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Carbamodithioate-Based Dual Functional Fluorescent Probe for Hg^{2+} and S^{2-}

Xiaohong Cheng · Shuang Li · Zhicheng Zhong · Song Wang · Ping He

Abstract Carbamodithioate-based compound **T1** was designed and synthesized as a dual-functional probe for Hg^{2+} ions and S^{2-} anions. The underlying signaling mechanism was intramolecular charge transfer (ICT). It could serve as a direct probe towards Hg^{2+} ions through "on-off" fluorescence changes and an indirect probe towards S^{2-} anions through "on-off-on" fluorescence changes.

Keywords Dual-functional probe · Fluorescence · Carbamodithioate · Mercury · Sulfide anion

Introduction

In recent years, mercury pollution has been becoming a global problem and receiving much attention [1–3]. Both human

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activities including gold mining, solid waste incineration, fossil fuel combustion [4, 5], and nonanthropogenic sources such as volcanic and oceanic emissions as well as forest fire [6, 7], have caused the fast increase of environmental Hg^{2+} level. It is estimated by the US Environmental Protection Agency (EPA) that the total mercury released into the environment reaches to ~7,500 t per year [8, 9]. Once introduced into environment, ionic mercury could be converted by bacteria in the environment to methyl mercury, which could subsequently bioaccumulate through the food chain and cause various neurological damage [10–12]. Therefore, to prevent the possible mercury pollutions, mainly from food and water, the monitoring of mercuric ions (Hg^{2+}), one of the most usual and stable form of mercury pollution, becomes an increasing demand. Thanks to the great efforts of scientists, a number of Hg^{2+} sensors have been developed with good performance, for example, the redox, colorimetric and fluorescent Hg^{2+} sensors by using proteins [13–17], nucleic acids [18–22], DNAs [23–27], nano particles [28–40] and several types of small molecules [41–56] as Hg^{2+} acceptors. However, many of the reported systems suffered from different limitations, for example, low selectivity, expensive and sophisticated instrumentation, complicated sample preparation processes, high cost (e.g., enzymes), and the use of unstable molecules (e.g., RNA) [57]. Thus, the design of new fluorescent sensors for Hg^{2+} ions with excellent performance is still needed.

In the field of supramolecular chemistry, the progress in receptors for anions has attracted considerable attention in recent decades due to the fact that a large number of chemical, biological, and environmental processes involve molecular recognition of anionic species [58–64]. Among these anions, sulfide anion is one of the toxic anions, which could irritate mucous membranes and even cause unconsciousness and respiratory paralysis upon continuous and high concentration exposure of sulfide anion. Once being protonated, it becomes even more toxic. Actually, sulfide anion is widely used in

industrial settings and produced as a byproduct in a large scale. Also, it can be formed in several ways in the biosystem, for example, the microbial reduction of sulfate by anaerobic bacteria, and the conversion from the sulfur-containing amino acids in meat proteins [65–68]. Thus, the detection of sulfide anion is becoming very important from industrial, environmental, and biological points of view. A variety of detection techniques have been developed for the determination of sulfide anion [69–73], in which fluorimetry has received considerable attention due to its high sensitivity and easy detection.

Generally, in comparison with the relatively large number of cation chemosensors, the development of anion chemosensors is still a challenging area [74–77]. So far, most of the anion chemosensors have been designed based on the attachment of a dye to an anion-binding site; however, this mechanism does not always work well, leading to the comparatively scarce number of anion chemosensors as mentioned above. Considering that many anions can form stable complexes with cations, we are wondering if it is possible to probe anions by utilizing the reported good cation chemosensors. That is to say, the anions might snatch cations from the formed complex of the cations and their corresponding chemosensors, with a detectable optical signal. This is really possible, if the stability constant of the complex formed by the anion and the cation is larger than that of the complex of the cation and its chemosensor.

