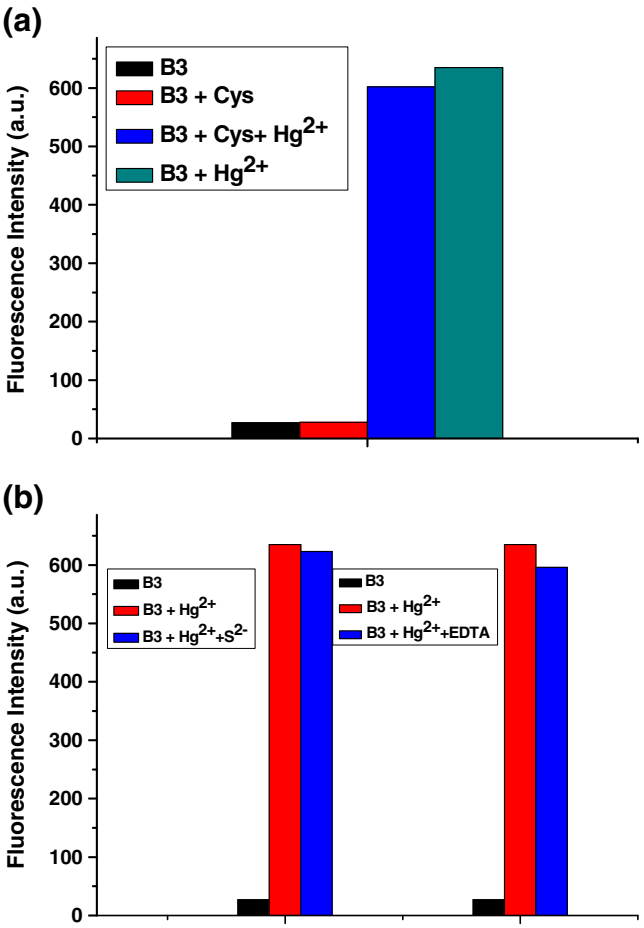


Fig. 7 **a** Fluorescence responses of **B3** (10 μM) to Hg^{2+} (50 μM) in the presence of cysteine (50 μM) in ethanol/HEPES buffer (20 mM HEPES, 100 mM $NaNO_3$, 1:1, v/v, pH 7.2) solution. **b** Fluorescence spectral changes of **B3**-Hg^{2+} upon addition of excess S^{2-}(50 μM) and EDTA (50 μM) ethanol/HEPES buffer (20 mM HEPES, 100 mM $NaNO_3$, 1:1, v/v, pH 7.2) solution

Fluorescent Detection of Hg^{2+} in Sulfur-Rich Environments

It was known that cysteine could form a stable complex with Hg^{2+} [44–47]. Therefore, for the next detection of Hg^{2+} in sulfur-rich environment, we investigated the effect of cysteine on the detection of Hg^{2+} in buffer solutions. As a comparison, we also investigated the effect of S^{2-} and EDTA.

As shown in Fig. 7a, when added Hg^{2+} (50 μM) into the mixed solution of **B3** (10 μM) and cysteine (50 μM), the obvious fluorescence enhancement (blue bar) was observed, which is very close to the enhancement induced by Hg^{2+} only (grey bar). When added S^{2-} (50 μM) and EDTA (50 μM) into the solution of **B3**-Hg^{2+}, respectively (Fig. 7b), the fluorescence enhancement only showed a slight change, indicating that the complex **B3**-Hg^{2+} was very stable and that the sensor **B3** could detect Hg^{2+} in the sulfur-rich environment.

Conclusions

We have demonstrated a BODIPY derivative **B3** as a fluorescence turn-on sensor for Hg^{2+}. This sensor exhibits very high selectivity and sensitivity for Hg^{2+} in the presence of various metal ions and anions in the aqueous solution. Moreover, it also performed well in natural conditions and sulfur-rich environments. Due to these excellent properties, **B3** can be further applied for the detection of Hg^{2+} in really environmental samples.

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