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Tridentate Lysine-Based Fluorescent Sensor for Hg(II) in Aqueous Solution

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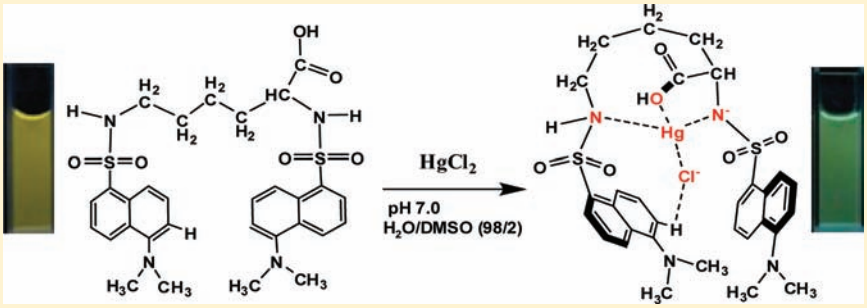
Supporting Information

ABSTRACT:



A novel homoplastic podand fluorescent sensor based on flexible hydrophilic lysine was prepared. Lysine with two dansyl groups-appended at both ends supplied a possibility for a tridentate binding toward Hg(II) and finally resulted in a unique selectivity to Hg(II) over other transition-metal ions with a hypersensitivity (detection limit 2.0 nM) in neutral buffered aqueous solutions. Notably, the coordination of chloride ion to the complex of sensor-Hg(II) brought forth that the trend in the NMR chemical shift for hydrogen and carbon atoms of the sensor was contrary to the findings in the former reports, which shows upfield shifts for the hydrogens and the alkane carbons but downfield shifts for the dansyl carbons, respectively.

INTRODUCTION

Mercury and most of its compounds are extremely toxic, and they enter the environment through a variety of natural and anthropogenic sources,[1−3] causing widespread concern due to their serious impact to the environment and public health. A major source of human exposure is Hg(II) in contaminated natural water, and therefore, a simple and fast detection of mercury ion in aqueous solution is desirable.

Applying fluorescent sensors to detect heavy metal ions are favored over other common analytical methods due to their advantages such as high sensitivity, good selectivity, quick response, and local observation (e.g., observation by fluorescence imaging spectroscopy).[4] In general, a typical fluorescent sensor includes a receptor for recognition and a fluorophore for signaling the recognition event, which are connected by a flexible linker.[5] The dansyl group is a common fluorophore due to its intense absorption, strong fluorescence in the visible region, and high sensitivity to the environment.[6] Therefore, numerous dansyl fluorescent sensors have been developed and applied for the detection of heavy metal ions.[3,7,8] For example, we previously reported water-soluble dansyl fluorescent sensors based on hydrophilic amino acids which could detect Hg(II) in aqueous solutions with high selectivity and sensitivity.[8] Both the easily deprotonated imino group on the sulfonamide moiety and the carboxyl group, as coordination ligands, played important roles in metal ion recognition. Therefore, the two sulfonamide groups at both ends of the flexible sensor presumably form a homoplastic podand conformation with the metal ion. Also, the introduction of the carboxyl group in coordinating with the metal ion will further stabilize the podand conformation. Here, we designed a novel lysine fluorescent sensor with two dansyl groups at both ends. The sensitive dansyl groups to the chemical microenvironment act as a fluorescent-shift signal source. The flexible alkane chain of lysine probably distorts to favor the chelation of the two sulfonamide groups with metal ions in aqueous solutions.[9] The dual sulfonamide and carboxyl groups in the sensor can produce tridentate chelation with metal ions. The experimental results indicated that the sensor displayed a rapid and specific response to Hg(II) in neutral buffered aqueous solutions.

