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# 3-(Pyridine-4-thione)BODIPY as a chemodosimeter for detection of Hg(II) ions

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## 1. Introduction

The development of chemosensors for the selective and efficient detection of chemically and biologically important ionic species has brought interest for many researchers in recent years [1–4]. The design of selective and sensitive sensors for the target guests generally requires conjugation of well established and efficient binding site with a suitable signaling moiety as a basic requirement. Many fluorophores have been used as signaling unit because of their desirable characteristics in both sensitivity and ease of signal transduction. There is a tremendous need for chemosensors which can show high selectivity and sensitivity for heavy metal cations such as  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Hg^{2+}$  since such metal cations can cause severe risks for human health and the environment [5–8]. Among the metal cations, mercury ion (Hg<sup>2+</sup>) is considered as one of the most toxic cation for the environment because it is widely distributed in air, water and soil [4]. Mercury ion can accumulate in the human body and can cause a wide variety of diseases even in a low concentration, such as prenatal brain damage, serious cognitive and motion disorders and minimata disease [8,9]. Because of high toxic nature of mercury ions for human health, its detection using simple chemosensors has become main objective for researchers in recent years [8,10]. Several small-molecule-based Hg(II) sensors such as sensors based on rhodamine derivatives, coumarin derivatives and boron-dipyrromethene (BODIPY)

## ABSTRACT

A new chemodosimeter for detection of Hg(II) ions based on boron-dipyrromethene (BODIPY) is developed. The 3-(pyridine-4-thione)BODIPY was synthesized in high yield by treating 3-(pyridine-4-one)BODIPY with Lawesson's reagent. The 3-(pyridine-4-thione) BODIPY was confirmed by HR-MS mass, <sup>1</sup>H, <sup>1</sup>H–<sup>1</sup>H COSY, <sup>19</sup>F and <sup>11</sup>B NMR techniques. In <sup>1</sup>H NMR, the protons which are adjacent to sulfur in 3-(pyridine-4-thione)BODIPY showed ~1 ppm downfield shift compared to equivalent protons in 3-(pyridine-4-thione)BODIPY. The absorption and electrochemical properties experienced slight changes in 3-(pyridine-4-thione)BODIPY compared to 3-(pyridine-4-one)BODIPY. Furthermore, 3-(pyridine-4-thione)BODIPY is very weakly fluorescent compared to 3-(pyridine-4-one)BODIPY. Furthermore, 3-(pyridine-4-thione)BODIPY can be used as an exclusive chemodosimeter for Hg<sup>2+</sup> ion as it shows significant enhancement in the fluorescence intensity and a dramatic visible color change from pink to fluorescent green in the presence of Hg(II) ions.

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derivatives have been synthesized and demonstrated their use for Hg<sup>2+</sup> ions detection [3,10–26]. Among the fluorophores, BODIPY based chemosensors have received tremendous attention in recent years because of their advantageous characteristics, such as sharp absorption with high intensity in visible to near NIR region, high fluorescence quantum yields and tunable redox properties [27–30]. Interestingly, the reports on BODIPY based sensors for Hg<sup>2+</sup> ions detection are few and the selected examples **I**–**V** are shown in Fig. 1 [10,12,14,17]. Hence, there is a scope to develop more BODIPY based chemosensor for Hg<sup>2+</sup> ions detection and in this paper, we report the synthesis of a new BODIPY based chemodosimeter 3-(pyridine-4-thione)-8-(4-methoxyphenyl)-4,4-difluoro-4-bora-3a,4a-diazas-indacene(1), which is useful for the selective detection of Hg(II) ions. The BODIPY chemodosimeter 1 is designed by keeping in mind that Hg(II) has high affinity for sulfur and causes desulfurization reaction which may reflect in the significant changes in the color as well as fluorescence properties of BODIPY.

