

# Highly Selective and Anions Controlled Fluorescent Sensor for $\text{Hg}^{2+}$ in Aqueous Environment

Jianjun Du · Jiangli Fan · Xiaojun Peng · Honglin Li · Jingyun Wang · Shiguo Sun

Received: 24 September 2007 / Accepted: 22 January 2008 / Published online: 12 February 2008  
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**Abstract** A highly selective PET fluorescent sensor **B1** for  $\text{Hg}^{2+}$  containing a BODIPY fluorophore and a  $\text{NS}_2\text{O}_2$  penta-chelating receptor has been synthesized and characterized. Its absorption maximum wavelength (498 nm) and emission maximum wavelength (512 nm) are both in the visible range. The fluorescence quantum yields of the **B1** and  $\text{Hg}^{2+}$ -bound states of **BHg1** are 0.008 and 0.58 in 70% aqueous ethanol solution, respectively. The  $\text{pK}_a$  of 1.97 is the lowest in metal ions PET chemo sensors reported up till now as we know. Thus, **B1** can detect the  $\text{Hg}^{2+}$  in a wide pH span, which indicates that it has more potential and further practical applications for biology and toxicology. Furthermore, **BHg1** also displays response to some anions such as  $\text{Cl}^-$  ( $\text{Br}^-$ ),  $\text{CO}_3^{2-}$ ,  $\text{SCN}^-$  and  $\text{CH}_3\text{COO}^-$ , which is attributed to the significant coordinating ability of these anions to  $\text{Hg}^{2+}$ .

**Keywords** Mercury · Sensor · Fluorescence · Anions

## Introduction

Mercury is one of the most toxic and dangerous heavy metal elements [1–3], and its contamination is widespread and occurs through various processes, e.g. volcanic emissions, mining, solid waste incineration, and the combustion of fossil fuels [4–6]. Of particular concern, is the concentration in the food chain, and bioaccumulation of mercury in animals [7–9]. It is frightening that mercury-

containing chemicals have been linked with a number of human health problems, including minamata, myocardial infarction, and some kinds of autism, and can lead to damage of the brain, kidneys, central nervous system, immune system and endocrine system [10, 11]. Thus much attention has been focused on developing new methods to monitor  $\text{Hg}^{2+}$  in biological and environmental samples.

The usual methods for determination of total mercury are atomic absorption spectroscopy [12] and inductively coupled plasma mass spectrometry [13]. These often require expensive and sophisticated instrumentation or sample preparation. So a variety of selective  $\text{Hg}^{2+}$  sensors were devised using multifarious strategies like redox-active [14, 15], fluorogenic [16–18], and chromogenic [19, 20] chemosensors.

Recently, much effort has been made to design  $\text{Hg}^{2+}$  fluorescent sensors with high sensitivities and selectivities, quick response times and easy signal detection [21–24], in which both the thioether-rich-metal-binding  $\text{NS}_2$  [25–27] and the macrocycles of  $\text{NS}_2\text{O}_2$  or  $\text{NS}_4$  [30–32] were used as receptors for  $\text{Hg}^{2+}$ . However, there are some important factors which limit their application in biological and environmental systems: (1) their fluorescence is often quenched by many heavy and transition metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  [33, 34]; (2) poor solubilities in aqueous solution; (3) interference by protons; (4) interference from other competing metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ; (5) low fluorescence enhancement for  $\text{Hg}^{2+}$  and background fluorescence interference from organisms. Herein, we report a new  $\text{Hg}^{2+}$  sensor **B1**, which shows large fluorescence enhancement (160-fold), and quick binding respond to  $\text{Hg}^{2+}$  in aqueous ethanol solution. We chose Boradiazaindacene (BODIPY) as the fluorophore because of its outstanding photophysical properties such as visible absorption and emission with high quantum yield, large extinction coefficient, good photo-stability and successful

J. Du · J. Fan (✉) · X. Peng (✉) · H. Li · J. Wang · S. Sun  
State Key Laboratory of Fine Chemicals,  
Dalian University of Technology,  
158 Zhongshan Road,  
Dalian 116012, People's Republic of China  
e-mail: fanjl@dlut.edu.cn  
e-mail: pengxj@dlut.edu.cn

application in sensors [35–39]. The NS<sub>2</sub>O<sub>2</sub> chelate receptor could both bring excellent selectivity for Hg<sup>2+</sup> and water solubility of **B1**. It is interesting that **B1** system frequently results in the co-occurrence of multiple phenomena, some of which may involve both Hg<sup>2+</sup> and anions [31].

