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RESEARCH ARTICLE

Carbamodithioate-based fluorescent chemosensor for Hg(II): a staged response approach and investigation into the sensing mechanism

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Abstract

Carbamodithioate-based compound **C1** was designed and synthesized as a new fluorescent probe for Hg^{2+} ions. Upon the addition of Hg^{2+} ions, it displayed a rare staged response: the emission spectra of **C1** first showed an apparent red-shift, followed by a dramatic decrease. To investigate the sensing mechanism, control compounds **C2** with the same phenanthroimidazole unit and **C3** with the same carbamodithioate functionality were synthesized. On comparison, the first step sensing process was ascribed to decreasing photoinduced electron transfer on the coordination of Hg^{2+} with the lone pair electrons of the nitrogen atom on the phenanthroimidazole ring. The affinity of Hg^{2+} and the carbamodithioate unit with four sulfur atoms then induced changes in intramolecular charge transfer efficiency and the second step fluorescent response.

KEYWORDS

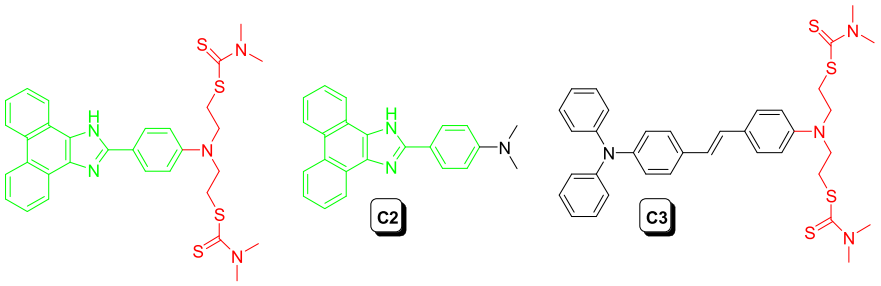
Fluorescent probe, intramolecular charge transfer, mercury, photoinduced electron transfer, stage response approach

The detection of some analytes, including metal ions, anions, explosives, proteins, DNA and RNA in certain samples is very important in medical diagnosis, combating terrorism, environmental monitoring, etc. For example, mercuric ions (Hg^{2+}), one of the more severe environmental pollutants, are very harmful to humans. Specifically, methylmercury, a product of the microbial biomethylation of Hg^{2+}, is known to cause brain damage and other chronic diseases.[1–6] Therefore, monitoring of Hg^{2+}, one of the most common and stable forms of mercury pollution, is increasingly required. The ability to recognize and sense biologically and environmentally important metal ions using a fluorescence technique has become significant in chemical sensing in recent years. Among the various methods available for the detection of Hg^{2+} ions, techniques based on fluorescence sensors have many number of advantages in terms of their high sensitivity, specificity, simplicity of implementation and fast response times.[7,8] Thanks to the enthusiastic efforts of scientists, many good chemosensors for Hg^{2+} ions have been reported, and some design rules have been summarized.[9–22]

In terms of sensor design, acyclic receptors are generally more popular than cyclic structures because synthesis of a cyclic structure is usually expensive.[23] Among these acyclic receptors, the carbamodithioate moiety was first used by Roundhill and co-workers to create upper-rim-substituted calix [4]arenes as selective extractants.[24] However, it has rarely been utilized for metal-sensing purposes. According to Pearson's hard and soft acids and bases theory, Hg^{2+} (soft acid) can preferentially interact with the sulfur atom (soft base).[25] Therefore, it is expected that the carbamodithioate moiety containing four sulfur atoms has exceptionally strong affinity towards Hg^{2+}. To further our interest in fluorescent sensor development for Hg^{2+} detection,[26–29] we herein reported an acceptor–spacer-donor system **C1**, comprising a phenanthroimidazole moiety as the fluorophore and carbamodithioate functionalities as ligating groups. Compound **C1** could serve as a new fluorescent chemosensor for Hg^{2+} and displayed a rare staged response: the emission spectra of **C1** first showed an apparent red-shift, followed by a dramatic decrease. Moreover, control compounds **C2** and **C3** were synthesized to investigate the sensing mechanism systematically (Scheme 1). We described the new fluorescent chemosensor for Hg^{2+} ions in detail.

1 | EXPERIMENTAL

Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. All other reagents were of



SCHEME 1 Structural comparison of probe **C1** and references **C2** and **C3**

analytical reagent grade and used without further purification. Double-distilled water was used in all experiments.

The ^{1}H and ^{13}C NMR spectra were measured on Varian Mercury300 spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. The electrospray ionization mass spectra (ESI-MS) were measured on a Finnigan LCQ advantage mass spectrometer. Elemental analyses were performed using a CARLOERBA-1106 microelemental analyzer. Photoluminescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer.