## 2. Experimental section

### 2.1. Chemicals

Toluene was dried over sodium benzophenone ketyl and chloroform and acetonitrile dried over calcium hydride prior to use.  $BF_3 \cdot OEt_2$  and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) obtained from Spectrochem (India) were used as obtained. Metal acetates are used for the studies. All other chemicals used for the synthesis were reagent grade unless otherwise specified. Column





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Fig. 1. The reported BODIPY Hg(II)-sensors I-V along with our compound 1.

chromatography was performed on silica (60–120 mesh) or alumina.

### 2.2. Instrumentation

<sup>1</sup>H NMR spectra ( $\delta$  in ppm) were recorded using Bruker 400 MHz spectrometer. <sup>13</sup>C NMR spectra were recorded on Bruker operating at 100.6 MHz <sup>19</sup>F NMR spectra were recorded on Bruker 376.4 MHz spectrometer. <sup>11</sup>B NMR spectra were recorded on Bruker spectrometer operating at 128.3 MHz. TMS was used as an internal reference for recording <sup>1</sup>H (of residual proton;  $\delta$  7.26) and <sup>13</sup>C ( $\delta$  77.0 signal) in CDCl<sub>3</sub>. Absorption and steady-state fluorescence spectra were obtained with Perkin–Elmer Lambda-35 and PC1 Photon Counting Spectrofluorometer manufactured by ISS, USA instruments respectively. Fluorescence spectra were recorded at 25 °C in a 1 cm quartz fluorescence cuvette. The fluorescence quantum yields ( $\Phi_f$ ) were estimated from the emission and absorption spectra by comparative method at the excitation wavelength of 488 nm using Rhodamine 6G ( $\Phi_f = 0.88$ ) [31]. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies were carried out with electrochemical

system utilizing the three electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxillary electrode) and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Half wave potentials were measured using DPV and also calculated manually by taking the average of the cathodic and anodic peak potentials. All potentials were calibrated versus saturated calomel electrode by the addition of ferrocene as an internal standard, taking  $E_{1/2}$  (Fc/ Fc<sup>+</sup>) = 0.42 V, vs SCE. High-resolution mass spectrum was obtained from Q-TOF instrument by electron spray ionization (ESI) technique.

## 2.3. Details of Hg(II) ion sensing studies

All the solvents used were of analytical grade and were purified and dried by routine procedures immediately before use. Stock solutions of the Hg(II) (1 mM) in H<sub>2</sub>O–CH<sub>3</sub>OH mixture (1:1) and **1** (10  $\mu$ M) in CHCl<sub>3</sub> were prepared. Fluorescence titration experiments were performed by placing 2.5 mL solution of **1** (10  $\mu$ M) in a quartz cuvette of 1 cm path length and various amounts of Hg(II) ions were



Scheme 1. Synthesis of 3-(Pyridine-4-thione)BODIPY 1.

added incrementally by means of a micropipette. The excitation wavelength used was 488 nm, and emission was collected from 500 to 800 nm. The association constant has been estimated by using the following standard Benesi–Hildebrand equation [34]:

$$\frac{1}{I-I_0} = \frac{1}{I_1 - I_0} + \frac{1}{(I_1 - I_0)K_{\rm a}[M^+]}$$

where  $I_0$  is the fluorescence intensity of **1** before addition of Hg(II), I is the fluorescence intensity in the presence of Hg(II),  $I_1$  is the

intensity upon saturation with Hg(II), and  $K_a$  is the association constant of the complex formed.

## 2.4. 3-(Pyridine-4-one)-8-(4-methoxyphenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene 2

The compound **2** was synthesized by treating the 3-bromo boron-dipyrromethene [32] **3** (100 mg, 0.26 mmol) with 4-hydroxypyridine (38 mg, 0.39 mmol) in  $CH_3CN$  (15 mL) in the



Fig. 2. (a) Comparison of <sup>1</sup>H NMR spectra for compounds 1 and 2. (b) <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum for compound 1.

b

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Photophysical data of com	pounds <b>1</b> and <b>2</b> in	different solvents.