## Experimental

### Materials and general methods

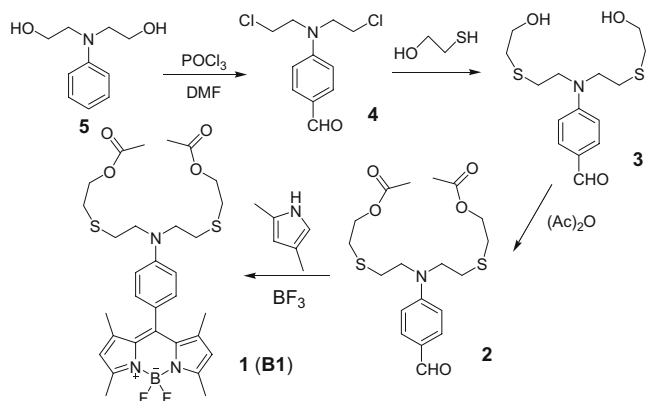
All the solvents were of analytical grade. The solutions of metal ions were prepared from 50% Mn(NO<sub>3</sub>)<sub>2</sub>, Pb(ClO<sub>4</sub>)<sub>2</sub> · 8H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, Zn(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O, Ca(NO<sub>3</sub>)<sub>2</sub>, NaNO<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, KNO<sub>3</sub>, Cd(NO<sub>3</sub>)<sub>2</sub> · 2H<sub>2</sub>O, AgClO<sub>4</sub>, Hg(ClO<sub>4</sub>)<sub>2</sub> · xH<sub>2</sub>O, Cr(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, respectively, and were dissolved in distilled water. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a VARIAN INOVA-400 spectrometer with chemical shifts reported as ppm (in CDCl<sub>3</sub>, TMS as internal standard). Mass spectrometric data were obtained on a HP1100LC/MSD MS spectrometer and a LC/Q-ToF MS spectrometer. Fluorescence measurements were performed on a PTI-700 Felix and Time-Master system, and the slit width was 3 nm for both excitation and emission. Absorption spectra were measured on Lambda 35 UV/vis spectrophotometer. All pH measurements were made with a Model PHS-3C meter.

### Synthetic procedures

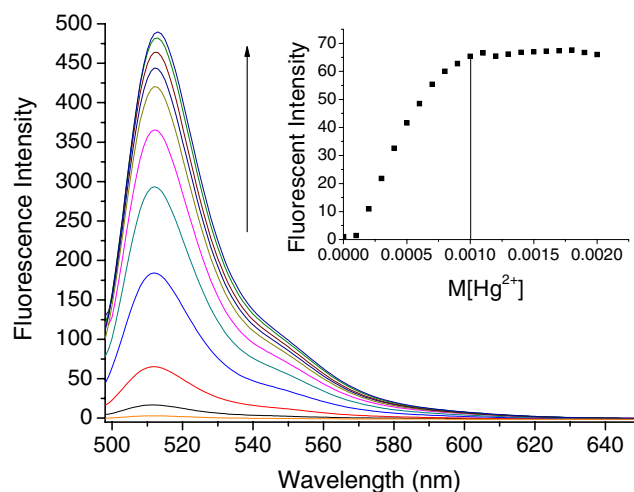
The synthetic route for **B1** is shown in Scheme 1 [40].