1.1 | Synthesis of compound C1

A mixture of 9,10-phenanthroquinone (208 mg, 1 mmol), compound **1** (623 mg, 1.5 mmol) and ammonium acetate (1.23 g, 16 mmol) in acetate acid (AcOH) (10 ml) was heated to 100°C for 30 min. The above hot solution was then cooled to room temperature, and the resulting yellow solid was collected by filtration and washed successively with acetate acid (AcOH), dilute sodium hydrogen carbonate solution and water. The crude product was further dried under reduced vacuum, and then purified by silica gel column chromatography using acetone as the eluent to afford compound **C1** as a yellow solid (259.2 mg, 43%). ^{1}H NMR (300 MHz, d_6-Acetone): δ=3.30 (m, 10H), 3.57 (m, 6H), 3.71 (s, 4H), 7.61–7.76 (m, 4H), 8.05–8.07 (d, J = 6.0 Hz, 2H), 8.49–8.61 (m, 4H), 8.82–8.88 (m, 2H). MS (ESI), m/z $[M + H]^+$: 604.0, calcd, 604.2. $C_{31}H_{33}N_5S_4$ (EA) (%, found/calcd): C, 61.69/61.57; H, 5.96/5.57; N, 11.29/11.60.

1.2 | Synthesis of compound C2

Compound **C2** was obtained by following a procedure similar to that for **C1**, using 9,10-phenanthroquinone (208 mg, 1 mmol), 4-(dimethylamino)benzaldehyde (223.6 mg, 1.5 mmol) and ammonium acetate (1.23 g, 16 mmol) in glacial AcOH (10 ml), with acetone: petroleum ether (1:1, v/v) as the eluent to afford compound **C2** as a yellow solid (63 mg, 31.5%). ^{1}H NMR (300 MHz, d_6-Acetone): δ=2.98–3.10 (m, 6H), 6.88–6.90 (d, J = 6.0, 2H), 7.60–7.66 (m, 4H), 8.16–8.18 (m, 2H), 8.56 (s, 2H), 8.82–8.85 (d, J = 9.0, 2H). MS (ESI), m/z $[M + H]^+$: 338.3, calcd, 338.2. $C_{23}H_{19}N_3$ (EA) (%, found/calcd): C, 81.67/81.87; H, 5.86/5.68; N, 12.58/12.45.

1.3 | Synthesis of compound C3

Under an argon atmosphere, compound **1** (416 mg, 1 mmol) and diethyl 4-(diphenylamino)benzylphosphonate (727 mg, 2 mmol) were dissolved in 30 ml THF, and NaH (0.2 g, 3.7 mmol) in 10 ml THF was added dropwise to the solution. After reacting overnight at room temperature, the solvent was removed under reduced pressure to give the crude product. The crude product was purified by silica gel column chromatography using dichloromethane: petroleum ether (1:1, v/v) as the eluent to give compound **C3** as a yellow solid (177 mg, 27%).^{1}H NMR (300 MHz, $CDCl_3$): δ=3.39 (s, 6H), 3.51–3.58 (m, 10H), 3.69–3.71 (m, 4H), 6.91 (s, 1H), 6.94–6.95 (m, 2H), 6.98 (s, 2H), 7.01–7.04 (m, 5H), 7.08–7.10 (m, 4H), 7.31 (s, 1H), 7.34–7.36 (d, J = 3.0, 2H), 7.38 (s, 1H), 7.41–7.44 (d, J = 4.5, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=34.2, 42.0, 45.8, 50.4, 112.7, 115.1, 123.6, 124.1, 124.7, 125.5, 127.3, 128.1, 129.7, 132.5, 133.6, 146.2, 147.2, 147.5, 196.8 ppm. MS (ESI), m/z $[M + H]^+$: 656.1, calcd, 656.2. $C_{36}H_{40}N_4S_4$ (EA) (%, found/calcd): C, 66.08/65.81; H, 5.91/6.14; N, 8.31/8.53.

1.4 | Preparation of solutions of metal ions

A 1 mmol quantity of each inorganic salt [$MgSO_4$, $MnSO_4{\cdot}2H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Pb(NO_3)_2$, $Ba(NO_3)_2$, $Ca(NO_3)_2{\cdot}4H_2O$, $CoCl_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $CdSO_4{\cdot}8H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$, LiCl, $NaNO_3$, KNO_3, $AgNO_3$ or $Hg(ClO_4)_2{\cdot}3H_2O$] was dissolved in distilled water (10 ml) to afford a 1×10^{-1} mol/l aqueous solution. The stock solutions were diluted to the desired concentrations with water when needed.

1.5 | Fluorescence titration of C1, C2 or C3 with Hg^{2+} ions

A solution of **C1**, **C2** or **C3** (1×10^{-5} mol/l) was prepared in THF. The solution of Hg^{2+} (1×10^{-3} mol/l) was prepared in distilled water. A solution of **C1**, **C2** or **C3** was placed in a quartz cell (10.0 mm wide) and the fluorescence spectrum was recorded. Aliquots of the Hg^{2+} ion solution were introduced and changes in the fluorescence intensity were recorded at room temperature each time.