RESULTS AND DISCUSSION

The fluorescent sensor based on lysine with double dansyl groups (**1**) was easily synthesized by three steps in 63.1% of yield according to the literature procedure[8,10] (Scheme 1). In buffer solutions of **1**, the addition of $HgCl_2$ induced a significant change

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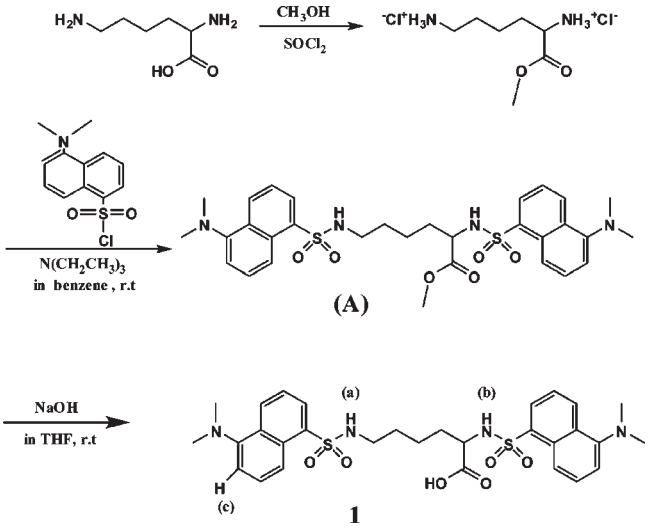
Scheme 1. Synthetic Route of 1



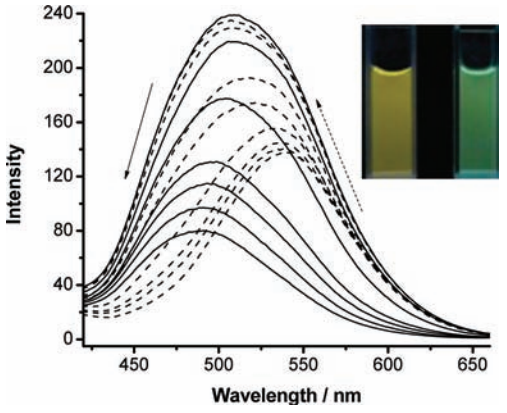


Figure 1. Fluorescent spectra of **1** (5.0 μM) in 10.0 mM NaH_2PO_4/Na_2HPO_4 buffered solution (DMSO-2%, pH 7.0) upon addition of various amounts of $HgCl_2$ (0.0, 8.0, 16.7, 33.4, 68.0, 83.5, 117.0, 134.0, 167.0, 334.0, 1167.0, 2837.0, 4500.0, 7800.0, 13000.0 nM) at an excitation wavelength of 340 nm. The inset shows fluorescence photographs of **1** (20.0 μM, left) and **1**-Hg(II) (20.0 μM/10.0 μM, right) under the excitation of 365 nm.

of fluorescent spectra with a gradual blue-shift ($\Delta\lambda_{max}$ = 51 nm, from 540 to 489 nm) (Figure 1).[11] Meanwhile, the fluorescence color of solutions changed from yellow to green under illumination with 365 nm light (inset in Figure 1), and the fluorescent visual color change plot was exhibited when the concentration of $HgCl_2$ is 0.3 μM. The significant blue-shift of the maximum emission was attributed to the deprotonation of the sulfonamide upon the cationic binding.[8,12] When the sulfonamide group interacted with the metal ion, the reduction of the charge density on the anionic nitrogen atom would inhibit the internal charge transfer (ICT) between the amino group and the dansyl group.

Upon the addition of $HgCl_2$, the fluorescent emission increased at first and then decreased (Figure S1a in the Supporting Information). At a low concentration of Hg(II) (0−0.167 μM), a polarity change in the microenvironment around the dansyl moieties probably bring on the enhancement of the emission intensity,[13] and the coordination of **1** and Hg(II) produced a blue-shift of