#### Compound 4

POCl<sub>3</sub> (58.8 ml, 1 mol) was slowly added dropwise into dry DMF (154.6 ml, 2 mol) in an ice bath with stirring for 0.5 h, then **5** (60.5 g, 0.33 mol) in dry DMF (150 ml) was added in portions in 20 min. The mixture was heated for



**Scheme 1** The synthesis of **B1**

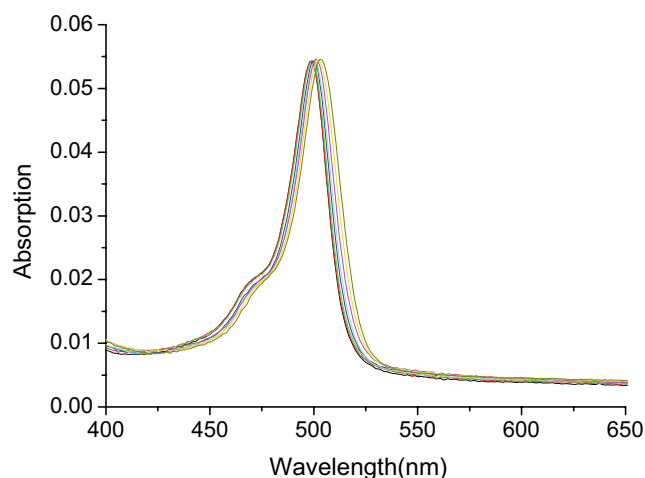


**Fig. 1** Fluorescence response of **B1** (1 μM) to different concentrations of Hg<sup>2+</sup> (0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 100.0 and 150.0 μM) with excitation at 490 nm in water–ethanol solution (water/ethanol=7/3, v/v, pH 7.0). Inset: saturation titration of **B1** with Hg<sup>2+</sup>

2.5 h at 90 °C. and cooled down to room temperature, poured into H<sub>2</sub>O (2 l), and neutralized to pH 6–8 with K<sub>2</sub>CO<sub>3</sub> to precipitate a white solid. The solid was filtrated, washed with H<sub>2</sub>O, and then dried with infrared lamp. The desired product (**4**) (47.08 g) was obtained in 58% yield. <sup>1</sup>H NMR (400MHz, DMSO-D), δ: 3.63(t, *J*=12 Hz, 4H), 3.84 (t, *J*=12 Hz, 4H), 6.77(d, *J*=8 Hz, 2H), 7.74(d, *J*=8 Hz, 2H), 9.8(s, 1H); <sup>13</sup>C NMR (400 MHz, DMSO-D), δ: 190.1, 151.5, 131.8, 125.7, 111.5, 51.7, 40.8; TOF MS (EI): *m/z* Calcd for C<sub>11</sub>H<sub>13</sub>NOC<sub>2</sub> 245.0374, Found 245.0378.

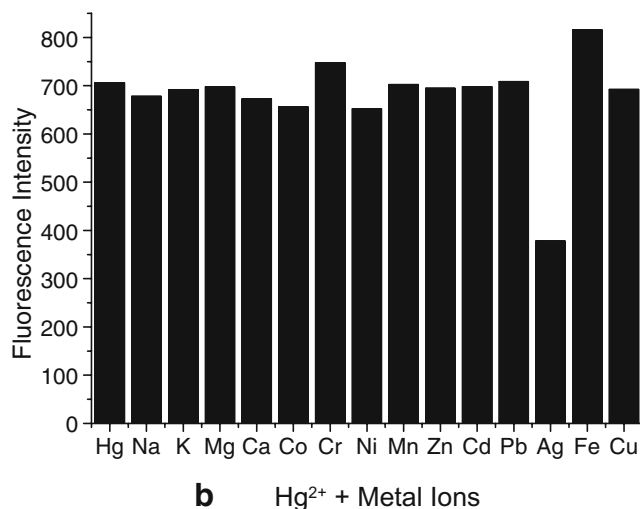
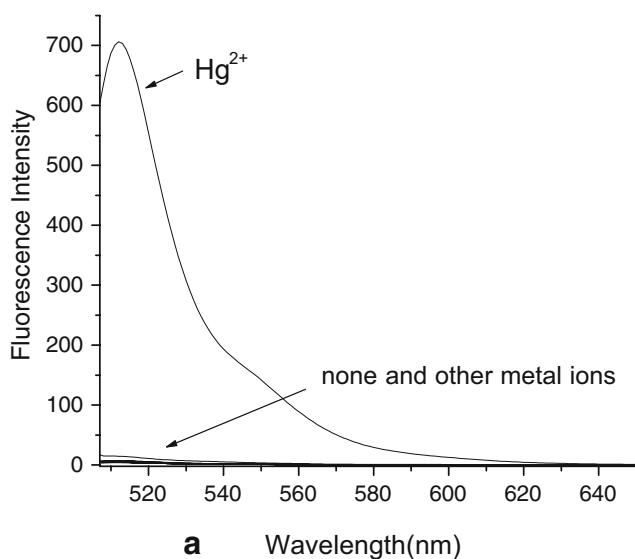
#### Compound 3