1.6 | Fluorescence titration of C1 + Hg^{2+} with S^{2-} anions

A solution of **C1** (1×10^{-5} mol/l) was prepared in THF. The solution of Hg^{2+} with the concentration of 25 μM was added to the above solution. The solution of NaS (1×10^{-3} mol/l) was prepared in distilled water. A solution of **C1** + Hg^{2+} was placed in a quartz cell (10.0 mm wide) and the fluorescence spectrum was recorded. Aliquots of the S^{2-} ion solution were introduced to the above **C1** + Hg^{2+} solution and changes in the fluorescence intensity were recorded at room temperature each time.

1.7 | Fluorescence intensity changes of C1 with different metal ions

A solution of **C1** (1×10^{-5} mol/l) was prepared in THF. The solutions of metal ions (1×10^{-1} mol/l) were prepared in distilled water. A solution of **C1** (3.0 ml) was placed in a quartz cell (10.0 mm wide) and the fluorescence spectrum was recorded. Different ion solutions were introduced and changes in the fluorescence intensity were recorded at room temperature each time.

1.8 | Fluorescence titration of C1 with Ag^+ ions

A solution of **C1** (1×10^{-5} mol/l) was prepared in THF. The solution of Hg^{2+} (1×10^{-3} mol/l) was prepared in distilled water. A solution of **C1** was placed in a quartz cell (10.0 mm wide) and the fluorescence spectrum was recorded. Aliquots of the Ag^+ ion solution were introduced and changes in the fluorescence intensity were recorded at room temperature each time.

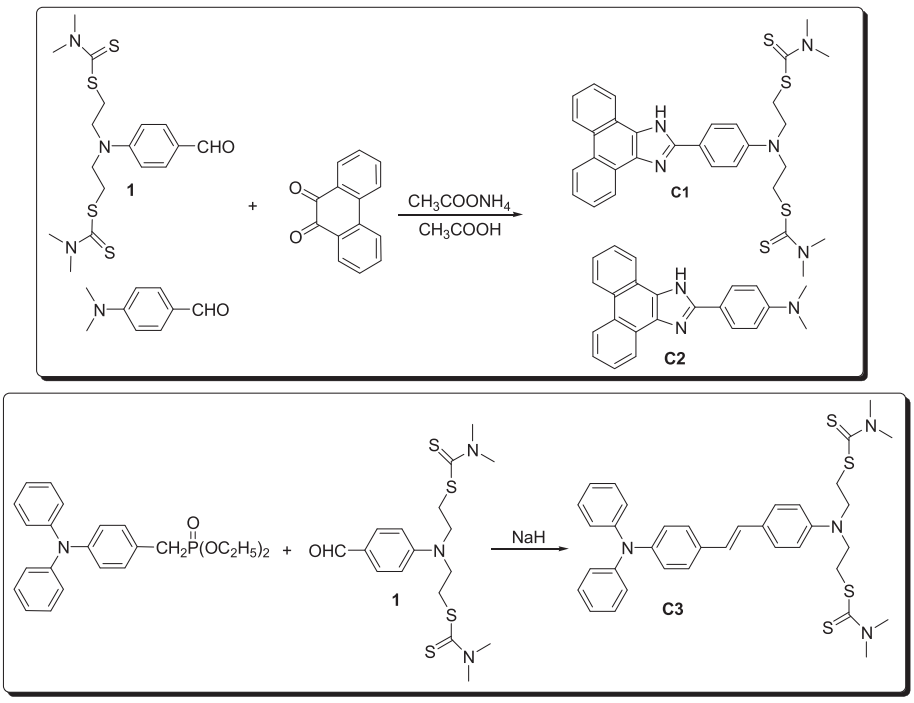
2 | RESULTS AND DISCUSSION

2.1 | Synthesis and structural characterization

Probe **C1** was readily synthesized in one step by coupling 9,10-phenanthroquinone with aldehyde **1** according to a reported procedure (Scheme 2),[23] and the reference compound **C2** was prepared using the same procedure by coupling 9,10-phenanthroquinone with 4-(dimethylamino)benzaldehyde. The Wittig reaction of aldehyde **1** with diethyl (4-(diphenylamino)benzyl) triphenyl)-phosphonate gave reference compound **C3**. The whole synthesis route was simple and the purification was easy. Their structures were well characterized by ^{1}H, ^{13}C NMR, ESI-MS, elemental analysis and ultraviolet/visible (UV/vis) spectra, and gave satisfactory spectral data (Figures S1–S8). Unfortunately, we failed to obtain the ^{13}C NMR spectra of compound **C1** and **C2** because of the poor solubility of the phenanthroimidazole moiety in them.