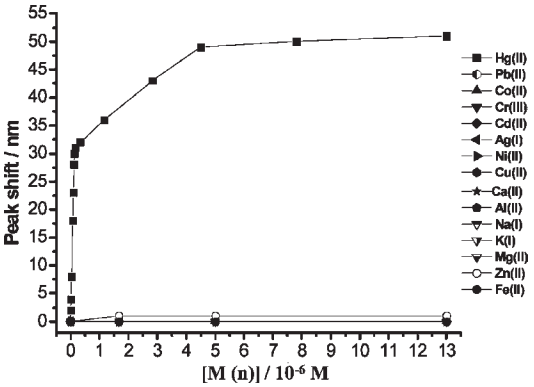


Figure 2. The blue-shift of the fluorescent maximum emission peak in 10.0 mM NaH_2PO_4/Na_2HPO_4 buffered solution (DMSO-2%, pH 7.0) of **1** (5.0 μM) in the presence of different concentrations of Hg(II) (0−13.0 μM) and Pb(II), Cr(III), Cd(II), Ag(I), Ni(II), Cu(II), Co(II), Zn(II), Al(III), Na(I), K(I), Ca(II), Fe(II), and Mg(II) (0−13.0 μM), respectively.

32 nm. Along with the addition of Hg(II) (0.167−4.5 μM), the quenching effect of the heavy metal ion induced the reduction of the emission intensity with another blue-shift ($\Delta\lambda$ = 17 nm). Hildebrand-Bebesi[14] plots gave binding constants of 2.1 × 10^6 and 3.0 × 10^5 L mol^{-1} for Hg(II) in aqueous solutions (1:1), respectively (Figure S1b,c in the Supporting Information). There is a blue-shift observed when more Hg(II) was added. These results showed that a more strong force between **1** and Hg(II) existed under low concentration of Hg(II), and the **1**-Hg(II) system gets saturated when the mole ratio of **1** and Hg(II) is 1:1. The phenomena possibly resulted from the dynamic coordination of **1** with Hg(II). Every mercury ion could generate the effective coordination with excessive **1** at the low concentration of Hg(II). Along with the addition of a concentration, Hg(II) displays two functions that one is coordination role and another is quencher.

Compound **1** was also applied to the detection of 14 other metal ions commonly found in surface water (Figure S2 in the Supporting Information). No obvious blue-shift of the maximum emission of **1** was observed upon the addition of these metal ions, including Pb(II), Co(II), Cu(II), Cr(III), Cd(II), Fe(II), etc. (Figure 2), but only slightly fluorescent quenching was observed. The results indicated a high selectivity of **1** toward Hg(II) over these metal ions with the fluorescent-shift signal in aqueous solutions. Moreover, a minimum detection limit of 2.0 nM was achieved for Hg(II) by compound **1**, which was much lower than the maximum allowable level of of the United States Environmental Protection Agency (EPA) for the mercury ion (10.0 nM) in drinking water.[15] In addition, the experiment results indicated a good reversibility for the response of 1 to Hg(II) (Figure S3 in the Supporting Information). We have also performed UV−vis spectral measurements of **1** to different metal ions. The results showed slight but regular UV−vis spectral responses of **1** to Hg(II) (Figure S6 in the Supporting Information). The decrease of bands at 248 and 330 nm upon addition of various amounts of $HgCl_2$ (0−75.0 μM) indicated that conformational changes of **1** were induced by Hg(II) binding. Differently, nearly no response could be observed when other metal ions were added.

The pH influence on the selectivity of compound **1** to Hg(II) was also studied, which showed that the fluorescent emission band of the **1**-Hg(II) complex was highly dependent on the solution pH. A larger blue-shift of the fluorescent emission peak

