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### **Graphical abstract**

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# A reversible fluorescent chemosensor for Mercury ions based on 1H-Imidazo[4,5-b]Phenazine derivatives

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### Abstract:

A series of non-sulfur, fluorescent sensors ( $S_6$ ,  $S_{6-1}$  or  $S_{6-2}$ ) for mercury ions bearing 1H-Imidazo[4,5-b]Phenazine derivatives have been designed and synthesized. Among there sensors, a furan group into the sensor  $S_6$  molecule was as the functional group, compound  $S_{6-1}$  containing the 5-(4-Nitrophenyl)-2-furan group was synthesized, and in order to establish the furan group's contribution to the sensor's fluorescent sensing abilities, compound  $S_{6-2}$  which without containing the furan group was also synthesized.  $S_6$  showed excellent fluorescent specific selectivity and high sensitivity for  $Hg^{2+}$  in aqueous solution. The detection limit of the sensor towards  $Hg^{2+}$  is  $1.6 \times 10^{-7}$  M, and other ions, including  $Fe^{3+}$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Cr^{3+}$ , and  $Mg^{2+}$ had nearly no influence on the probing behavior. Notably, this sensor serves as a recyclable component in sensing materials. The test strips based on  $S_6$  were fabricated, which could act as a convenient and efficient  $Hg^{2+}$  test kits.

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### **1. Introduction**

Mercury is one of the most hazardous species in nature, which may cause prenatal brain damage, cognitive and motion disorders, vision and hearing loss, and even death.<sup>1</sup> Development of a facile and selective method for Hg<sup>2+</sup> detection has long been demanded in the area of food safety and environmental protection. Numerous chemosensors for Hg<sup>2+</sup> with good properties have been reported.<sup>2</sup> Most of these traditional chemosensors contain a sulfur moiety and the sensing process involves an irreversible coordination of Hg<sup>2+</sup> to the S atom.<sup>3</sup> The mechanism for traditional sensors includes an affinity irreversible organic reaction driven by the extremely strong Hg–S affinity. (1) ring opening of spirocyclic systems (rhodamine and fluorescein, etc.),<sup>4</sup> (2) intramolecular cyclic guanylation of thiourea derivatives,<sup>5</sup> (3) conversion of thiocarbonyl compounds into their carbonyl analogues or a sequential desulfurization-lactonization reaction<sup>6</sup>(Scheme 1). This thiophilic approach will suffer from potential interference in sulfur-rich environments where mercury is abundant,<sup>7</sup>



**Scheme 1** Tactics for the sensing of  $Hg^{2+}$ .

and undesired oxidation of the probes containing a sulfur atom by air or oxidizing reagents also inevitably occurs. Other drawbacks may be the requirement for elevated

temperature or excess quantities of  $Hg^{2+}$  to drive these desulfurization reactions to completion. Correspondingly, most of the traditional chemosensors which contain a sulfur moiety and the sensing process involves an irreversible coordination of  $Hg^{2+}$  to the S atom were unrecyclable. So the recyclable sensors for  $Hg^{2+}$  are badly needed.

Furthermore, phenazine derivatives have been synthesized and been used for organic electronics for a long time,<sup>8</sup> but they have seldom been used in host-guest chemistry. Phenazines are ideal platforms for the development of cation, anion, and neutral molecule recognition. Moreover, among the different fluorogenic units, phenazine is very sensitive to conformational change. Phenazine-based fluorescent chemosensors are still very scarce, although in principle, well-designed ones should show very good performance.

In view of this requirement and as part of our research effort devoted into ion recognition,<sup>9</sup> an attempt was made to obtain a non-sulfur, recyclable and efficient fluorescent sensor which could sense  $Hg^{2+}$  with specific selectivity and high sensitivity in aqueous solution. This paper details the design and synthesis of a series of  $Hg^{2+}$  fluorescent sensors  $S_6$ ,  $S_{6-1}$  or  $S_{6-2}$  bearing 1H-Imidazo[4,5-b]Phenazine derivatives (Scheme 2). The strategies for the design of these sensors were as follows. The phenazine group acts as fluorophore, imidazole and furan groups into the same sensor molecule as the functional groups, to allow the coordination capacity required to coordinate a mercury ion. The sensors were designed to be easy to synthesize. In order to establish the substituent group's influence to the sensor's fluorescent sensing abilities for  $Hg^{2+}$ , compound  $S_{6-1}$  which containing the 5-(4-Nitrophenyl)-2-furan

group was synthesized, and in order to establish the furan group's contribution to the sensor's fluorescent sensing abilities for  $Hg^{2+}$ , compound  $S_{6-2}$  which without containing the furan group was also synthesized. Sensor  $S_6$  showed fluorescent selectivity for mercury ions in DMSO/H<sub>2</sub>O (6:4, v/v) HEPES buffer solutions (pH=7.2) over other common physiologically important metal ions. To the best of our knowledge, this is the first time that the Phenazine derivatives were used to the recognition of  $Hg^{2+}$  ions with high selectivity.