2.2 | Sensing properties

We tried to add Hg^{2+} ions to the diluted solution of compound **C1**, and investigate the sensing behavior of **C1** towards mercury ions. As shown in Figure 1, on increasing the concentration of Hg^{2+}, the fluorescent spectrum of compound **C1** displayed apparent changes. First, as the concentration of Hg^{2+} ions increased from 0 to 10 μM, the fluorescent intensity increased and the emission maximum gradually shifted from 414 to 422 nm. In fact, the emission spectrum changed immediately at Hg^{2+} concentration as low as 1 μM. To see the results more visually, we summarized the changes in intensity at 422 nm as a function of mercury concentrations. As shown in Figure S9, over a range of 0–10 μM, there was a good linear relationship between the intensity change and the concentration of Hg^{2+}. A linear regression curve could be simulated, and the point at which this line crossed the abscissa was taken as the limit of detection and equaled ~2.5×10^{-7} mol/l.[30] It suggested that compound **C1** could detect the presence of Hg^{2+} ions quantitatively. A Job plot was used to determine the binding stoichiometry of **C1** with Hg^{2+} ions. The total concentration of chemosensor **C1** and Hg^{2+} was held constant while the mole fraction of Hg^{2+} ions was altered; the increasing fluorescence value, ΔI ($\Delta I = I - I_0$, where I_0 and I are the fluorescence intensities at 422 nm in the absence and presence of Hg^{2+}, respectively) was plotted against the mole fraction. The maximum fluorescence increasing occurred at a mole fraction of 0.5, indicating the formation of a 1:1 complex (Figure S10).



SCHEME 2 Synthetic route for probe **C1** and the reference compounds **C2** and **C3**

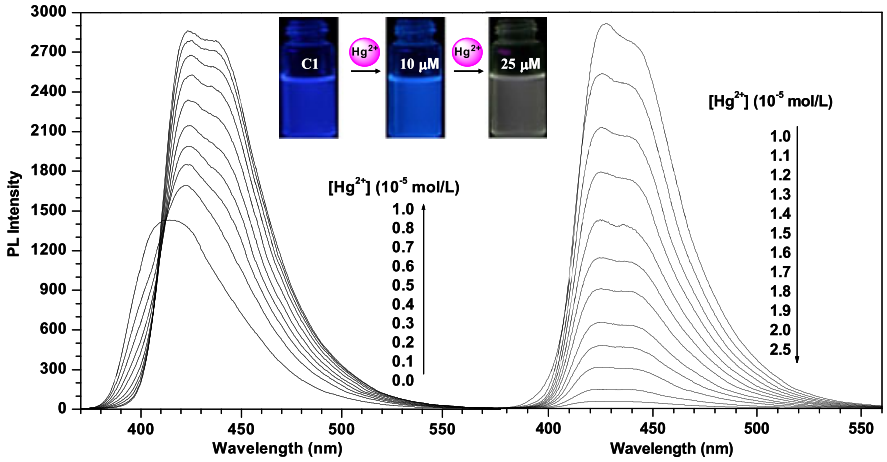


FIGURE 1 Fluorescent emission spectra of **C1** (10 μM, in THF) in the presence of different concentrations of Hg^{2+} (excited at 335 nm)

Surprisingly, with the continued addition of Hg^{2+} ions, the emission intensity centered at 422 nm declined dramatically. When 2.5 equiv. of mercury ions were added, the emission intensity at 422 nm reached a minimum with a 60-fold decrease compared with the intensity at a 10 μM Hg^{2+}. However, when the concentration reached 25 μM, no big change could be observed, even on further increasing the concentration of Hg^{2+} ions. With the aid of normal UV lamp it can be seen that the fluorescent color changes on addition of Hg^{2+} ions (Figure 1, inset).

The above experimental results showed that probe **C1** had a staged fluorescent response towards Hg^{2+} ions: first a red-shift and increase and subsequent decrease. This phenomenon was very rare and unanticipated. We then designed the reference compound **C2**, which possessed the same phenanthroimidazole moiety, and reference compound **C3**, which possessed the same carbamodithioate moiety, in order to explore the mutual interaction between probe **C1** and Hg^{2+} ions (Scheme 1). As demonstrated in Figure 2, on the addition of mercury ions from 0 to 10 μM, the emission spectra of reference **C2** displayed similar changes as in the case of probe **C1**. Moreover, the emission spectra of compound **C2** reached a plateau at a Hg^{2+} ion concentration of 10 μM (namely, 1.0 equiv. of Hg^{2+} ions) and there was no change in the fluorescence intensity on the subsequent addition of Hg^{2+} ions. Accordingly, we speculated that there was a 1:1 stoichiometry between compound **C2** and Hg^{2+} ions,[31] which led to the red-shift in the emission spectra at mercury ion concentrations of as 0–1.0 equiv. In compound **C2**, the *N*,*N*-dimethyl moiety was passive and there was almost no response with Hg^{2+} ions. Therefore, it was reasonable that both in compound **C1** and **C2**, the phenanthroimidazole moiety played the dominant role in the interaction with Hg^{2+} and led to the changes on emission spectra.