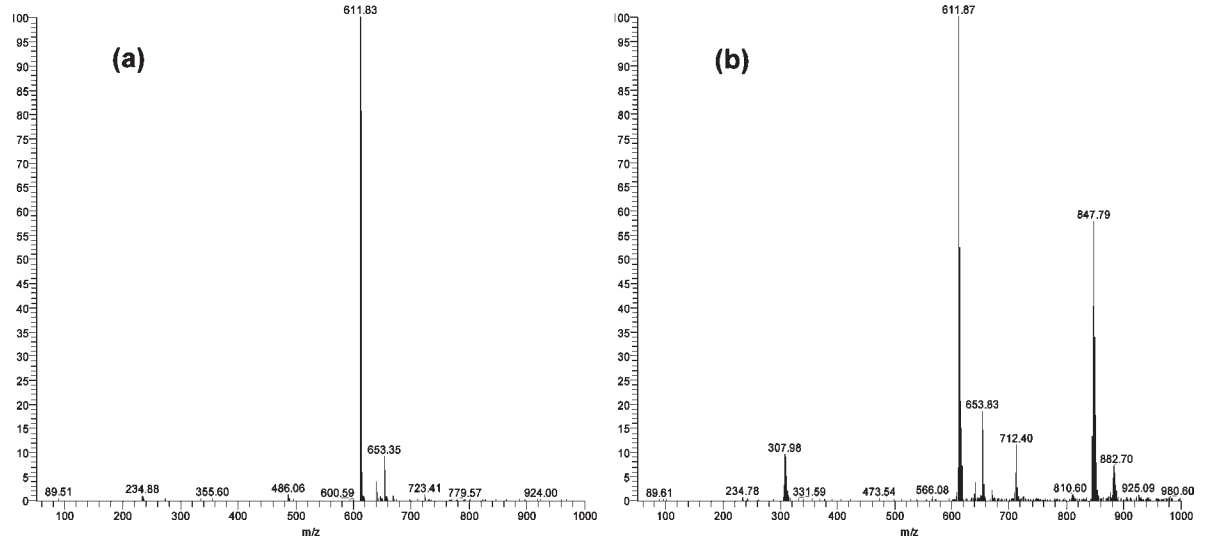


Figure 3. The ESI-MS mass spectra of **1** (a) and **1**-Hg(II) (b) in CH_3OH.

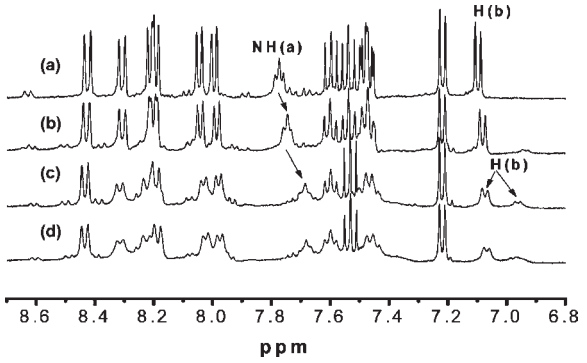


Figure 4. Selected region of the ^{1}H NMR spectra of (a) **1** (14.0 mM), (b) **1**-Hg(II) (2:1), (c) **1**-Hg(II) (1:1), and (d) **1**-Hg(II) (1:2) in DMSO-d_6/H_2O = 95:5.

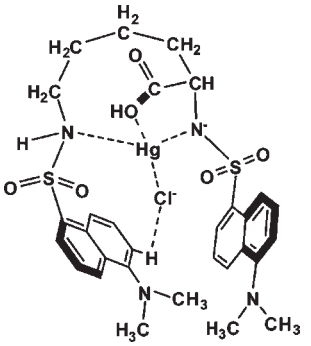


Figure 5. Proposed coordination model for **1**-Hg(II).

was observed when the pH was set between 6.0 and 7.0 (Figure S4 in the Supporting Information). These results were possible due to the low pH that would prevent the deprotonation of the sulfonamide, while the high pH would cause precipitation of mercuric hydroxide. Therefore, the detection of Hg(II) and other metal ions was carried out in 10.0 mM NaH_2PO_4/Na_2HPO_4 buffered solution (pH 7.0).

The interference of the potentially competing metal ions on Hg(II) detection was also investigated. The result showed that no obvious interference was observed in the presence of the common metal ions, including Pb(II), Cu(II), Cd(II), Fe(II), Na(I), Mg(II), Ca(II), etc. except Cr(III) and Co(II), as both had a minor influence on the maximum emission band shift of **1**-Hg(II) (Figure S5 in the Supporting Information).

In the ESI-MS of **1**-Hg(II), a peak at m/z 847.79 (calcd for $C_{30}H_{36}N_4S_2O_6$−HgCl = 847.80) corresponding to [**1** + HgCl] and another peak at m/z 882.70 (calcd for $C_{30}H_{36}N_4S_2O_6$−$HgCl_2$ = 883.25) corresponding to $[\mathbf{1} + HgCl_2]^-$ were clearly observed upon the addition of $HgCl_2$ (Figure 3). These results displayed a 1:1 stoichiometric ratio of **1** and Hg(II), being consistent with the result of a fluorometric titration measurement.