Scheme 2 Synthesis of compounds S<sub>6</sub>, S<sub>6-1</sub> and S<sub>6-2</sub>.

### 2. Experimental

### 2.1. Materials and physical methods

Fresh double distilled water was used throughout the experiment. All other reagents and solvents were commercially available at analytical grade and were used without

further purification. <sup>1</sup>H NMR spectra were recorded on a Mercury-400BB spectrometer at 400 MHz and <sup>13</sup>C NMR spectra were recorded on a Mercury-600BB spectrometer at 150 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS,  $\delta$  scale with solvent resonances as internal standards) Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer.

2.2. Synthesis of sensors  $S_6$ ,  $S_{6-1}$  and  $S_{6-2}$ .

2,3-diamino-phenazine was prepared following the reported procedure.<sup>8</sup>

5-(4-Nitrophenyl)-2-furaldehyde was prepared following the reported procedure.<sup>10</sup> Synthesis of Compounds S<sub>6</sub>, S<sub>6-1</sub> and S<sub>6-2</sub>:

2,3-diamino-phenazine (0.42g, 2mmol), 2-furaldehyde (0.24g, 2.5mmol) and catalytic amount of acetic acid (AcOH) were combined in hot absolute DMF (20 mL). The solution was stirred under reflux conditions for 8 hours, after cooling to room temperature, the brown precipitate was filtrated, washed with hot absolute ethanol three times, then recrystallized with DMF-H<sub>2</sub>O to get brown powdery product S<sub>6</sub>. The other compounds S<sub>6-1</sub> and S<sub>6-2</sub> was prepared by similar procedures.

**S**<sub>6</sub>: Yield: 72%; m.p.>300°C; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ 13.43 (s 1H), δ 8.45 (s 1H), 8.23~8.21 (m 3H), 8.17~8.16 (d J=4 1H), 7.90~7.87 (m 2H), 7.59~7.58 (d J=4 1H), 6.89~6.88 (m 1H); <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 150 MHz) δ 156.16, 154.46, 151.15, 147.08, 144.39, 141.77, 141.03, 140.13, 136.99, 129.76, 129.09, 128.58, 123.20, 115.04, 113.15, 102.37, 99.07; IR (KBr, cm<sup>-1</sup>) v: 3101 (NH), 1653 (C=N), 1620 (C=C); ESI-MS m/z:  $(M+H)^+$  Calcd for C<sub>17</sub>H<sub>10</sub>N<sub>5</sub>O 287.2; Found 287.2; Anal. Calcd.

For C<sub>17</sub>H<sub>10</sub>N<sub>5</sub>O: C, 71.32; H, 3.52; N, 19.57; O, 5.59; Found C, 71.26; H, 3.55; N, 19.56; O, 5.63.

**S**<sub>6-1</sub>: Yield: 75%; m.p.>300°C; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz)  $\delta$  13.56 (s 1H),  $\delta$ 8.34~8.32 (m 3H), 8.18~8.15 (m 5H), 7.84~7.81 (m 2H), 7.67~7.66 (d J=4 1H), 7.61~7.60 (d J=4 1H); IR (KBr, cm<sup>-1</sup>) v: 3106 (NH), 1643 (C=N); ESI-MS m/z: (M+H)<sup>+</sup> Calcd for C<sub>23</sub>H<sub>13</sub>N<sub>5</sub>O<sub>3</sub> 408.3; Found 408.4; Anal. Calcd. For C<sub>23</sub>H<sub>13</sub>N<sub>5</sub> O<sub>3</sub>: C, 67.81; H, 3.22; N, 17.19; O, 11.78; Found C, 67.78; H, 3.24; N, 17.16; O, 11.82.