With all these considerations in mind, here, we designed a "reporter-spacer-receptor" sensing system for mercury ions, namely, compound T1 (Scheme 1), which comprised a triphenylamine (TPA) moiety as the fluorophore moiety and carbamodithioate functionalities as ligating groups and electron-donor. According to the Pearson's hard and soft acids and bases theory, it is well known that Hg^{2+} (soft acid) can preferentially interact with the sulfur atom (soft base). Therefore, it was expected that the carbamodithioate unit in compound T1 had an exceptionally strong affinity towards Hg^{2+} and then formed the T1–Hg^{2+} complex, which would induce the changes on intramolecular charge transfer (ICT) efficiency and the concomitant emission spectra. If it was the case, the

compound T1 could act as a new fluorescent chemosensor towards Hg^{2+} ions. Furthermore, considering that sulfide anion could form very stable complex with mercury ions (HgS, $K_{sp}=4.0\times10^{-53}$) [78], we were wondering if the added sulfide anion could preferentially snatch mercury ion in the above T1–Hg^{2+} complex to form stable HgS species. This was really possible, if the stability constant of the complex formed by Hg^{2+} ions and S^{2-} anion was larger than that of the complex of Hg^{2+} ions and its chemosensor T1. As a result, the liberated carbamodithioate moiety of the sensor molecule T1 recovered its electron-donating ability with obvious fluorescence changes. If so, the potential Hg^{2+} ions chemosensor T1 could serve as an indirect chemosensor towards sulfide anion. Herein, we would like to describe the new dual-functional fluorescent chemosensor for mercury ion as well as sulfide anion in detail.

## Experimental

Materials and Instrumentations

Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. All other reagents were of analytical reagent grade and used without further purification. Doubly distilled water was used in all experiments.

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

Synthesis of Compound T1

Under the Argon atmosphere, compound 1 (416 mg, 1 mmol) and diethyl 4-(diphenylamino) benzylphosphonate (727 mg, 2 mmol) were dissolved in 30 mL of THF, and then NaH (89 mg, 3.7 mmol) in 10 mL of THF was added dropwise to

Scheme 1 The speculated sensing process of T1 towards Hg^{2+} and S^{2-}
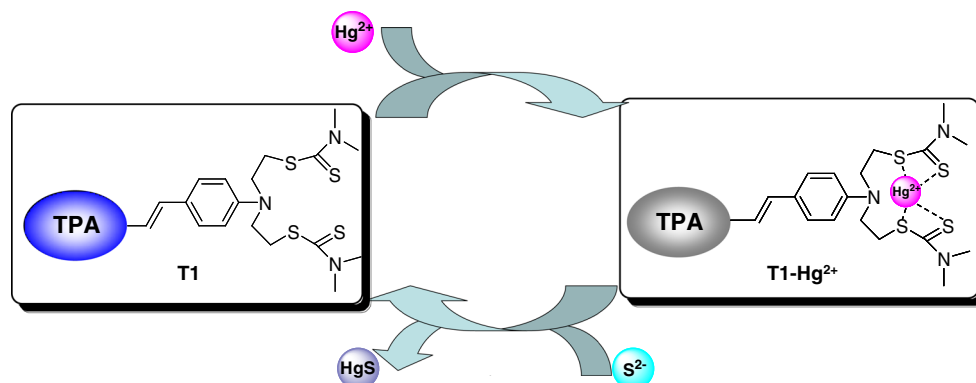
the solution. After reaction overnight at room temperature, the solvent was removed under reduced pressure to give the crude product. Then the crude product was purified by silica gel column chromatography using dichloromethane/petroleum ether (v/v, 1/1) as eluent to give compound **T1** as a yellow 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$_4$S$_4$ (EA) (%, found/calcd): C, 66.88/65.81; H, 5.907/6.14; N, 7.405/8.53.

Preparation of Solutions of Metal Ions

1 mmol of each inorganic salt (MgSO$_4$, MnSO$_4$·2H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, Pb(NO$_3$)$_2$, Ba(NO$_3$)$_2$, Ca(NO$_3$)$_2$·4H$_2$O, CoCl$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, Cu(NO$_3$)$_2$·3H$_2$O, CdSO$_4$·8H$_2$O, Cr(NO$_3$)$_3$·9H$_2$O, (NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O, LiCl, NaNO$_3$, KNO$_3$, AgNO$_3$ or Hg(ClO$_4$)$_2$·3H$_2$O) was dissolved in distilled water (10 mL) to afford 1×10^{-1} mol/L aqueous solution. The stock solutions were diluted to desired concentrations with water when needed.