To further investigate the binding model between **1** and Hg(II), NMR experiments were carried out in DMSO-d_6/H_2O = 95:5. Upon the addition of $HgCl_2$, the chemical shift of the protons changed at first and then it stopped changing further after the molar ratio of **1**/Hg(II) reached 1:1 (see Figure 4 and the Supporting Information), which confirmed again that **1** and Hg(II) forms a 1:1 complex.

Upon the addition of $HgCl_2$, a new resonance peak for the carboxyl proton and a downfield shift of the carboxyl carbon ($\Delta\delta$ = 0.35 ppm) were observed. In addition, an obvious upfield shift of the chiral carbon atom ($\Delta\delta$ = −0.268 ppm) and its hydrogen proton ($\Delta\delta$ = −0.412 ppm) were measured. These findings revealed the coordination between the carboxyl group and Hg(II). Furthermore, the obvious upfield shifts of NH(a) ($\Delta\delta$ = −0.088 ppm) and the neighboring alkane protons/carbons revealed the coordination between N(a) and Hg(II). However, only the chemical shift for NH(a) was observed in the ^{1}H NMR spectra of **1** but not for NH(b). This phenomenon possibly resulted from the rapid proton exchange between NH(b) and water in DMSO-d_6, and the nearby connection of the carboxyl group potentially favors the exchange. The easily deprotonated imino group on the sulfonamide moiety played an important role for the recognition of metal ions.[8] Furthermore, the larger change in the chemical shift for the dansyl group close to the carboxyl group than the other group indicated the coordination of deprotonated-N(b) to the mercury(II) center. On the basis of these results, a potential coordination model between **1** and Hg(II)

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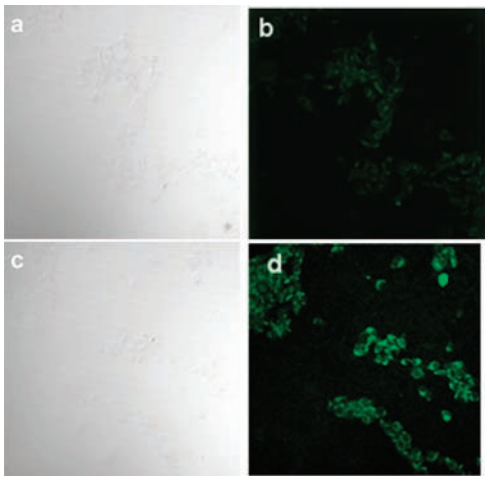

Figure 6. Bright field (a, c) and confocal fluorescence microphotographs (b, d) of live HeLa cells: (a, b) after 30 min exposure to 50.0 μM **1**; (c, d) after 30 min exposure to 50.0 μM **1** and further 30 min exposure to 50.0 μM $HgCl_2$. The conditions of the microscope were the same for parts a−d, and images were taken by a fluorescence microscope.

was proposed (Figure 5), which indicated a tridentate chelation between the fluorescent sensor and Hg(II), and the alkane chain distorted to favor the conformation. Interestingly, the trend in the NMR chemical shift for the dansyl and alkane groups was contrary to the findings in the former reports,[8] which showed that the hydrogens of the sensor were upfield shifted in the presence of Hg(II). Such a difference was probably ascribed to the coordination of chloride ion toward mercury(II),[16] as revealed by the mass spectra experiments. The electronegative chloride ion attaching to the metal ion increased the electron density of the N−Hg bond, enhancing the electron density around the attached hydrogen next to the sulfonamide group. In addition, the splitting patterns of H(c) suggested a special interaction between H(c) and the chloride ion. Considering the electronegative property of the chloride ion, it potentially interacts with the nearby electron-deficient hydrogen and further strengthens the special conformation of **1**-Hg(II). This coordination of chloride ion on **1**-Hg(II) is unique in the fluorescence sensoring for metal ions. When a little $HgCl_2$ was added into the solution of sensor **1**, the produced feeble NMR chemical shifts was consistent with the trend of chemical shifts under a higher concentration of Hg(II), which was in accord with the fluorescent results.