In order to explore the possible sensing mechanism of probe **C1** for Hg^{2+} ions from another aspect, reference **C3** was synthesized, which contained the same carbamodithioate moiety as compound **C1**, but not the phenanthroimidazole moiety. As a control, we added Hg^{2+} ions into a dilute solution of reference **C3** and investigated its response towards Hg^{2+} ions in THF in detail (Figure 3). The fluorescent

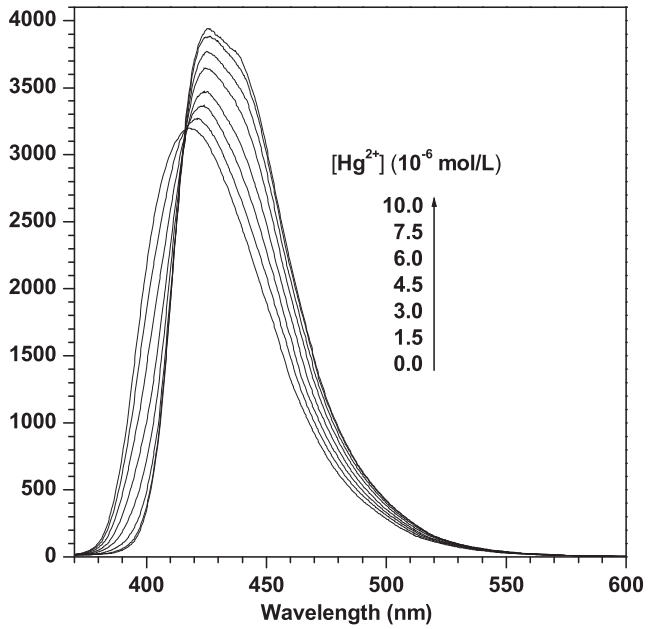


FIGURE 2 Fluorescent emission spectra of **C2** (10 μM, in THF) in the presence of different concentrations of Hg^{2+} (excited at 335 nm)

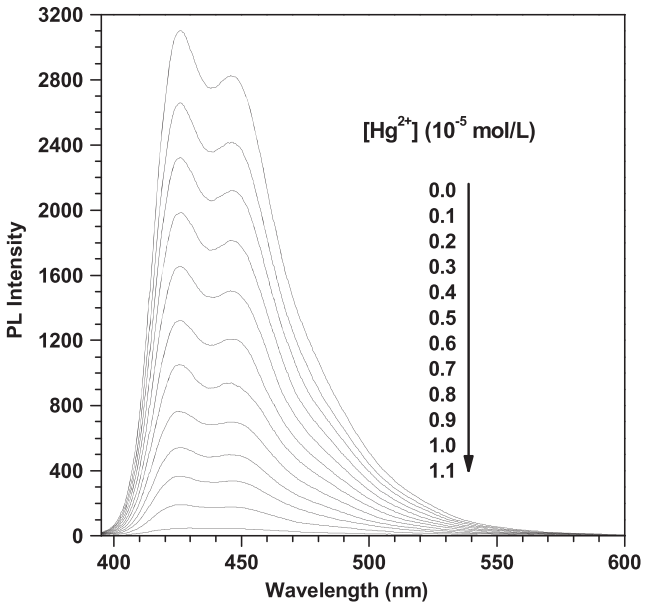


FIGURE 3 Fluorescent emission spectra of **C3** (10 μM, in THF) in the presence of different concentrations of Hg^{2+} (excited at 345 nm)

spectra of compound **C3** showed a monotonic decrease with increasing concentrations of Hg^{2+} ions: the emission intensity centered at 425 nm decreased as the concentration of Hg^{2+} ions changing from 0 to 11 μM. In compound **C3**, the triphenylamine moiety was passive towards Hg^{2+} ions and we speculated that the decrease in the emission spectra could be ascribed to the affinity of Hg^{2+} and the carbamodithioate unit in both compound **C1** and **C3** according to Pearson's hard and soft acids and bases theory.

We compared the chemical structures and sensing behavior of probe **C1** and references **C2** and **C3**. When we added Hg^{2+} ions to the solution of compound **C1**, there was a two-step change in the fluorescent spectra: red-shift and increase firstly and the consequence decrease. In compound **C2**, which contained the same phenanthroimidazole moiety as compound **C1**, the addition of Hg^{2+} ions only induced the red-shift and an increase in the emission spectra; however, with reference compound **C3**, which possessed the same carbamodithioate moiety as compound **C1**, the addition of Hg^{2+} ions induced a monotonic decrease in the emission intensity. Accordingly, we speculated the possible sensing mechanism (Scheme 3) between probe **C1** and Hg^{2+} ions: first, Hg^{2+} ions had strong affinity with the nitrogen atoms of the phenanthroimidazole moieties in **C1**, and **Complex 1** between the phenanthroimidazole moieties and Hg^{2+} ions was spontaneously formed, in a manner similar to previous cases of chelation-enhanced fluorescence (CHEF).[32–36] The CHEF effect depended directly on the photoinduced electron transfer (PET) mechanism. During the PET process, the lone pair electrons of the nitrogen atom of the imidazole ring were induced in the free ligand under the exciting radiation, quenching its fluorescence. While coordinating with Hg^{2+} ions, the same lone pair electrons became involved in metal–ligand bond formation, decreasing the PET quenching effect and leading to the CHEF effect. Correspondingly, the fluorescence intensity increased with a shift in the spectra from 414 to 422 nm. Afterwards, the continued addition of Hg^{2+} to the system induced a sharp decrease in the emission spectra at 422 nm. The association constant of **Complex 1** for Hg^{2+} was calculated to be ~1.7×10^5 M^{-1} using the equation in Scheme S1.[37] We speculated that the interaction between compound **C1** and Hg^{2+} ions was ascribed to formation of **Complex 2** due to the affinity between Hg^{2+} and the carbamodithioate unit containing four sulfur atoms, which would induce changes in the intramolecular charge transfer (ICT) efficiency and the concomitant emission spectra.[38] The above results were unexpected, but indicated that compound **C1** could act as a bifunctional probe towards Hg^{2+} ions, because both the fluorophore unit (phenanthroimidazole moiety) and the recognition (carbamodithioate moiety) had a sensing response to Hg^{2+}.