**S**<sub>6-2</sub>: Yield: 80%; m.p.>300°C; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ 13.44 (s 1H), δ 8.51 (s 1H), 8.38~8.37 (d J= 4 2H), 8.26~8.23 (d 3H), 7.89~7.88 (d J=4 2H), 7.67~7.66 (d 3H); <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 150 MHz) δ 159.55, 148.88, 141.87, 141.68, 140.51, 140.23, 139.84, 131.87, 131.88, 129.85, 129.55, 129.23, 129.22, 129.02, 128.80, 127.76, 127.75, 114.84, 105.91; IR (KBr, cm<sup>-1</sup>) v: 3168 (NH), 1693 (C=N); ESI-MS m/z: (M+H)<sup>+</sup> Calcd for C<sub>23</sub>H<sub>13</sub>N<sub>5</sub>O<sub>3</sub> 297.1; Found 297.2; Anal. Calcd. For C<sub>23</sub>H<sub>13</sub>N<sub>5</sub> O<sub>3</sub>: C, 77.01; H, 4.08; N, 18.91; Found C, 77.08; H, 4.04; N, 18.88.

2.3. General procedure for Fluorescence spectra experiments

All fluorescence spectra were recorded on a Shimadzu RF–5301 fluorescence spectrometer after the addition of perchlorate metal salts in DMSO, while keeping the ligand concentration constant ( $2.5 \times 10^{-5}$  M). The excitation wavelength was 416 nm. Solutions of metal ions were prepared from the perchlorate salts of Fe<sup>3+</sup>, Hg<sup>2+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup>, and Mg<sup>2+</sup>.

2.4. General procedure for <sup>1</sup>H NMR experiments

For <sup>1</sup>H NMR titrations, two stock solutions were prepared in DMSO- $d_6$ , one

containing the sensor only and the second containing an appropriate concentration of the metal. Aliquots of the two solutions were mixed directly in NMR tubes.

### 3. Results and discussion

In order to investigate the  $Hg^{2+}$  recognition abilities of the sensors  $S_6$ ,  $S_{6-1}$  and  $S_{6-2}$  in aqueous solution, we carried out a series of Host-Guest recognition experiments in DMSO/H<sub>2</sub>O (6:4/v:v) HEPES buffered solution at pH 7.2. The fluorescent measurements for  $S_6$ ,  $S_{6-1}$  and  $S_{6-2}$  were first performed in DMSO/H<sub>2</sub>O (6:4/v:v) HEPES buffered solution (pH=7.2). As shown in Figure (1), sensors  $S_6$  and  $S_{6-2}$  had strong emission maximum wavelength at 546 nm and 544 nm, but  $S_{6-1}$  emitted very weakly, indicating that the 5-aryl-furan unit directly bound to the phenazine group quenched the emission for the formation of the twisted intramolecular charge transfer state.<sup>11</sup> The recognition



Figure 1 Fluorescence spectra of  $S_6$  (25µM),  $S_{6-1}$  (25µM) or  $S_{6-2}$  (25µM).

profiles of the chemosensor  $S_6$  toward various metal cations,  $Fe^{3+}$ ,  $Hg^{2+}$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Cr^{3+}$ , and  $Mg^{2+}$ , were investigated by fluorescence spectroscopy in DMSO/H<sub>2</sub>O (6:4/v:v) HEPES buffered solution at pH 7.2. As shown in Figure (2), in the fluorescence spectrum, the emission of  $S_6$  appeared at the

maximum emission wavelength was 546 nm in DMSO/H<sub>2</sub>O (6:4, v/v) HEPES buffer

(pH 7.2) solution when excited at  $\lambda_{ex}{=}416$  nm. When 15 equivalents of  $Hg^{2{\scriptscriptstyle +}}$  was



**Figure 2** Fluorescence spectra of  $S_6$  upon an excitation at 416 nm in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) in the presence of Hg<sup>2+</sup> (15 equiv.). Inset: photograph from left to right shows the change in the fluorescence of  $S_6$ ,  $S_6$ -Hg<sup>2+</sup> (15 equiv.) in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4).