Compound	Solvent	$\lambda_{abs} (nm)$	$\log \epsilon_{max}$	$\lambda_{em} (nm)$	$\Phi_{\rm F}{}^{\rm a}$
1	n-Hexane	526	3.6	548	0.008
	CHCl <sub>3</sub>	524	4.5	548	0.008
	CH₃CN	509	3.9	548	0.007
2	n-Hexane	519	4.6	551	0.21
	CHCl <sub>3</sub>	517	4.7	551	0.20
	CH <sub>3</sub> CN	510	4.5	548	0.16

<sup>a</sup> Rhodamine ( $\Phi_F = 0.88$ ) was used as a reference, and the values were based on the peak height.

presence of Cs<sub>2</sub>CO<sub>3</sub> (129 mg, 0.39 mmol) under nitrogen atmosphere at refluxing temperature for 1 h. The progress of the reaction was followed by TLC analysis which showed the disappearance of spot corresponding to **3** and appearance of new spot corresponding to the desired compound. The crude compound was subjected to alumina gel column chromatography using petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (5:95) and afforded pure compound **2** as orange solid in 70% yield (72 mg). M.p. 212–213 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 3.93 (s, 3 H, OMe), 6.44 (d, *J* = 4.3 Hz, 1 H,  $\beta$ -py), 6.48 (d, *J* = 7.8 Hz,

> a <sub>0.50</sub> 0.45

> > 0.40 0.35

> > 0.30 0.25 0.20

> > 0.15 0.10

Absorbance

2 H, pyridyl), 6.65 (d, J = 4.2 Hz, 1 H,  $\beta$ -py), 6.98 (d, J = 4.3 Hz, 1 H,  $\beta$ -py), 7.08–7.10 (m, 3 H, BODIPY Ar +  $\beta$ -py), 7.55–7.57 (m, 2 H, BODIPY Ar), 7.76 (d, J = 6.24 Hz, 2 H, pyridyl), 7.98 (s, 1 H,  $\beta$ -py). <sup>19</sup>F NMR (376.4 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): -141.59 (q,  $J_{B-F} = 60.2$  Hz). <sup>11</sup>B NMR (128.3 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 0.48 (t,  $J_{B-F} = 29.5$  Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 55.76, 112.26, 113.45, 114.53, 118.57, 120.36, 125.55, 129.88, 131.17, 132.71, 133.27, 135.31, 139.77, 146.18, 148.30, 149.87, 162.77, 179.38. HR-MS mass calcd for C<sub>21</sub>H<sub>16</sub>BF<sub>2</sub>N<sub>3</sub>O<sub>2</sub> 392.1398 found 392.1382 [M + H]<sup>+</sup>

## 2.5. 3-(Pyridine-4-thione)-8-(4-methoxyphenyl)-4,4-difluoro-4bora-3a,4a-diaza-s-indacene 1

Compound **2** (100.0 mg, 0.25 mmol) and 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-dithione (Lawesson's Reagent) (103 mg, 0.25 mmol) were dissolved in dry toluene, and the reaction mixture was refluxed for 2 h. The solvent was removed on rotary evaporator under reduced pressure, and the crude compound was purified by chromatography on alumina using petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (5:95) to afford compound **1** as violet solid in 50% yield (52 mg). M.p. 174–175 °C; <sup>1</sup>H NMR (400 MHz,

2

1



**Fig. 3.** (a) Comparison of UV–vis absorption spectra of 1 (––––) and 2 (–) recorded at 10  $\mu$ M concentration in CHCl<sub>3</sub>. (b) Comparison of first reduction waves along with differential pulse voltammograms of 1 and 2 in dichloromethane containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV/s scan speed (c) and comparison of emission spectra of 1 (––––) and 2 (–) recorded at 10  $\mu$ M concentration in CHCl<sub>3</sub>. (b) Comparison of first reduction waves along with