Furthermore, considering that mercury ions were able to form a very stable complex with sulfide anion (HgS, $K_{sp} = 4.0 \times 10^{-53}$),[39] we added an aqueous solution of sodium sulfide to the **C1**–Hg^{2+} complex to investigate the reversibility of the sensing system. We fixed the concentration of **C1** at 10 μM and that of the added Hg^{2+} ions at 25 μM (Figure 4, blue line) considering that the addition of 25 μM of Hg^{2+} ions led to the minimum emission intensity during the fluorescent titration

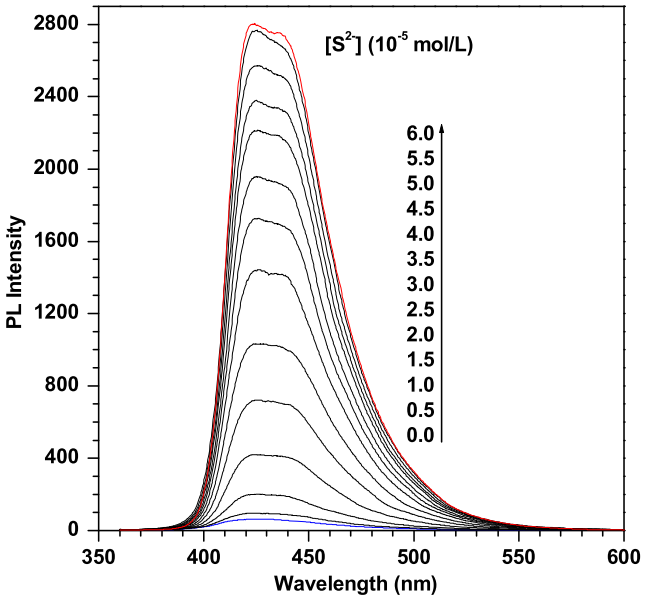
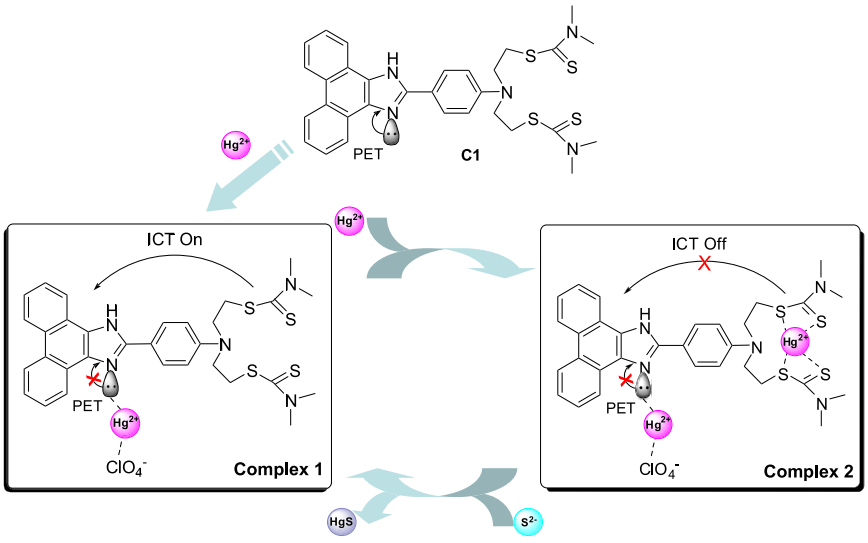


FIGURE 4 Fluorescent emission spectra of **C1** + Hg^{2+} (Hg^{2+}: 25 μM, blue line, excited at 335 nm) in the presence of different concentrations of S^{2-} and **C1** + Hg^{2+} (Hg^{2+}: 10 μM, red line, excited at 335 nm) for comparison



SCHEME 3 Postulated sensing process of **C1** towards Hg^{2+}

experiment. Upon addition of the sulfide anion, the fluorescent intensity at 422 nm increased as expected. As shown in Figure 4, the emission spectra became closer to that of **C1** + Hg^{2+} (Hg^{2+}: 10 μM, Figure 4, red line) with increasing concentrations of S^{2-} anion. However, the emission spectra reached a plateau when the concentration of S^{2-} anions was 60 μM. These experimental results indicated that addition of the sulfide anion could preferentially snatch mercury ion in **Complex 2** to form stable HgS species, as we reported previously.[40] As a result, the liberated carbamodithioate moiety recovered its electron-donating ability during the ICT process with recovery of the fluorescence. Therefore, to summarize: the transformation from **Complex 1** to **Complex 2** was reversible on addition of S^{2-} anions. However, the transformation from **C1** to **Complex 1** was irreversible because no blue-shift in the emission spectra could be observed, even on further increasing the concentration of S^{2-} anions.