**Figure 3** (a) Fluorescence emission data for a 1:15 mixture of  $S_6$  (25µM) and different metal ions: 1)only  $S_6$ , 2) Fe<sup>3+</sup>, 3) Hg<sup>2+</sup>, 4) Ca<sup>2+</sup>, 5) Cu<sup>2+</sup>, 6) Co<sup>2+</sup>, 7) Ni<sup>2+</sup>, 8) Cd<sup>2+</sup>, 9) Pb<sup>2+</sup>, 10) Zn<sup>2+</sup>, 11) Cr<sup>3+</sup> and 12) Mg<sup>2+</sup>; as their perchlorate salts, in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) solution. (excitation wavelength = 416 nm). (b) Visual fluorescence emissions of sensor  $S_6$  after the addition of Fe<sup>3+</sup>, Hg<sup>2+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup> and Mg<sup>2+</sup> (15 equiv.) in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) on excitation at 365 nm using UV lamp at room temperature.

added to the DMSO/H<sub>2</sub>O (6:4, v/v) HEPES buffer (pH 7.2) solutions of sensor S<sub>6</sub>, the fluorescence emission band at 546 nm is red-shifted to 562 nm. The apparent fluorescence emission color change from yellow to jacinth could be distinguished by the naked eye. To validate the selectivity of sensor S<sub>6</sub>, the same tests were also applied using Fe<sup>3+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup>, and Mg<sup>2+</sup> ions, and none of these anions induced any significant changes in the fluorescent spectrum of the sensor (Figure 3). Therefore, in DMSO/H<sub>2</sub>O solution, S<sub>6</sub> showed specific



**Figure 4** Fluorescence emission data for a 1:15 mixture of  $S_{6-1}$  (25µM) and different metal ions: 1)only  $S_6$ , 2) Fe<sup>3+</sup>, 3) Hg<sup>2+</sup>, 4) Ca<sup>2+</sup>, 5) Cu<sup>2+</sup>, 6) Co<sup>2+</sup>, 7) Ni<sup>2+</sup>, 8) Cd<sup>2+</sup>, 9) Pb<sup>2+</sup>, 10) Zn<sup>2+</sup>, 11) Cr<sup>3+</sup> and 12) Mg<sup>2+</sup>; as their perchlorate salts, in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) solution. (excitation wavelength = 436 nm).

fluorescent selectivity to  $Hg^{2+}$ . The same tests were applied to  $S_{6-1}$  (Figure 4) and  $S_{6-2}$  (Figure 5). In this case, when various cations were added to the DMSO/H<sub>2</sub>O (6:4/v:v, pH=7.2) solutions of  $S_{6-1}$  or  $S_{6-2}$ , no obvious changes were observed. In corresponding fluorescent spectrum of  $S_{6-1}$  or  $S_{6-2}$ , there is no selectivity for the recognition of  $Hg^{2+}$ , which indicated that  $S_{6-1}$  or  $S_{6-2}$  couldn't fluorescent and selectively sense  $Hg^{2+}$  under these conditions.



**Figure 5** Fluorescence emission data for a 1:15 mixture of  $S_{6-2}$  (25µM) and different metal ions: 1)only  $S_6$ , 2) Fe<sup>3+</sup>, 3) Hg<sup>2+</sup>, 4) Ca<sup>2+</sup>, 5) Cu<sup>2+</sup>, 6) Co<sup>2+</sup>, 7) Ni<sup>2+</sup>, 8) Cd<sup>2+</sup>, 9) Pb<sup>2+</sup>, 10) Zn<sup>2+</sup>, 11) Cr<sup>3+</sup> and 12) Mg<sup>2+</sup>; as their perchlorate salts, in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) solution. (excitation wavelength = 403 nm).

Therefore, according to these results we can find that the furan moiety acted as a functional group and played a crucial role in the process of colorimetric recognition. The sensor S<sub>6</sub> employ furan moiety as functional group, which possess fluorescent Hg<sup>2+</sup> cations. Because for abilities the  $S_{6-1}$ employ response the 5-(4-Nitrophenyl)-2-furan group as functional group, and the nitrophenyl group in the molecule can enhance the the twisted intramolecular charge transfer ability, the fluorescent capability of  $S_{6-1}$  is too weak to fluorescent recognize any cations.<sup>12</sup> At the same time, because the S<sub>6-2</sub> has no furan unit as functional group, S<sub>6-2</sub> has no fluorescent capability to fluorescent recognize any cations.

As  $S_6$  showed specific selectivity for  $Hg^{2+}$ , a series of experiments was carried out to investigate the  $Hg^{2+}$  recognition capability and mechanism of  $S_6$ . To gain an insight into the stoichiometry of the  $S_6$ - $Hg^{2+}$  complex, the method of continuous variations



Figure 6 The Job's plot examined between  $Hg^{2+}$  and  $S_6$ , indicating the 1 : 1 stoichiometry for  $S_6-Hg^{2+}$  clearly.