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CDCl<sub>3</sub>, δ in ppm): 3.94 (s, 3 H, OMe), 6.47 (d, J = 4.2 Hz, 1 H, β-py), 6.68 (d, J = 4.2 Hz, 1 H, β-py), 6.98 (d, J = 4.2 Hz, 1 H, β-py), 7.09 (d, J = 8.6 Hz, 2 H, BODIPY Ar), 7.12 (d, J = 4.2 Hz, 1 H, β-py) 7.46 (d, J = 7.3 Hz, 2 H, pyridyl), 7.55–7.58 (m, 4 H, BODIPY Ar + pyridyl), 8.0 (s, 1 H, β-py). <sup>19</sup>F NMR (376.4 MHz, CDCl<sub>3</sub>, δ in ppm): -141.09 (q,  $J_{B-F} = 60.2$  Hz). <sup>11</sup>B NMR (128.3 MHz, CDCl<sub>3</sub>, δ in ppm): 0.51 (t,  $J_{B-F} = 29.5$  Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ in ppm): 55.83, 112.09, 114.62, 120.80, 125.51, 130.85, 132.89, 133.50, 133.81, 146.98, 148.59, 162.91, 195.88. HR-MS mass calcd for C<sub>21</sub>H<sub>16</sub>BF<sub>2</sub>N<sub>3</sub>OS 408.1153 found 408.1160 [M + H]<sup>+</sup>.

## 3. Results and discussions

To synthesize 3-(pyridine-4-thione) BODIPY 1, we need an access to the key precursor 3-(pyridine-4-one) BODIPY 2. We showed earlier that 3,5-dibromo BODIPY on reaction with 2- and 4hydroxypyridines forms 3,5-bis(pyridone)-BODIPYs and with 3hydroxypridine, it forms 3,5-bis(oxypyridine)BODIPY [33]. We adopted similar synthetic strategy to prepare 3-(pyridine-4-one) BODIPY 2 by using 3-bromo BODIPY [32] as a precursor. Treatment of 3-bromo BODIPY with 4-hydroxypyridine using Cs<sub>2</sub>CO<sub>3</sub> as a base under reflux conditions for 1 h followed by standard work-up and column chromatographic purification afforded compound 2 in 70% yield (Scheme 1). The target 3-pyridine-(4-thione) BODIPY 1 was synthesized by treating 2 with one equivalent of Lawesson's reagent in toluene under reflux conditions for 2 h (Scheme 1). The crude compound was subjected to silica gel column chromatographic purification and afforded pure compound **1** as green solid in 50% vield. The BODIPYs 1 and 2 are readily soluble in common organic solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>OH, toluene etc and confirmed the identities by molecular ion peaks in HR-MS mass spectra (Supporting Information). The compounds 1 and 2 were characterized further by 1D & 2D NMR, absorption, fluorescence and electrochemical techniques. <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F and <sup>11</sup>B NMR were used to characterize the compounds **1** and **2** and the comparison of  ${}^{1}$ H NMR spectra of compounds 1 with 2 is presented in Fig. 2a. We used  ${}^{1}H-{}^{1}H$  COSY NMR to identify all signals of BODIPY **1** and spectrum is presented in Fig. 2b. In compounds 1 and 2, because of unsymmetrical substitution, the five pyrrole protons of BODIPY core (represented as a, b, c, d and e) appeared as five sets of signals. The protons of pyridine-4-one in compound 2 and pyridine-4thione in compound 1 represented as f and g appeared as two sets of signals and the four meso-aryl protons in compounds 1 and 2 also appeared as two sets of signals. As clear from the Fig. 2a, there is no significant shifts in the pyrrole protons of BODIPY core (a-e protons) when pyridine-4-one in compound 2 was changed to pyridine-4-thione in compound 1. However, the pyridine-4-thione protons represented as f and g in compound 1 showed shifts as compared to pyridine-4-one protons in compound 2. The proton 'f' experienced  $\sim 0.2$  ppm upfield shift whereas proton 'g' experienced nearly 1 ppm downfield shift in compound 1 compared to the same protons in compound 2. The compounds 1 and 2 showed a triplet in <sup>11</sup>B NMR at  $\sim$  0.51 ppm and a single quartet in <sup>19</sup>F NMR spectra because of coupling with  ${}^{11}B(I = 3/2, J = 32 \text{ Hz})$  and appears at ~ -141 ppm like other reported BODIPYs [34].