To confirm, the reaction mixture of **C1** with Hg^{2+} was characterized by ESI-MS spectrometry. The ESI-MS spectrum of **C1** in Figure 5 (left) revealed a main peak at 604.0 nm before the addition of mercury ions, corresponding to [**C1** + H]$^+$ (m/z_{calcd} = 604.2). After addition of a small amount of Hg^{2+} (Hg^{2+}: **C1** < 1:1), a relatively weak peak at ~ 804.1 appeared, coinciding exactly with the adduct species of [**C1** + Hg]$^{2+}$, namely, **Complex 1** (m/z_{calcd} = 804.5). We then added Hg^{2+} ions (Hg^{2+}: **C1** > 1:1) into the above solution continually and observed that the previous peak at 804.1 disappeared, and another apparent peak at 1004.8 emerged, corresponding to the adduct species [**C1** + 2Hg]$^{4+}$, namely, **Complex 2** (m/z_{calcd} = 1005.1). The changes in the ESI-MS spectrum of **C1** with and without the presence of Hg^{2+} ions provided some evidence of a 'two-step' interaction between probe **C1** and Hg^{2+} ions, and both the fluorophore unit (phenanthroimidazole moiety) and the recognition unit (carbamodithioate moiety) had a sensing response towards Hg^{2+}.

To assess the specificity of the sensing behavior of **C1**, various ions were examined in parallel under the same conditions. Surprisingly, upon the addition of other ions such as Mg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Fe^{3+}, Al^{3+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Fe^{2+}, Li^+, Na^+ and K^+, there was hardly any change in the emission spectra (Figure S11). Therefore, it could be concluded that **C1** displayed extremely good selectivity for Hg^{2+}, rather than of the other ions examined. Moreover, to test the reproducibility of the sensing behavior of compound **C1** towards Hg^{2+} ions, we studied the fluorescent properties of **C1** in the presence and absence of Hg^{2+} ions in acetone. As shown in Figures S12 and S12, **C1** displayed both high sensitivity and good selectivity towards Hg^{2+} ions as in THF. Meanwhile, considering that Hg^{2+} and Ag^+ ions possessed some similarities, for instance, both are soft acid ions and have special affinity towards sulfur,[41,42] and sometimes Hg^{2+} chemosensors gave a response to trace silver ions, we also investigated the sensing behavior of **C1** towards silver ions. As shown in Figure 6, upon the