Preparation of Solutions of Anions

1 mmol of inorganic salt (NaOAc·3H$_2$O, NaF, NaNO$_2$, NaHCO$_3$, NaNO$_3$, Na$_2$SO$_3$, Na$_2$SO$_4$, Na$_2$HPO$_4$·12H$_2$O, NaIO$_3$, NaCl, NaCN, Na$_3$PO$_4$, NaHSO$_3$, NaHSO$_4$, KBr, KI, Na$_2$S$_2$O$_3$·5H$_2$O or Na$_2$S) was dissolved in distilled water (10 mL) to afford 1×10^{-1} mol/L aqueous solution. The stock solutions were diluted to desired concentrations with water prior to the experiment.

Fluorescence Titration of T1 with Hg^{2+} Ions

A solution of **T1** (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 **T1** was placed in a quartz cell (10.0 mm width) and the fluorescence spectrum was recorded. The Hg^{2+} ion solution was introduced in portions and fluorescence intensity changes were recorded at room temperature each time.

Fluorescence Titration of T1 with Ag$^+$ Ions

A solution of **T1** (1×10^{-5} mol/L) was prepared in THF. The solution of Ag$^+$ (1×10^{-3} mol/L) was prepared in distilled water. A solution of **T1** was placed in a quartz cell (10.0 mm width) and the fluorescence spectrum was recorded. The Ag$^+$ ion solution was introduced in portions and fluorescence intensity changes were recorded at room temperature each time.

Fluorescence Intensity Changes of T1 with Different Metal Ions

A solution of **T1** (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 **T1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the fluorescence spectrum was recorded. Different ion solutions were introduced and the changes of the fluorescence intensity were recorded at room temperature each time.

Fluorescence Titration of T1+Hg^{2+} with S^{2-} Anions

A solution of **T1** (1×10^{-5} mol/L) was prepared in THF. The solution of Hg^{2+} with the concentration of 20 μM was added to the above solution. The solution of NaS (1×10^{-3} mol/L) was prepared in distilled water. A solution of **T1**+Hg^{2+} was placed in a quartz cell (10.0 mm width) and the fluorescence spectrum was recorded. The S^{2-}ion solution was introduced in portions to the above **T1**+Hg^{2+} solution and fluorescence intensity changes were recorded at room temperature each time.

Results and Discussion

Synthesis and Structural Characterization

The general synthetic procedure presented in Scheme 2. The Wittig reaction of the obtained aldehyde **1** [79] with diethyl ((4-(diphenylamino)benzyl) triphenyl)-phosphonate gave probe **T1**. The whole synthetic route was simple and the purification was easy. The target compound **T1** exhibited good solubility in common organic solvents, such as CHCl$_3$, CH$_2$Cl$_2$, acetone, DMF, DMSO and THF. Its structure was well characterized by ^{1}H, ^{13}C NMR, ESI-MS and elemental analysis, and all gave satisfactory spectral data.

Sensing Properties towards Hg^{2+} Ions

Compound **T1** emitted strong blue fluorescence with the maximum emission wavelength centered at about 425 nm and the maximum absorption wavelength at about 360 nm. Then, we tried to add Hg^{2+} ions into the diluted solution of compound **T1**, and investigated the sensing behavior of **T1** towards mercury ions carefully. As shown in Fig. 1, excitingly, the emission spectra displayed apparent decrease with the

Scheme 2 The structure of probe **T1**
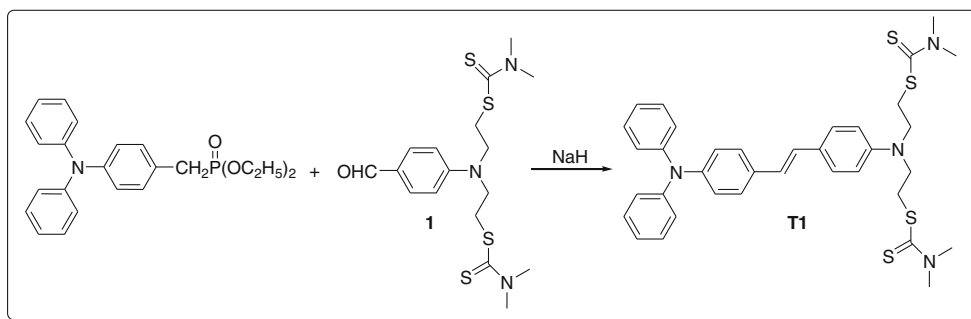
increasing of Hg^{2+} ions. In fact, the emission intensity at 425 nm decreased immediately to about 84 % of the original one at the concentration of Hg^{2+} ions as low as 1 μM. With the increasing of the concentration of Hg^{2+} ions in the test system, the emission intensity decreased correspondingly. When 1.1 equiv of mercury ions were added, the emission intensity reached the minimum with 64-fold decrease. However, when the concentration reached 11 μM, further increasing the concentration of Hg^{2+} ions to 13 μM, no big difference could be observed.