The absorption spectra of compounds **1** and **2** were recorded in CHCl<sub>3</sub> and the data is given in Table 1. The comparison of normalized absorption spectra of compounds **1** and **2** is shown in Fig. 3a. In general BODIPYs exhibit a strong  $S_0 \rightarrow S_1$  transition at ~500 nm with a vibronic transition on the higher energy side as a shoulder and an ill-defined weak band corresponding to the  $S_0 \rightarrow S_2$  transition at ~400 nm [34]. The compounds **1** and **2** showed typical absorption features like any other BODIPY. However, the compound **1** showed ~8 nm red shift in  $S_0 \rightarrow S_1$  transition compared to compound **2** indicating the alteration in electronic properties of

BODIPY core on changing pyridine-4-one in compound 2 to pyridine-4-thione in compound 1. This is also clearly reflected in difference in their colors in CHCl<sub>3</sub> solution (Supporting Information). The absorption spectra recorded for compounds 1 and 2 in different solvents of varying polarity followed the same trend like any other BODIPY (Table 1) [34]. The redox properties of compounds 1 and 2 were investigated in CH<sub>2</sub>Cl<sub>2</sub> by cyclic voltammetry and differential pulse voltammetry at different scan rates (50-150 mV/s) using tetrabutylammonium perchlorate as the supporting electrolyte. The comparison of first reduction wave of compounds 1 and 2 is shown in Fig. 3b. The compounds 1 and 2 showed one reversible ( $E_{1/2}^{red} = -0.66$  and -0.60 V respectively) and one irreversible reduction  $(E_{1/2}^{\text{red}} = -1.70 \text{ and } -1.47 \text{ V} \text{ respectively})$ but no oxidation supporting the electron deficient nature of BOD-IPY compounds 1 and 2. The first reduction potential of compounds 1 and 2 are almost in the same range indicating that the compounds **1** and **2** are equally electron deficient. The fluorescence properties of compounds 1 and 2 were studied in different solvents (Table 1) and the comparison of fluorescence spectra of compounds 1 and 2 recorded in CHCl<sub>3</sub> under identical experimental conditions is shown in Fig. 3c. As is clear from the Fig. 3c that compound 2 is decently fluorescent with emission peak maxima of 551 nm and quantum yield of 0.20 whereas the compound **1** is very weakly fluorescent with emission peak maxima at 548 nm, and quantum yield of 0.008. The low fluorescence behavior of **1** was tentatively



**Fig. 4.** (a) Fluorescence emission changes ( $\lambda_{ex} = 488 \text{ nm}$ ) of compound **1** (10  $\mu$ M) upon addition of different concentrations of Hg<sup>2+</sup> in CHCl<sub>3</sub>. The Hg<sup>2+</sup> concentration were varied from 0 to 100  $\mu$ M. The inset shows the plot of *I/lo* vs. different concentrations of Hg<sup>2+</sup> ions. (b) Emission spectra of **1** (10  $\mu$ M) in the presence of 60  $\mu$ M of Hg<sup>2+</sup> ions and 100  $\mu$ M of each Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> ions.



**Fig. 5.** Color change of **1** (10  $\mu$ M) in the presence of different metal ions (Hg<sup>2+</sup> in 0.6 equivalents and other metal ions in excess). From left to right: Pb<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, K<sup>+</sup>, Hg<sup>2+</sup>, Na<sup>+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup>.

ascribed to the internal heavy atom effect of sulfur. The empty d-orbitals of sulfur atom with an appropriate symmetry interact with the  $\pi$ -system of BODIPY resulting in the low quantum yield of **1**. Thus, the study clearly indicates that the conversion of pyridine-4-one in compound **2** to pyridine-4-thione in compound **1** reduces the fluorescence significantly.