Na (0.46 g, 0.02 mol) was added into ethanol (11.2 ml, 0.24 mol) along with stirring. After Na reacted completely,

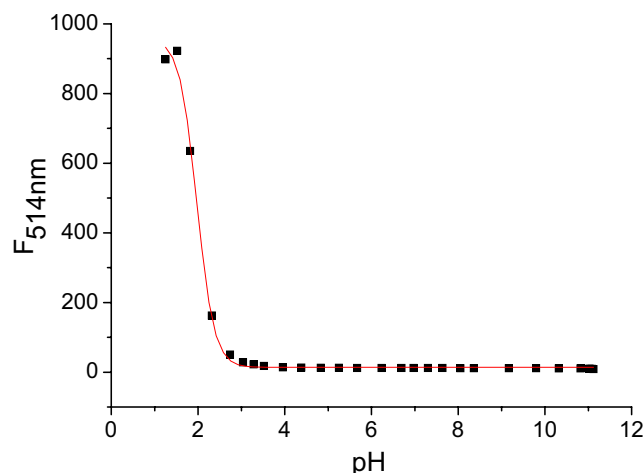


**Fig. 2** Absorption spectra in water–ethanol solution (water/ethanol=7/3, v/v, pH 7.0) in the presence of increasing concentrations of Hg<sup>2+</sup> (0, 10.0, 50.0, 60.0, 70.0, 100.0, 150.0 and 200.0 μM). The concentration of **B1** was 1 μM

2-mercaptoethanol (1.4 ml, 0.02 mol) was added into the solution with stirring for 1 h at room temperature. Then **4** (2.46 g, 0.01 mol) in DMF (5 ml) was added in portions. 1 h later, the mixture was heated up to 60 °C for another 1 h. The desired product **3** (3.24 g) was obtained as brown solid in 98% yield through column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>/acetone, 2/1, v/v). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ: 2.78(m, *J*=12 Hz, 8H), 2.82(s, 2 H), 3.66(t, *J*=16 Hz, 4H), 3.80(t, *J*=12 Hz, 4H), 6.70(d, *J*=12 Hz, 2H), 7.73(d, *J*=8 Hz, 2H), 9.71(s, 1H); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>), δ: 190.5, 151.7, 132.6, 125.9, 111.2, 61.5, 51.6, 35.5, 29.2; TOF MS (ES): *m/z* Calcd. for C<sub>15</sub>H<sub>23</sub>NO<sub>3</sub>S<sub>2</sub>: 364.0808, Found: 364.0812.