Because of its chemical and spectroscopic properties, **1** should be an ideal probe for the monitoring of mercury ions in living cells. To test this idea, in vivo detection of Hg(II) in HeLa cells was evaluated. Before the measurement, HeLa cells were incubated for 30 min with **1** (50.0 μM) to allow the probe to permeate into the cells. Fluorescence microscopic images (Figure 6) showed that the fluorescence intensity of the cells increased upon addition of Hg(II) (50.0 μM) into the medium after incubation for another 30 min at 37 °C. The cells displayed dramatically different brightness between parts b and d of Figure 6, and the results indicated that **1** have migrated into the cells and it can be applied to monitor intracellular Hg(II) in live cells.

CONCLUSIONS

In summary, our experimental results indicated that based on a tridentate binding model, **1** is an attractive sensor for the fast detection of Hg(II) in aqueous solution with unique selectivity. The sensor exhibited fluorescent shift in its emission spectra in response to Hg(II) in water, allowing hypersensitive Hg(II) detection (detection limit up to 2.0 nM). In addition, the coordination of chloride ion toward **1**-Hg(II) led to extraordinary changes in the NMR spectra of **1**. Furthermore, **1** can be applied for the monitoring of Hg(II) in living cells, implicating its potential applications in biological sampling and studying the toxicity or bioactivity of Hg(II) in biological applications. Thus, this sensor of Hg(II) has superiorities: (i) good water-solubility; (ii) hypersensitivity for Hg(II) detection; (iii) special homoplastic podand structure and the coordination with $[HgCl]^+$, which is rarely reported for the fluorescence sensors of Hg(II); (iv) can also monitor Hg(II) in living cells. Because of the specific interactions of metal ions with the amino acids and the dansyl group, modification of the bond site in other sensors is actively undertaken in our laboratory to develop more advanced fluorescent-shift sensors for metal ion recognition in water. These studies will provide a foundation for future design of more novel fluorescent-shift sensors.

EXPERIMENTAL SECTION

Materials and Methods. All chemicals were obtained from commercial suppliers and used without further purification. NMR experiments were performed on a Varian NMR Systems 400 MHz spectrometer using TMS as an internal standard. Mass spectra were measured on an LCQ DACAXP MAX mass spectrometer (Finnigan). Fluorescence spectra were measured on a Hitachi F-2500 fluorescence spectrophotometer. UV−vis spectra were obtained on a Shimadzu UV-1700 spectrophotometer at room temperature.

Synthesis of 1. *Compound* L*-Lysine Methyl Ester Dihydrochloride.* A volume of 5 mL of anhydrous methanol in flasks was first cooled to 0 °C in an ice−water bath for 5 min, followed by dropwise addition of thionyl chloride (1.0 mL). L-Lysine solid (1.0 g, 6.85 mmol) was added to the above methanol solution, and the resulting mixture was first stirred for 10 min at 0 °C in an ice−water bath and then under room temperature for 2 h before refluxing at 70−80 °C for another 30 min. Finally, the reaction mixture was cooled to room temperature, followed by evaporation of methanol. Then, anhydrous ether (40.0 mL) was added to wash the residue solid and cooled to 4 °C for 2 h. The mixture was filtered to remove the solvent, getting the milky white solid product of L-lysine methyl ester dihydrochloride with a 96.0% yield.[10a] The final product was characterized by ^{1}H NMR. ^{1}H NMR spectrum (D_2O) (ppm): 3.938 (t, 1H, CH), 3.616 (s, 3H, OCH_3), 2.774 (t, 2H, CH_2), 1.775 (m, 2H,CH_2), 1.487 (m, 2H,CH_2), 1.273 (m, 2H,CH_2).