(Job's method)<sup>13</sup> was used. When the molar fraction of sensor  $S_6$  was 0.5, the fluorescence intensity value approached a maximum, which demonstrated the formation of a 1:1 complex between the sensor  $S_6$  and  $Hg^{2+}$  (Figure 6).



**Figure 7** (a) Fluorescence spectra of  $S_6$  (25µM) in the presence of different concentration of Hg<sup>2+</sup> (0-5.58 equiv.) in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4). (b) A plot of fluorescence intensity depending on the concentration of Hg<sup>2+</sup> in the range from 0 to 5.58 equivalents.

The binding properties of sensor  $S_6$  with  $Hg^{2+}$  were further studied by fluorescence emission spectral variation experiments (Figure 7). It turned out that DMSO/H<sub>2</sub>O (6:4/v:v, pH=7.2) solutions of  $S_6$ , with an increasing amount of  $Hg^{2+}$ , the emission peak at 546 nm gradually shifted to 562 nm. The binding constant Ks of the metal complex

was determined as  $1.8 \times 10^4$  M<sup>-1</sup>. And the detection limit of the fluorescent spectrum changes calculated as  $1.6 \times 10^{-7}$  M for Hg<sup>2+</sup>cation, which pointing to the high detection sensitivity.



**Figure 8** IR spectra of compound  $S_6$  and  $S_6$ -Hg<sup>2+</sup> complex in KBr disks.

The recognition mechanism of the sensor  $S_6$  with  $Hg^{2+}$  were investigated by IR spectra and <sup>1</sup>H NMR titration methods. In the IR spectra of  $S_6$ , the stretching vibration absorption peaks of imidazole N-H, imidazole C=N and furan C=C appeared at 3100, 1651 and 1625 cm<sup>-1</sup> respectively. However, when  $S_6$  coordinated with  $Hg^{2+}$ , the stretching vibration absorption peaks of imidazole N-H shifted to 3124 cm<sup>-1</sup>, while, the stretching vibration absorption peaks of imidazole C=N and furan C=C shifted to 1618 cm<sup>-1</sup>, which indicated that  $S_6$  complexed with  $Hg^{2+}$  via O-Hg<sup>2+</sup>-N coordination bond as shown in Figure (8).

The results of <sup>1</sup>H NMR titration experiments also support this presumption. As shown in Figure (9), after adding 1.0 equivalents of  $Hg^{2+}$ , the NH peak at 13.4 ppm disappeared. At the same time, the signal of the hydrogen atoms in the benzene and



**Figure 9** <sup>1</sup>H NMR spectra (400 MHz, DMSO- $d_6$ ) of free S<sub>6</sub> and in the presence of Hg<sup>2+</sup>,  $\Gamma$ , respectively.

furan rings showed a significant downfield shift, indicating a charge transfer from the benzene and furan groups to the  $Hg^{2+}$  ions. After adding 2.0 equivalents of  $\Gamma$  to the above system, one new peak appeared at 8.8 ppm, which can be attributed to the NH protons. Because of the negative electron character of  $\Gamma$ , the N-H signal in the top line and bottom line is different.<sup>14</sup> And, the signal of the hydrogen atoms in the benzene and furan rings showed a significant upfield shift. Based on the above findings, we propose that the reaction mechanism in this system may proceed through the route depicted in Figure (10).



Figure 10 The proposed structures of  $S_6$  for  $Hg^{2+}$  and  $I^-$  ions.

An important feature of the sensor is its high selectivity toward the analyte over other

competitive species. The variations of fluorescent spectrum of sensor  $S_6$  in DMSO/H<sub>2</sub>O binary solutions caused by the metal ions Fe<sup>3+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup>, and Mg<sup>2+</sup> were recorded in Figure (3). It is noticeable that the miscellaneous competitive metal ions did not lead to any significant interference. In the presence of these ions, the Hg<sup>2+</sup> still produced similar emission changes (Figure 11). These results shown that the selectivity of sensor S<sub>6</sub> toward Hg<sup>2+</sup> was not affected by the presence of other cations and suggested that it could be used as a fluorescent chemosensor for Hg<sup>2+</sup>.