To see the results more visually, we summarized the intensity changes at 425 nm as a function of mercury concentrations. As demonstrated in Fig. 2, in the range of 0~10 μM, there was a good linear relationship between the intensity change and the concentration of Hg^{2+} ions. A linear regression curve could be simulated, and the point at which this line crossed the abscissa axis was taken as the detection limit and equaled approximately 3×10^{-7} mol/L [80]. The association constant of **T1** for Hg^{2+} was calculated to be ~1.3×10^{5} M^{-1} [81] using the equation in Scheme S1. It suggested that compound **T1** could act as a "switching-off" fluorescent

chemosensor; especially, it could detect the presence of Hg^{2+} ions quantitatively. A Job plot was used to determine the binding stoichiometry of **T1** with Hg^{2+} ions. The total concentration of chemosensor **T1** and Hg^{2+} was held constant while the mole fraction of Hg^{2+} ions was altered; the fluorescence quenching value, ΔF ($\Delta F = FL_0 - FL$, where FL_0 and FL represents fluorescence intensities at 425 nm in the absence and presence of Hg^{2+}, respectively) was plotted against the mole fraction (Fig. S1). The maximum fluorescence quenching occurred at mole fraction 0.5, indicating the formation of 1:1 complex. The fluorescent titration experimental results indicated that the addition of Hg^{2+} ions to the solution of **T1** induced the changes on ICT efficiency and the concomitant emission spectra. According to the Pearson's hard and soft acids and bases theory, it is well known that Hg^{2+} (soft acid) can preferentially interact with the sulfur atom (soft base) [82]. Therefore, we speculated the interaction between compound **T1** and Hg^{2+} ions was ascribed to the exceptionally strong affinity of Hg^{2+} and the carbamodithioate unit which contained four sulfur atoms, as shown in Scheme 1.
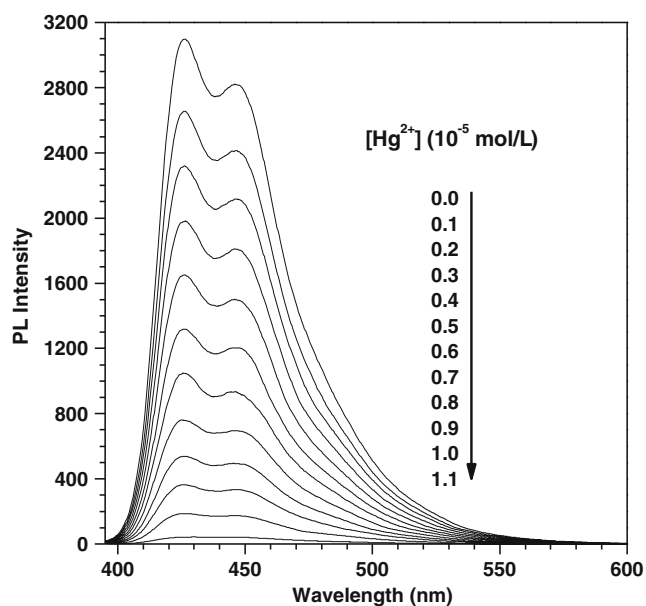
Fig. 1 Fluorescent emission spectra of **T1** (10 μM, in THF) in the presence of different concentrations of Hg^{2+}
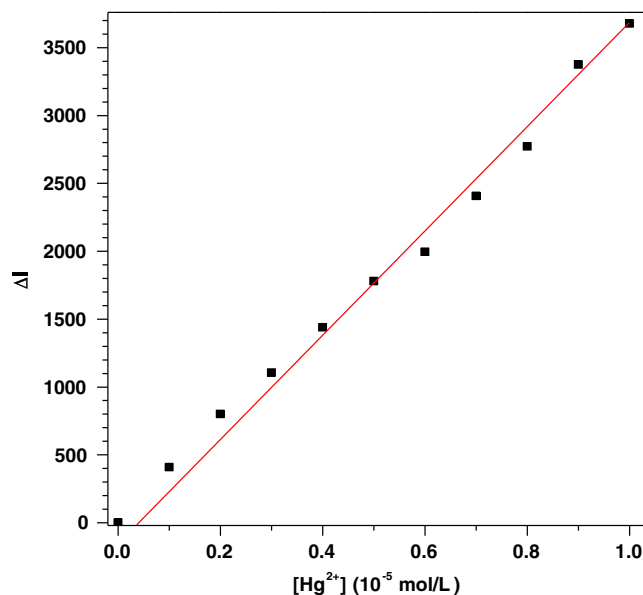
Fig. 2 Plot of fluorescence titration of **T1** with Hg^{2+} ($\Delta I = I_0 - I$, where I_0 and I represents the fluorescence intensities at 425 nm in the absence and presence of Hg^{2+}, respectively)
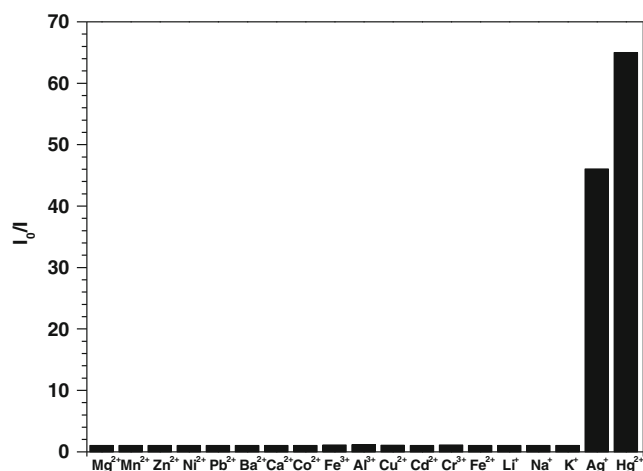
Fig. 3 Emission intensity changes (at 425 nm) of **T1** in the presence of Hg^{2+} and Ag^+ (15 μM) and other metal ions (50 μM)