The 3-(pyridine-4-thione)BODIPY **1** can be used as an exclusive chemodosimeter for  $Hg^{2+}$  ions which we investigated by emission studies. Since compound **1** is completely insoluble in water and very sparingly soluble in methanol, the studies were carried out by dissolving compound **1** in CHCl<sub>3</sub> and titrated with Hg(II) ion in water/methanol mixture (1:1). The fluorescence spectral response of compound **1** with the increasing addition of Hg(II) ions is shown in Fig. 4a. Upon addition of Hg(II), a gradual increase in the intensity of fluorescence was observed. The fluorescence titration profile of 1 versus concentration of Hg(II) ions revealed that the gradual enhancement of the emission intensity was obtained with the increasing addition of Hg(II) ions up to 60  $\mu$ M (Inset in Fig. 4a) and the detection limit was found to be 3 ppm. This is also clearly evident in the increase of fluorescence of solution 1 on addition of Hg(II) ions. Upon addition of Hg(II) ions to solution of compound 1, the non-fluorescent solution gradually changed to bright green fluorescent solution under Uv lamp. Under the same titration conditions, we tested compound **1** by adding various other metal ions such as Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> but there is no change in the fluorescence intensity (Fig. 4b) as well as color of the solution (Fig. 5). These observations indicate that 3-(pyridine-4-thione)BODIPY dye 1 can serve as a sensitive naked eye sensor for Hg<sup>2+</sup> ions. From the Benesi–Hildebrand equation [35], the association constant calculated was  $1.6 \times 10^6 \text{ M}^{-1}$  [36]. Furthermore, we attributed tentatively the increase in the fluorescence intensity of compound **1** upon addition of Hg<sup>2+</sup> ion to the  $Hg^{2+}$  ion induced desulfurization of compound **1** to form strongly fluorescent compound 2 (Scheme 2). Thus, compound 1 can act as chemodosimeter for Hg<sup>2+</sup> ion. This hypothesis is further supported by electron spray ionization (ESI-MS) analysis. In the absence of Hg(II), a peak was observed at m/z 408.11 corresponding to



**Scheme 2.** Hg<sup>2+</sup> induced desulfurization of compound **1**.

 $[1 + H]^+$ . After the addition of one equivalent of Hg(OAc)<sub>2</sub> to the solution of **1**, the peak at m/z 408.11 disappeared with the appearance of a new peak at m/z 392.13 corresponds to the compound  $[2 + H]^+$ .

## 4. Conclusion

We synthesized 3-(Pyridine-4-thione)-8-(4-methoxyphenyl)-4, 4-difluoro-4-bora-3a, 4a-diaza-s-indacene(1) in high yield and used it as a chemodosimeter for the detection of Hg(II) ions. In addition, the dye 1 can be used as colorimetric sensor for Hg(II) ions, as detection of Hg(II) ions induces clear visible color for naked eye. The high selectivity of 1 for Hg<sup>2+</sup> ions was attributed tentatively to Hg<sup>2+</sup>-induced desulfurization mechanism. It is anticipated that 1 could contribute to the development of mercury ion sensors.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2012.03.015.