**Fig. 3** **a** Fluorescence spectra of **B1** (1 μM) in the presence of different metal ions (100 μM) in water–ethanol solution (water/ethanol=7/3, v/v, pH 7.0). **b** Fluorescence responses of **B1** (1 μM) to Hg<sup>2+</sup> (100 μM) in the presence of selected metal ions (100 μM) in water–ethanol solution (water/ethanol=7/3, v/v, pH 7.0). From left to right: Hg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Ag<sup>+</sup>, Fe<sup>3+</sup>, and Cu<sup>2+</sup>. Excitation: 498 nm



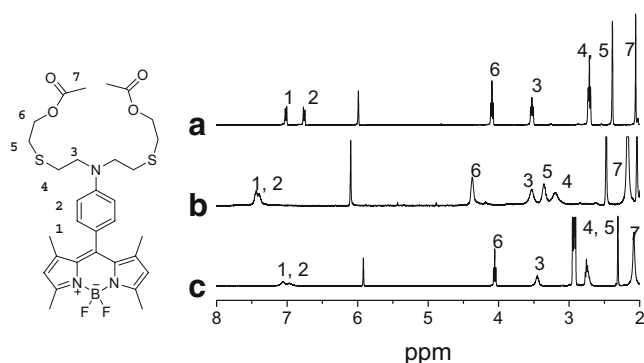
**Fig. 4** Fluorescence intensity  $F_{514}$  of **B1** vs. pH. The concentration of **B1** was 1 μM, excitation wavelength was 498 nm. The pH was adjusted by 1 M HCl and 1 M NaOH

#### Compound 2

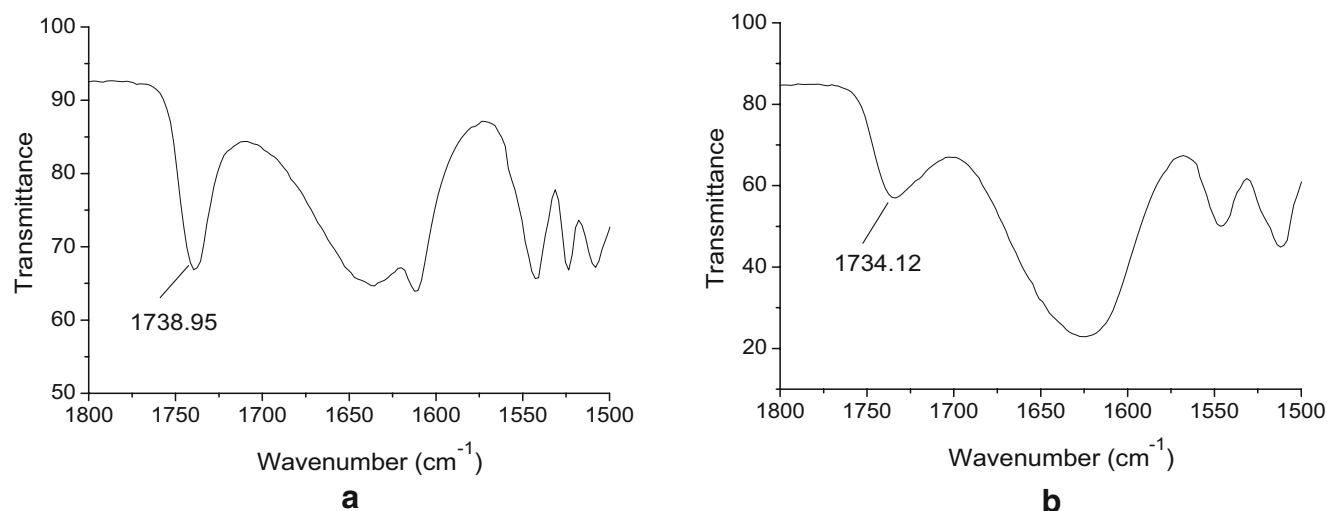
Acetic anhydride (8.5 ml, 1.54 mol) and piperidine (6.2 ml, 0.197 mol) were added to a solution of dichloromethane dissolved with **3** (1.5 g, 4.6 mmol). Then the mixture was refluxed overnight under nitrogen. The desired product **2** (1.83 g) was obtained as brown oil in 96% yield through column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>/acetone, 4/1, v/v). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ: 2.09(s, 6H), 2.83(m, *J*=20 Hz, 8H), 3.67(t, *J*=16 Hz, 4H), 4.25(t, *J*=16 Hz, 4H), 6.74(d, *J*=8 Hz, 2H), 7.77(d, *J*=8 Hz, 2H), 9.8(s, 1H); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>), δ: 190.3, 170.9, 151.5, 132.5, 126.3, 111.3, 63.5, 51.6, 30.9, 29.4, 21.1; TOF MS (ES): *m/z* Calcd for C<sub>19</sub>H<sub>27</sub>NO<sub>5</sub>S<sub>2</sub>: 448.1019, Found: 448.1026.