Compound (***A***). L-Lysine methyl ester dihydrochloride (0.10 g, 0.46 mmol) prepared above was suspended in anhydrous benzene (20.0 mL), followed by dropwise addition of NEt_3 (0.15 mL, 1.1 mmol) and thereafter dansyl chloride (0.26 g, 0.51 mmol). The resulting mixture was stirred under a nitrogen atmosphere for 5 min and cooled to 0 °C in an ice−water bath. Then the mixture was allowed to warm to room temperature and stirred for 32 h at room temperature.[8,10b] Then benzene was evaporated, and the product was further purified by column chromatography. The yield of jade-green solid is 66.8%. The final product (**A**) was characterized by ^{1}H NMR. ^{1}H NMR spectrum ($CDCl_3$) (ppm): 8.530 (t, 2H), 8.250 (t, 2H), 8.196 (t, 2H), 7.590−7.571 (m, 2H), 7.520−7.502 (m, 2H), 7.216−7.159 (m, 2H), 3.744 (m, 1H, CH), 3.256 (s, 3H, OCH_3), 2.895 (s, 6H, NCH_3), 2.855 (s, 6H, NCH_3), 2.653 (m, 2H, CH_2), 2.327 (t, 1H, CH_2), 2.220 (t, 1H, CH_2), 2.013 (m, 2H, CH_2), 1.622 (m, 2H, CH_2).

Compound ***1***. (**A**) was hydrolyzed in THF (60.0 mL) with HCl (3.0 mL) for 2 h at room temperature and then first washed by saturated

$NaHCO_3$ solution and followed by washing with water to neutralize. The hydrolyzed product (**1**) was purified by column chromatography, and the structure was characterized by NMR. ^{1}H NMR spectrum (DMSO-d_6/H_2O, 95:5, v/v) (ppm): 8.479−8.458 (d, 1H), 8.361−8.340 (d, 1H), 8.264−8.227 (m, 2H), 8.097−8.079 (d, 1H), 8.046−8.029 (d, 1H), 7.816 (t, 1H, $NHCH_2$), 7.660−7.620 (t, 1H), 7.602−7.561 (t, 1H), 7.541−7.495 (m, 2H), 7.270−7.251 (d, 1H), 7.149−7.130 (d, 1H), 3.237 (s, 1H, CH), 2.835 (s, 6H, NCH_3), 2.726 (s, 6H, NCH_3), 2.353 (s, 2H, $NHCH_2$), 1.395−1.323 (d, 2H, $CHCH_2$), 1.169−1.049 (d, 2H, $NHCH_2CH_2$), 0.887 (s, 2H, $CHCH_2CH_2$). ^{13}C NMR spectrum (DMSO-d_6/H_2O, 95:5, v/v) (ppm): 173.760, 151.630, 151.515, 136.573, 136.331, 129.605, 129.570, 129.361, 129.266, 128.446, 128.364, 128.098, 128.049, 123.913, 123.754, 119.574, 119.481, 115.433, 115.293, 57.130, 45.409, 45.305, 42.675, 32.454, 29.339, 21.825. ESI-MS (m/z): 611.83; calcd for $C_{30}H_{37}N_4S_2O_6$, 612.21.

Measurements of Fluorescent Spectra. All the fluorescent experiments were carried out in 10.0 mM NaH_2PO_4/Na_2HPO_4 buffered solution (DMSO-2%, pH 7.0) at 298 K. Fluorescence titration was performed in aqueous solution using the respective chloride salt of metal ions (except for $AgNO_3$ and $Cr(NO_3)_3$).

■ ASSOCIATED CONTENT

Supporting Information. Experimental details, fitting procedure of the association constant, additional spectroscopic data, and NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The addition of a modicum DMSO in solution (2%) results in the fluorescence response of sensor **1** to Hg(II) to be more stable with time. Although the initial responses of **1** to Hg(II) in pure water are similar, they can not be kept stable for a long time. The additions of $HgCl_2$ and $Hg(NO_3)_2$ result in the same fluorescent recognition effect for **1**. Also, some common anions, such as NO_3^-, CH_3COO^-, SO_4^{2-}, could not interfere with the **1**-Hg(II) binding.

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