### References

- de Silva AP, Fox DB, Huxley AJM, Moody TS. Combining luminescence, coordination and electron transfer for signalling purposes. Coord Chem Rev 2000; 205(1):41–57.
- [2] Prodi L, Bolletta F, Montalti M, Zaccheroni N. Luminescent chemosensors for transition metal ions. Coord Chem Rev 2000;205(1):59–83.
- [3] Nolan EM, Lippard SJ. A "turn-on" fluorescent sensor for the selective detection of mercuric ion in aqueous media. J Am Chem Soc 2003;125(47): 14270-1.
- [4] Descalzo AB, Martínez-Máñez R, Radeglia R, Rurack K, Soto J. Coupling selectivity with sensitivity in an integrated chemosensor framework: design of a Hg<sup>2+</sup>-responsive probe, operating above 500 nm. J Am Chem Soc 2003; 125(12):3418–9.
- [5] de Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher JT, et al. Signaling recognition events with fluorescent sensors and switches. Chem Rev 1997;97(5):1515–66.
- [6] He X, Liu H, Li Y, Wang S, Wang N, Xiao J, et al. Gold nanoparticle-based fluorometric and colorimetric sensing of copper(II) ions. Adv Mater 2005; 17(23):2811–5.
- [7] Yoon S, Albers AE, Wong AP, Chang CJ. Screening mercury levels in fish with a selective fluorescent chemosensor. J Am Chem Soc 2005;127(46):16030–1.
- [8] Nolan EM, Lippard SJ. Tools and tactics for the optical detection of mercuric ion. Chem Rev 2008;108(9):3443–80.
- [9] Clarkson TW, Magos L, Myers GJ. The toxicology of mercury of current exposures and clinical manifestations. N Engl J Med 2003;349(18):1731-7.
- [10] Yuan M, Li Y, Li J, Li C, Liu X, Lv J, et al. A colorimetric and fluorometric dual-modal assay for mercury ion by a molecule. Org Lett 2007;9(12):2313–6.
  [11] Wang J, Qian X, Cui J. Detecting Hg<sup>2+</sup> ions with an ICT fluorescent sensor
- [11] Wang J, Qian X, Cui J. Detecting Hg<sup>2+</sup> ions with an ICT fluorescent sensor molecule: remarkable emission spectra shift and unique selectivity. J Org Chem 2006;71(11):4308–11.
- [12] Moon SY, Cha NR, Kim YH, Chang S-K. New Hg<sup>2+</sup>-selective chromo- and fluoroionophore based upon 8-hydroxyquinoline. J Org Chem 2003;69(1): 181–3.
- [13] Coskun A, Akkaya EU. Signal ratio amplification via modulation of resonance energy transfer: proof of principle in an emission ratiometric Hg (II) sensor. Am Chem Soc 2006;128(45):14474–5.
- [14] Coskun A, Yilmaz MD, Akkaya EU. Bis(2-pyridyl)-substituted boratriazaindacene as an NIR-emitting chemosensor for Hg(II). Org Lett 2007;9(4): 607–9.
- [15] Sun H-B, Liu S-J, Ma T-C, Song N-N, Zhao Q, Huang W. An excellent BODIPY dye containing a benzo[2,1,3]thiadiazole bridge as a highly selective colorimetric and fluorescent probe for Hg<sup>2+</sup> with naked-eye detection. New J Chem 2011;35(6):1194–7.
- [16] Wang J, Qian X. A series of polyamide receptor based PET fluorescent sensor molecules: positively cooperative Hg<sup>2+</sup> ion binding with high sensitivity. Org Lett 2006;8(17):3721–4.