#### Compound 1 (B1)

**2** (310 mg, 0.75 mmol) and 2,4-dimethylpyrrole (3 ml, 2 mmol) were dissolved in anhydrous methylene chloride (160 ml) under argon atmosphere. Then one drop of trifluoroacetic acid was added into the solution, and the



**Fig. 5** <sup>1</sup>H NMR spectra of **a** free **B1** in CD<sub>3</sub>CN, **b** **BHg1** complex (1 equiv of Hg(ClO<sub>4</sub>)<sub>2</sub> was added into **a**), **c** **BHg1-Br<sup>-</sup>** complex (1.5 equiv of tetrabutylammonium bromide was added into **b**)



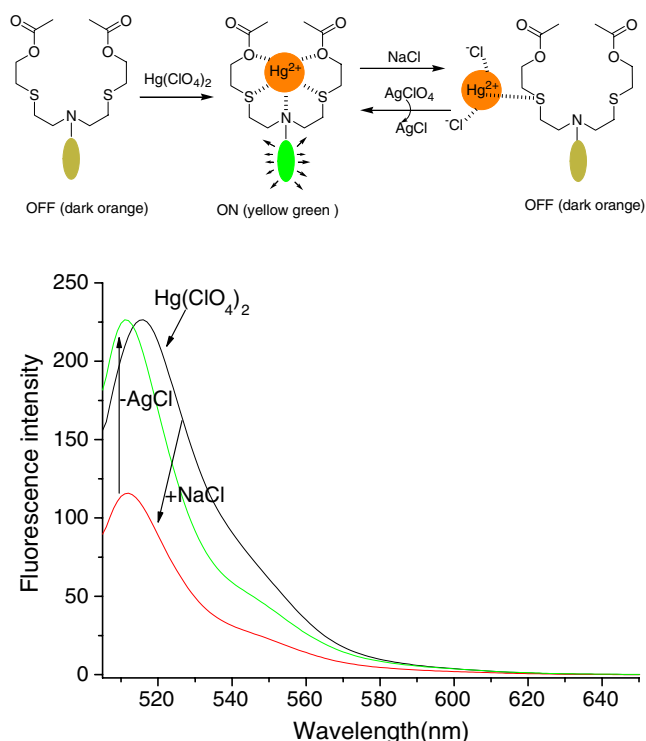
**Fig. 6** The partial IR spectra of **B1** (20 mM) **a** and **BHg1** (1 equiv of  $\text{Hg}(\text{ClO}_4)_2$  in  $\text{CH}_3\text{CN}$ ) **b**

solution was stirred for 5 h at room temperature. A solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 360 mg, 2.16 mmol) in  $\text{CH}_2\text{Cl}_2$  was added with syringe, and the reaction was continued for another 4 h. Then triethylamine (2 ml) was added followed by  $\text{BF}_3 \cdot \text{OEt}_2$  (4 ml) during 30 min and stirred overnight. After concentrated in vacuo, the residue was purified by column chromatography (silica,  $\text{CH}_2\text{Cl}_2/\text{acetone}$ , 10/1, v/v) the desired product **1** (123 mg) was obtained as brown solid in 23% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.48(s, 6H),