Fig. 5 Emission spectra of **T1**+Hg^{2+} (**T1**:10 μM; Hg^{2+}:11 μM, the blue line) in the presence of different concentrations of S^{2-}, with that of **T1** (10 μM, the red line) for comparison

To assess the specificity of the **T1**'s sensing behavior, various ions were examined in parallel under the same conditions (Fig. 3). 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 nearly no changes on the emission spectra even though the concentrations of these cations were higher than that of mercury ions (the response of Ag^+ ions would be discussed later). Therefore, it could be concluded that **T1** displayed an extremely good selectivity for Hg^{2+} only, instead of the other ions examined. Meanwhile, considering that Hg^{2+} and Ag^+ ions possessed some similarities, for instance, both of them were soft acid ions and had special affinity towards sulfur element [83], and sometimes the Hg^{2+} chemosensors really gave response to trace silver ions, we also investigated the
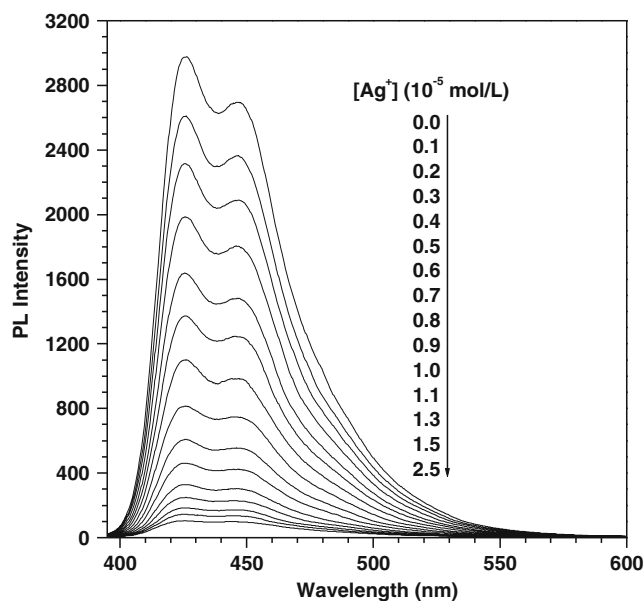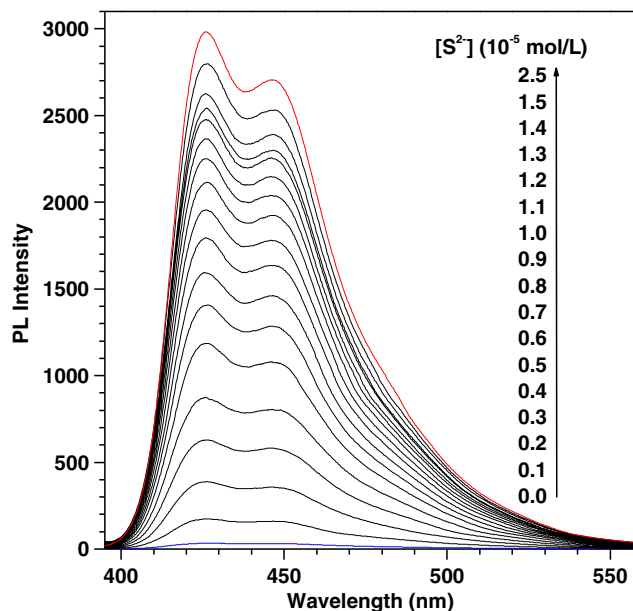
sensing behavior of **T1** towards silver ions. As shown in Fig. 3, upon the addition of silver ions, similar phenomena as in the case of Hg^{2+} ions were observed: the fluorescent intensity at 425 nm decreased gradually. Accordingly, we summarized the intensity changes at 425 nm as a function of silver ions concentrations. As demonstrated in Fig. S2, there was a good linear relationship between the intensity change and the concentration of Ag^{2+} ions with the detection limit of 1×10^{-6} mol/L. The association constant of **T1** for Ag^{2+} ions was determined to be $\sim 9.7 \times 10^4$ M^{-1} based on the fluorescent titration results [81]. However, the sensitivity was not so high as that of Hg^{2+} ions. The results were unexpected but reasonable. We speculated the possible reason was that
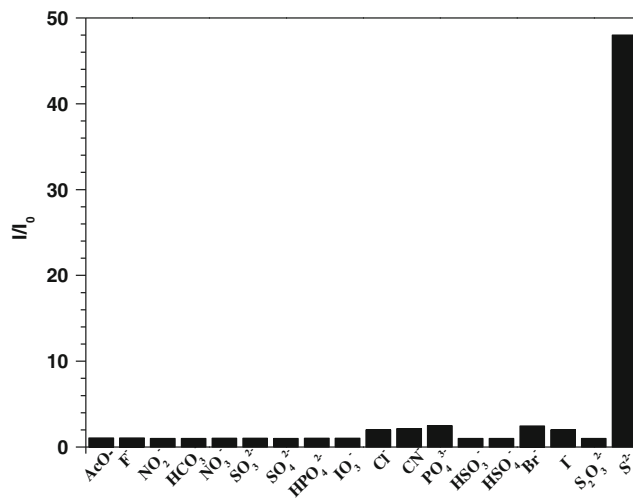

Fig. 4 Fluorescent emission spectra of **T1** (10 μM, in THF) in the presence of different concentrations of Ag^+

Fig. 6 Emission intensities of **T1**+Hg^{2+} (11 μM) in the presence of different anions (100 μM)

silver was also soft acid ions which could have an exceptionally strong affinity with the carbamodithioate unit in compound **T1** and then formed the **T1**–Ag^+ complex, leading to the changes on emission intensity. The obtained experimental results were unexpected but quite important: compound **T1** 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 [84] Fig. 4.