Figure 11 Fluorescence spectra of  $S_6$  and  $S_6$ -Hg<sup>2+</sup>in the presence of 15 equivalents of various metal ions in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) HEPES buffered solution at pH 7.2, room temperature.

The selectivity of  $S_6$  to  $Hg^{2+}$  was also examined over a wide range of pH values. No apparent changes of the fluorescence spectra were observed, and the detection of  $Hg^{2+}$  can work well in the range of pH 2.0-10.0 (Figure 12).



Figure 12 Influence of pH on the fluorescence of  $S_6$ -Hg<sup>2+</sup> in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4).

Excitation wavelength is 416 nm.



**Figure 13** Emission spectra showing the reversible complexation between  $S_6$  and  $Hg^{2+}$  (5.0 equiv.) by introduction of  $\Gamma$  (10.0 equiv.).

The reversibility of the chemosensor function was tested by addition of  $\Gamma$  to the mercury-sensor complex. The  $\Gamma$  ion is well-known to bind strongly to Hg<sup>2+</sup> ions.<sup>15</sup> Addition of  $\Gamma$  to a solution of the S<sub>6</sub>–Hg<sup>2+</sup> complex induced the opposite trend in the fluorescent spectra to that observed on titration with Hg<sup>2+</sup>. Upon addition of 40 equivalents of  $\Gamma$ , the optical fluorescence intensity returned to the levels observed for the free compound S<sub>6</sub>. The addition of  $\Gamma$  to the S<sub>6</sub>–Hg<sup>2+</sup> complex shows that the process of titrating sensor S<sub>6</sub> with Hg<sup>2+</sup> is reversible, and the reversible process could



be repeated at several times with little fluorescent efficiency loss (Figure 13, 14).

**Figure 14** Fluorescence emission spectra of S<sub>6</sub> (25 $\mu$ M) in the presence of Hg<sup>2+</sup> (15 equiv.) or  $\Gamma$  (40 equiv.) in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) solution. The excitation wavelength was 416 nm. Inset: photograph from left to right shows the change in the fluorescence of only S<sub>6</sub>, S<sub>6</sub>-Hg<sup>2+</sup> (15 equiv.) and S<sub>6</sub>-Hg<sup>2+</sup> (15 equiv.) plus  $\Gamma$  (40 equiv.) in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) solution on excitation at 365 nm.

To investigate the practical application of chemosensor  $S_6$ , test strips were prepared by immersing filter papers into a DMSO solution of  $S_6$  (0.1 M) and then drying in air. The test strips containing  $S_6$  was utilized to sense  $Hg^{2+}$  and other metal ions. As shown in Figure (15), when  $Hg^{2+}$  and the other ions were added on the test kits respectively, the obvious color change was observed only with  $Hg^{2+}$  solution under the 365nm UV lamp. And potentially competitive ions exerted no influence on the detection of  $Hg^{2+}$  by the test strips. Therefore, the test strips could conveniently detect  $Hg^{2+}$  in solutions.



Figure 15 Photographs of  $S_6$  on test papers (A) only  $S_6$ , (B) after immersion into DMSO/H<sub>2</sub>O

(PH=7.2, v/v=6:4) solutions with  $Hg^{2+}$ , C) after immersion into DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) solutions with others ions, (D) after immersion into DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) solutions with  $Hg^{2+}$  and other ions under irradiation at 365 nm.

### 4. Conclusion

A non-sulfur, recyclable sensor  $S_6$  of mercury ions has been designed and synthesized. The sensor was bearing 1H-Imidazo[4,5-b]Phenazine derivatives, which shown brilliant fluorescent response for  $Hg^{2+}$  ions in aqueous solution. The detection limit of the sensor towards  $Hg^{2+}$  is  $1.6 \times 10^{-7}$  M, and other ions, including Fe<sup>3+</sup>, Ca<sup>2+</sup>,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Cr^{3+}$ , and  $Mg^{2+}$  had nearly no influence on the probing behavior. Notably, this sensor serves as a recyclable component in sensing materials. In addition, test strips based on S<sub>6</sub> were fabricated, which also exhibits a good selectivity to  $Hg^{2+}$  as in solution. We believe the test strips could act as a convenient and efficient  $Hg^{2+}$  test kit.

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#### Supplementary data

These data include the Spectral data, MS data and copies of <sup>1</sup>H/<sup>13</sup>C NMR of the

compounds described in this article. Supplementary data associated with this article can be found in the online version.