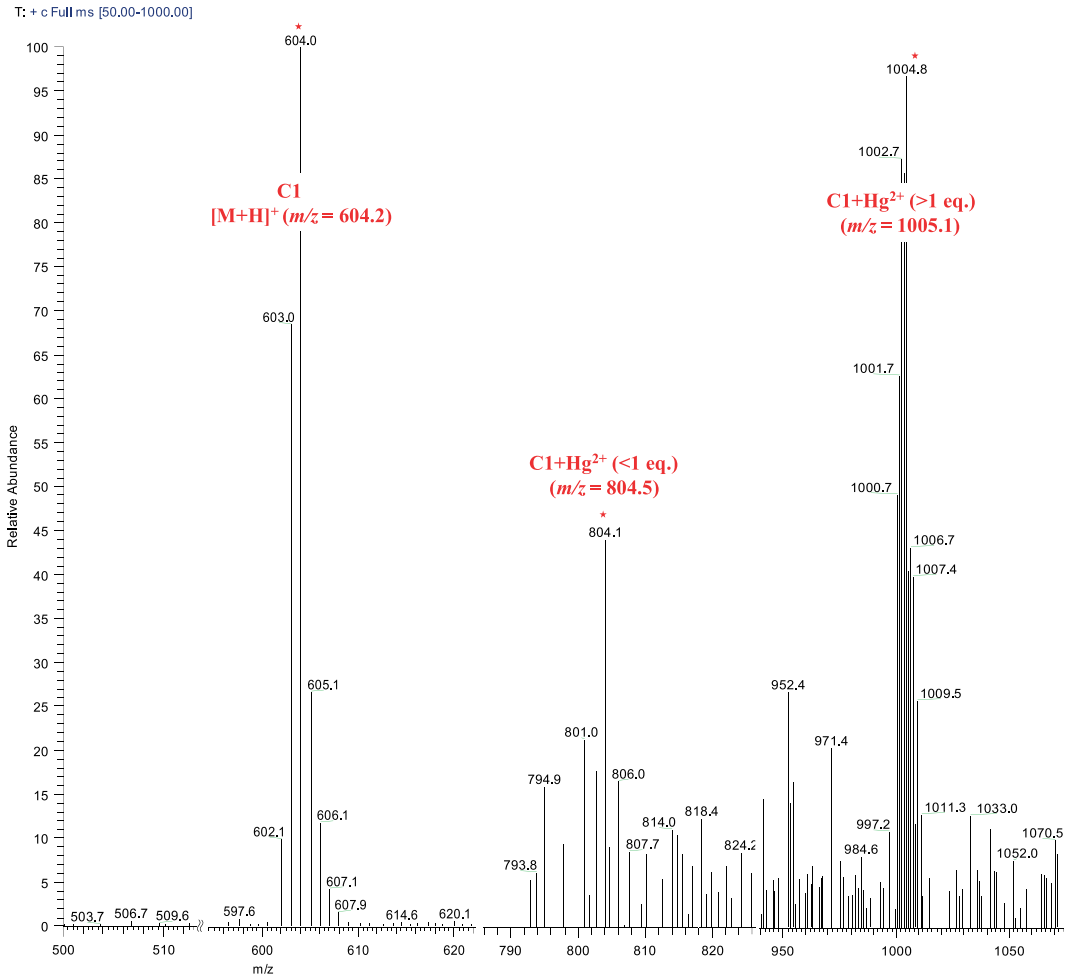


FIGURE 5 ESI-MS spectra of **C1** and **C1** + Hg^{2+}

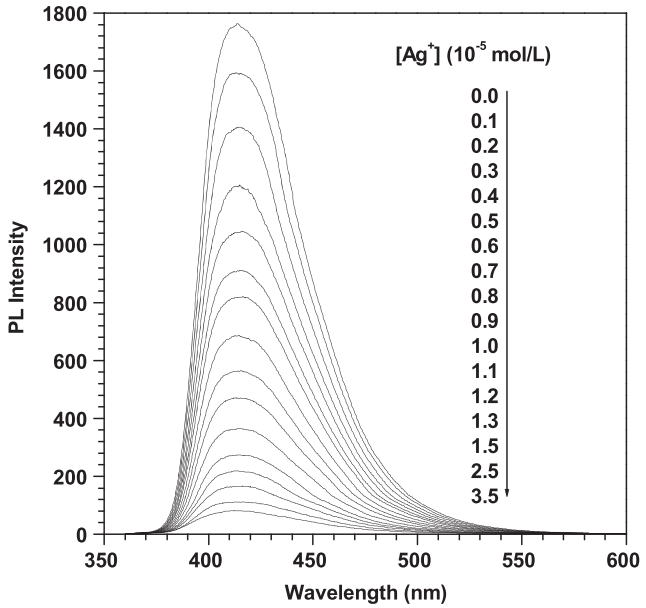


FIGURE 6 Fluorescent emission spectra of **C1** (10 μM, in THF) in the presence of different concentrations of Ag^+ (excited at 335 nm)

addition of silver ions, the sensing system exhibited different changes from those seen on the addition of Hg^{2+} ions: the fluorescent intensity centered at ~414 nm declined gradually with the increasing amounts of Ag^+. In order to investigate the sensing mechanism between **C1** and Ag^+ ions, we inspected the responses of reference compounds **C2** and **C3** towards Ag^+ (Figures S14 and S15). Although we added an excess of silver ions, there were hardly any changes in the emission spectra of reference **C2**. However, the changes to compound **C3** displayed a similar trend to that of **C1**: the fluorescent intensity declined gradually with increasing amounts of Ag^+ ions. Therefore, it was obvious that both compounds **C1** and **C3**, which contained the carbamodithioate moiety, had a fluorescent response towards Ag^+. By contrast, reference **C2** showed virtually no change upon the addition of silver ions due to the lack of a carbamodithioate unit. Based on these results, we conjectured that the sensing response of **C1** towards Ag^+ ions could be ascribed to interaction of the carbamodithioate moiety and Ag^+ ions. The obtained experimental results were unexpected but quite important. On the one hand, compound **C1** could also be regarded as a good probe towards Ag^+ ions, since it was also necessary to probe Ag^+ ions due to its strong toxicity to the human and our environment.[43,44] On the other hand, compound **C1** could discriminate Hg^{2+} and Ag^+ ions through different fluorescent response.

3 | CONCLUSIONS

In conclusion, compound **C1** was designed and synthesized as a new fluorescent chemosensor for Hg^{2+} and Ag^+ ions. Upon excitation, the emission spectra of **C1** showed a 'two-step' change upon the addition of Hg^{2+}, but a 'one-step' change upon the addition of Ag^+ ions. To investigate its sensing mechanism, control compounds **C2** with the same phenanthroimidazole unit and **C3** with the same carbamodithioate functionalities, were synthesized. Comparison of **C2** and **C3** with **C1** indicated that compound **C1** could act as a bifunctional probe towards Hg^{2+} ions, because both the fluorophore unit and the recognition unit had a sensing response to Hg^{2+}. The results reported here might provide some useful information for the design of new probes for metal ions, namely that subtle adjustment to the chemical structure dramatically affected the sensing property in the present system. Further study on the design of probes for toxic metal ions with better performance is still in progress in our laboratory.

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ABBREVIATIONS USED

AcOH	Acetic acid
CHEF	Chelation-enhanced fluorescence
ESI-MS	Electrospray ionization mass spectra
ICT	Intramolecular charge transfer
PET	Photoinduced electron transfer
THF	Tetrahydrofuran
TMS	Tetramethylsilane
UV/vis	Ultraviolet/visible

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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