Sensing Properties towards S^{2-} Anion

As mentioned in the introduction section, sulfide anion could form very stable complex with mercury ions with the solubility-product constant (K_{sp}) of HgS was as low as 4.0×10^{-53}. Meanwhile, the previous titration experiments demonstrated that compound **T1** could act as a "switching-off" chemosensor towards mercury ions through the formation of **T1**–Hg^{2+} complex with the association constant of $1.3 \times 10^5 M^{-1}$. With the both considerations in mind, it was reasonable that the addition of sulfide anion could preferentially snatch mercury ion in the above **T1**–Hg^{2+} complex to form stable HgS species. As a result, the liberated carbamodithioate moiety of the sensor molecule **T1** recovered its electron-donating ability with the fluorescence recovery. If it was the case, the Hg^{2+} ions chemosensor **T1** could serve as an indirect chemosensor towards sulfide anion with the fluorescence "switching-on". We added the aqueous solution of sodium sulfide into the **T1**–Hg^{2+} complex and investigated the indirect sensing response to S^{2-}.

Fortunately, upon the addition of sulfide anion, the fluorescent intensity at 425 nm of the complex of **T1** and mercury ions increased as expected. Therefore, we could now give the following summary: at first, the addition of Hg^{2+} ions to the solution of **T1** caused the decrease of the emission peak at 425 nm, indicating the formation of the complex of **T1** and Hg^{2+} ions; then in the second stage, due to the much higher stability constant of S^{2-} anion and Hg^{2+} ions, the added S^{2-} anion could snatch the mercury ions from the **T1**–Hg^{2+} complex, resulting in a sharply increased fluorescent intensity. Thus, it was reasonable that when more Hg^{2+} ions were added, more S^{2-} anion was needed to coordinate with the mercury ions added in the first step to give an obvious optical signal. Therefore, we fixed the concentration of **T1** at 10 μM and the added Hg^{2+} ions as 11 μM considered that the addition of 11 μM of Hg^{2+} ions induced the emission intensity reaching the minimum during the fluorescent titration experiment. Under this condition, we presented the response of **T1**–Hg^{2+} complex towards S^{2-} anion to inspect the sensitivity of the mixture system. As demonstrated in Fig. 5, the emission intensity at 425 nm increased immediately to about 15-fold of the original one at the concentration of S^{2-} anions as low as 3 μM. Finally, the detection limit of **T1**–Hg^{2+} complex for S^{2-} anion was found to be 30 ± 5 nM (when the lowest fluorescence increase

equals to three fold of the instrument noise). In fact, the emission spectra became more and more close to that of compound **T1** with the increasing concentrations of S^{2-} anion (Fig. 5, the red line).

To evaluate the S^{2-}-selective nature of **T1**, possible emission changes caused by other anions, including AcO^-, F^-, NO_2^-, HCO_3^-, NO_3^-, SO_3^{2-}, SO_4^{2-}, HPO_4^{2-}, IO_3^-, Cl^-, CN^-, PO_4^{3-}, HSO_3^-, HSO_4^-, Br^-, I^-, and $S_2O_3^{2-}$ were studied. It was found that anions other than sulfide anion did not lead to apparent changes in the fluorescent intensity of the solution of **T1**–Hg^{2+} complex. The good selectivity and high sensitivity of the **T1**–Hg^{2+} complex towards sulfide anion made compound **T1** a promising candidate as a good sulfide probe through an indirect approach Fig. 6.

Summary

In summary, we developed a carbamodithioate-based fluorescent chemosensor **T1**. On the one hand, compound **T1** could act as "on-off" chemosensor towards Hg^{2+} ions through the strong affinity between carbamodithioate unit and Hg^{2+} ions. Even at the concentration of Hg^{2+} ions as low as 1 μM, the emission intensity at 425 nm decreased immediately to about 84 % of the original one. On the other, compound **T1** could also act as "on-off-on" chemosensor for S^{2-} anions indirectly because the addition of S^{2-} anion could preferentially snatch mercury ion in the above **T1**–Hg^{2+} complex and then restored the emission spectra. Upon the addition of trace S^{2-} anion, the emission intensity of **T1**–Hg^{2+} complex increased immediately and the mixture system displayed high selectivity to S^{2-} anion over other anions. The present experimental results further confirmed the successful sensing properties of the indirect strategy. Further study on the design of dual-functional probes for cations as well as anions with better performance is still in progress in our lab.

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