- [17] Lu H, Zhang S, Liu H, Wang Y, Shen Z, Liu C, et al. Experimentation and theoretic calculation of a BODIPY sensor based on photoinduced electron transfer for ions detection. J Phys Chem A 2009;113(51):14081–6.
- [18] Csokai V, Kádár M, Ha Mai DL, Varga O, Tóth K, Kubinyi M, et al. Synthesis, optical and electroanalytical characterizations of a thiacalix[4](N-phenylazacrown-5) ether "BODIPY ionophore. Tetrahedron 2008;64(6):1058–63.
- [19] Lu H, Xiong L, Liu H, Yu M, Shen Z, Li F, et al. A highly selective and sensitive fluorescent turn-on sensor for Hg<sup>2+</sup> and its application in live cell imaging. Org Biomol Chem 2009;7(12):2554–8.
- [20] Song KC, Kim JS, Park SM, Chung K-C, Ahn S, Chang S-K. Fluorogenic Hg<sup>2+</sup>selective chemodosimeter derived from 8-hydroxyquinoline. Org Lett 2006; 8(16):3413-6.
- [21] Zhang Q-Q, Ge J-F, Xu Q-F, Yang X-B, Cao X-Q, Li N-J, et al. A selective, sensitive probe for mercury(II) ions based on oxazine-thione. Tetrahedron Lett 2011;52(5):595–7.
- [22] Voutsadaki S, Tsikalas GK, Klontzas E, Froudakis GE, Katerinopoulos HE. A "turn-on" coumarin-based fluorescent sensor with high selectivity for mercury ions in aqueous media. Chem Commun 2010;46(19): 3292-4.
- [23] Pu Q, Sun Q. Application of 2-mercaptobenzothiazole-modified silica gel to on-line preconcentration and separation of silver for its atomic absorption spectrometric determination. Analyst 1998;123(2):239–43.
- [24] Ceresa A, Radu A, Peper S, Bakker E, Pretsch E. Rational design of potentiometric trace level ion sensors. A Ag<sup>+</sup>-selective electrode with a 100 ppt detection limit. Anal Chem 2002;74(16):4027–36.
- [25] Zhang X-B, Guo C-C, Li Z-Z, Shen G-L, Yu R-Q. An optical fiber chemical sensor for mercury ions based on a porphyrin dimer. Anal Chem 2002; 74(4):821-5.

- [26] Huang C-C, Chang H-T. Selective gold-nanoparticle-based turn-on fluorescent sensors for detection of mercury(II) in aqueous solution. Anal Chem 2006; 78(24):8332-8.
- [27] Loudet A, Burgess K. BODIPY dyes and their derivatives: syntheses and spectroscopic properties. Chem Rev 2007;107(11):4891–932.
- [28] Ziessel R, Ulrich G, Harriman A. The chemistry of bodipy: a new El dorado for fluorescence tools. New J Chem 2007;31(4):496-501.
- [29] Ulrich G, Ziessel R, Harriman A. The chemistry of fluorescent bodipy dyes: versatility unsurpassed. Angew Chem Int Ed 2008;47(7):1184–201.
- [30] Zhang ZXB, Su J, Shen L, Xie Y, Tian H. Color-tunable solid-state emission of 2,2'biindenyl-based fluorophores. Angew Chem Int Ed 2011;50(49):11645-7.
   [31] Oin W. Leen V. Rohand T. Dehaen W. Dedecker P. Van der Auweraer M et al.
- [31] Qin W, Leen V, Rohand T, Dehaen W, Dedecker P, Van der Auweraer M, et al. Synthesis, spectroscopy, crystal structure, electrochemistry, and quantum chemical and molecular dynamics calculations of a 3-anilino difluoroboron dipyrromethene dye. J Phys Chem A 2009;113(2):439–47.
- [32] Khan TK, Ravikanth M. Synthesis of covalently linked boron-dipyrromethenechromophore conjugates using 3-bromo boron-dipyrromethene as a key precursor. Tetrahedron 2011;67(32):5816–24.
- [33] Khan TK, Rao MR, Ravikanth M. Synthesis and photophysical properties of 3,5bis(oxopyridinyl)- and 3,5-bis(pyridinyloxy)-substituted boron-dipyrromethenes. Eur J Org Chem 2010;12:2314–23.
- [34] Kee HL, Kirmaier C, Yu L, Thamyongkit P, Youngblood WJ, Calder ME, et al. Structural control of the photodynamics of boron-dipyrrin complexes. J Phys Chem B 2005;109(43):20433-43.
- [35] Benesi HA, Hildebrand JH. J Am Chem Soc 1949;71:2703-7.
- [36] Wu J-S, Hwang I-C, Kim KS, Kim JS. Rhodamine-based Hg<sup>2+</sup>-selective chemodosimeter in aqueous solution: fluorescent OFF-ON. Org Lett 2007;9(5): 907-10.