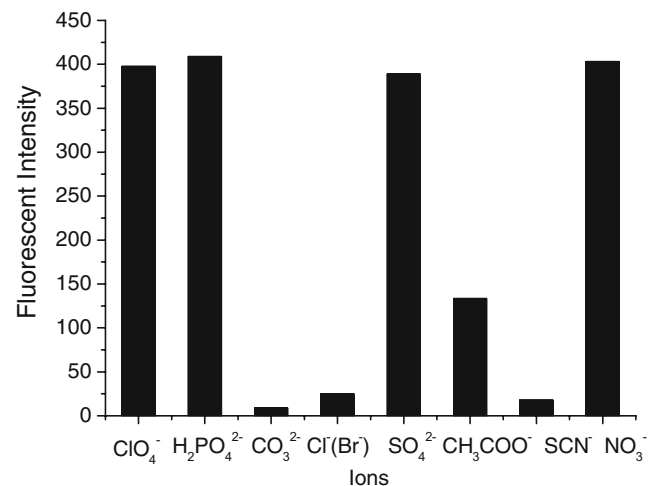
2.07(s, 6H), 2.55(s, 6H), 2.81(t,  $J=12$  Hz, 8H), 3.62(t,  $J=12$  Hz, 4H), 4.24(t,  $J=12$ Hz, 4H), 5.97(s, 2H), 6.77(d,  $J=8$  Hz, 2H), 7.09(d,  $J=8$  Hz, 2H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 170.9, 155.1, 147.2, 143.2, 132.3, 129.5, 123.1, 121.1, 112.3, 63.5, 51.7, 32.1, 30.9, 29.9, 29.5, 22.9, 21.1; TOF MS (ES):  $m/z$  Calcd for  $\text{C}_{31}\text{H}_{40}\text{BF}_2\text{N}_3\text{O}_4\text{S}_2$  632.2603, Found: 632.2600.

## Results and discussion

The free **B1** exhibits a characteristic BODIPY absorption band in the visible region centered at 498 nm and a corresponding emission maximum at 512 nm. It is virtually non-fluorescent with a very low quantum yield ( $\Phi$ ) 0.008, which is indicative of efficient photo-induced electron transfer (PET) quenching from the  $\text{NS}_2\text{O}_2$  receptor to the



**Fig. 7** Changes of Fluorescence-Switching by addition of salts in water–ethanol solution (water/ethanol=7/3, v/v, pH 7.0)



**Fig. 8** Anion-dependent enhancement in the fluorescent emission spectrum of **BHg1** for different anions in water–ethanol solution (water/ethanol=7/3, v/v, pH 7.0)

BODIPY fluorophore. The phenyl group is only a linker between the acceptor and fluorophore, as the stereo-effect of two near methyl groups leads to the aryl group being non-planar with BODIPY [36].

Upon addition of saturated  $\text{Hg}^{2+}$ , the fluorescence intensity of **BHg1** increased by over 160-fold ( $\Phi=0.58$ , Fig. 1) accompanied by a slight red shift in absorption spectrum (Fig. 2). This dramatic turn-on response should be due to the coordination of  $\text{Hg}^{2+}$  with the  $\text{NS}_2\text{O}_2$  acceptor and the inhibition of the PET. The saturation titration for **B1** (inset graph in Fig. 1) reveals formation of a 1:1 stoichiometry for the **BHg1** complex. From the curve in Fig. 1, the dissociation constants  $4.0\pm 0.3\times 10^{-5}$  M was obtained.

The perchlorate or nitrate salts of  $\text{Hg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Fe}^{3+}$ , and  $\text{Cu}^{2+}$  ions were used to evaluate the selectivity of metal ion binding properties of **B1** (Fig. 3a). As expected, **B1** exhibits excellent fluorescence selectivity towards  $\text{Hg}^{2+}$  over all other alkali and alkaline earth metal ions, transition and heavy metal ions. The competition experiments were conducted in the presence of  $\text{Hg}^{2+}$  mixed with above metal ions at 100  $\mu\text{M}$  (Fig. 3b). The fluorescence emission profiles were unperturbed except for a little quenching by  $\text{Ag}^+$ , which indicated its excellent fluorescence anti-jamming ability against other metal ions.

Fluorescent sensors based on photo-induced electron transfer are usually disturbed by protons in the detection of metal ions.