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#### List of Figures and schemes:

Figure 1 Fluorescence spectra of  $S_6 (25\mu M)$ ,  $S_{6-1} (25\mu M)$  or  $S_{6-2} (25\mu M)$ .

**Figure 2** Fluorescence spectra of S<sub>6</sub> upon an excitation at 416 nm in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) in the presence of Hg<sup>2+</sup> (15 equiv.). Inset: photograph from left to right shows the change in the fluorescence of S<sub>6</sub>, S<sub>6</sub>-Hg<sup>2+</sup> (15 equiv.) in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4).

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**Figure 5** Fluorescence emission data for a 1:15 mixture of  $S_{6-2}$  (25µM) and different metal ions: 1)only  $S_6$ , 2) Fe<sup>3+</sup>, 3) Hg<sup>2+</sup>, 4) Ca<sup>2+</sup>, 5) Cu<sup>2+</sup>, 6) Co<sup>2+</sup>, 7) Ni<sup>2+</sup>, 8) Cd<sup>2+</sup>, 9) Pb<sup>2+</sup>, 10) Zn<sup>2+</sup>, 11) Cr<sup>3+</sup> and 12) Mg<sup>2+</sup>; as their perchlorate salts, in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) solution. (excitation wavelength = 403 nm).

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**Figure 7** (a) Fluorescence spectra of  $S_6$  (25µM) in the presence of different concentration of Hg<sup>2+</sup> (0-5.58 equiv.) in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4). (b) A plot of fluorescence intensity depending on the concentration of Hg<sup>2+</sup> in the range from 0 to 5.58 equivalents.

**Figure 8** IR spectra of compound  $S_6$  and  $S_6$ -Hg<sup>2+</sup> complex in KBr disks.

Figure 9 <sup>1</sup>H NMR spectra (400 MHz, DMSO- $d_6$ ) of free S<sub>6</sub> and in the presence of Hg<sup>2+</sup>,  $\Gamma$ ,

respectively.

Figure 10 The proposed structures of  $S_6$  for  $Hg^{2+}$  and  $\Gamma$  ions.

Figure 11 Fluorescence spectra of  $S_6$  and  $S_6$ -Hg<sup>2+</sup>in the presence of 15 equivalents of various metal ions in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) HEPES buffered solution at pH 7.2, room temperature.

Figure 12 Influence of pH on the fluorescence of  $S_6$ -Hg<sup>2+</sup> in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4). Excitation wavelength is 416 nm.

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Scheme 1 Tactics for the sensing of  $Hg^{2+}$ .

Scheme 2 Synthesis of compounds  $S_6$ ,  $S_{6-1}$  and  $S_{6-2}$ .

### **Figures and schemes:**



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This work, recyclable

Scheme 1 Tactics for the sensing of Hg<sup>2+</sup>



Scheme 2 Synthesis of compound  $S_6$ ,  $S_{6-1}$  and  $S_{6-2}$ .

## Supporting Information

# A reversible fluorescent chemosensor for Mercury ions based on 1H-Imidazo[4,5-b]Phenazine derivatives

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**Figure S1** Absorbance spectra of S<sub>6</sub> (25  $\mu$ M) in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) in the presence of Hg<sup>2+</sup> (15 equiv.).



Figure S2 Absorbance spectra of S<sub>6-1</sub> (25  $\mu$ M) in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) in the presence of Hg<sup>2+</sup> (15 equiv.).



**Figure S3** Absorbance spectra of S<sub>6-2</sub> (25  $\mu$ M) in DMSO/H<sub>2</sub>O (PH=7.2, v/v=6:4) in the presence of Hg<sup>2+</sup> (15 equiv.).

### ESI-MS spectrum of S<sub>6</sub> compound



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### ESI-MS spectrum of S<sub>6-1</sub> compound



### ESI-MS spectrum of $S_{6-2}$ compound



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### <sup>1</sup>H NMR spectra of compound S<sub>6</sub>



### <sup>1</sup>H NMR spectra of compound S<sub>6-1</sub>



## $^1\mathrm{H}$ NMR spectra of compound $\mathrm{S}_{6\text{-}2}$





# <sup>13</sup>C NMR spectra of compound S<sub>6</sub>

# $^{13}\mathrm{C}$ NMR spectra of compound $\mathrm{S}_{6\text{-}2}$