In some cases, the  $pK_a$  are as high as 7–9. [25–29] As seen in Fig. 4, **B1** displays gradually intense fluorescence only at  $\text{pH}<3$ . When  $\text{pH}>3$ , however, the fluorescence intensities are very low and maintain constant. The  $pK_a$  is 1.97 from the sigmoidal curve, which is the lowest  $pK_a$  in metal ions PET chemosensors reported up till now.

Compared the  $^1\text{H}$  NMR of **BHg1**( $\text{Hg}(\text{ClO}_4)_2$ )(Fig. 5b) with that of the **B1** (Fig. 5a), several protons such as 3, 4, 5 and 6 shift to the down-field, which indicates that  $\text{Hg}^{2+}$  coordinates with the  $\text{NS}_2\text{O}_2$  receptor. After adding  $\text{Br}^-$  into the complex, those down-shift protons shift back to their incipient position again. (Fig. 5c) Moreover, Fig. 6 shows the partial IR spectra of **B1** (25 mM) with 1 equiv of  $\text{Hg}(\text{ClO}_4)_2$  in  $\text{CH}_3\text{CN}$ . Little shift of carbonyl IR absorption was observed in the  $\text{Hg}^{2+}$ -coordination, which implies that no binding occurs between the carbonyl group and  $\text{Hg}^{2+}$ .

Surprisingly, the fluorescence enhancement of **B1** with  $\text{Hg}(\text{ClO}_4)_2$  may change with the addition of different anions. For instance,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{SO}_4^{2-}$  have no interference on the fluorescence enhancement;  $\text{Cl}^-$  ( $\text{Br}^-$ ),  $\text{CO}_3^{2-}$ ,  $\text{SCN}^-$  and  $\text{CH}_3\text{COO}^-$ , however, inhibit the fluorescence enhancement to different extents (Figs. 7 and 8). The inhibition is reversible. For example, the bright fluorescence solution of **BHg1**( $\text{Hg}(\text{ClO}_4)_2$ ) became dark on the addition of  $\text{NaCl}$  aq. solution; while, the system returned bright with the drop

addition of  $\text{AgClO}_4$  solution (Fig. 7). This is attributed to the significant coordinating ability of these latter anions to  $\text{Hg}^{2+}$ .

Lee has found the similar anion-controlled effect in his chromogenic  $\text{Hg}^{2+}$  coordination recently[31]. In our cases of  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{SO}_4^{2-}$ , the coordination abilities of these anions to  $\text{Hg}^{2+}$  are weak,  $\text{Hg}^{2+}$  was endo-coordinated in the middle of  $\text{NS}_2\text{O}_2$  ligand of **B1** where photo-induced electron transfer (PET) process was inhibited and great fluorescence enhancement was observed. In the cases of  $\text{Cl}^-$  ( $\text{Br}^-$ ),  $\text{CO}_3^{2-}$ ,  $\text{SCN}^-$  and  $\text{CH}_3\text{COO}^-$ , however, the coordinating abilities of these anions to  $\text{Hg}^{2+}$  are much stronger than N-ligand of **B1**, and  $\text{Hg}^{2+}$  combines with the anion to form  $\text{HgX}$  ( $X=\text{anion}$ ) which coordinates the S-atom out side of the  $\text{NS}_2\text{O}_2$  ligand (Fig. 7). Therefore, the PET from the N-donor of **B1** was not inhibited by  $\text{Hg}^{2+}$ . The reversible processes suggest that anions could control the fluorescence enhancement through formation of endo- or exo-metal complexes with  $\text{Hg}^{2+}$ .

In conclusion, a new  $\text{Hg}^{2+}$  induced and anion-controlled water-soluble fluorescent sensor **B1** has been presented. **B1** displays high selectivity and large fluorescence enhancement for  $\text{Hg}^{2+}$ , and its fluorescence emission is pH-independent under a large physiological pH range, which indicates that it has potential applications for biological toxicities.

**Acknowledgements** This work was supported by the National Science Foundation of China (20376010 and 20472012).

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