

O-Phenylenediamine-Cysteine Nanosphere Having Conjugated Structures: A Highly Selective Fluorescent Probe for Mercury Ion

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Abstract. A sensitive fluorescent o-phenylenediamine-cysteine copolymer dots (O-Cys) detection system for Hg²⁺ was synthesized by a facile and one step hydrothermal method. As a sensitive fluorescent probe, the O-Cys showed excellent linear relationships with detection limit as low as 1.0×10⁻¹¹ M with the concentrations of Hg²⁺ increasing from 2×10⁻¹¹ M to 9×10⁻¹¹ M. What's more, the O-Cys for the detection of Hg²⁺ was superior to most current methods and fluorescent material. At the same time, the working mechanism of O-Cys for Hg²⁺ detection was also explored. Hg²⁺ had higher fluorescent quenching ability for as-prepared O-Cys because Hg²⁺ was interaction with amino group (-NH₂) and thiol group (-SH) via a series of contrast test. And -SH enhanced the ability of Hg²⁺ detection to some extent. Therefore, this paper provided a good exponent of detection Hg²⁺ with low detection limit.

Keywords: o-phenylenediamine-cysteine, nanosphere, Hg²⁺ detection, fluorescent probe.

1 Introduction

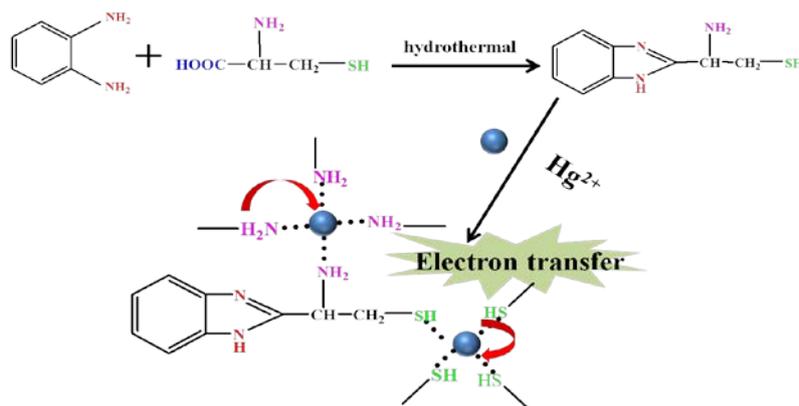
Environmental contamination and human live in an environment full of heavy metal ions (such as Cu²⁺, Cd²⁺, Ni²⁺, Ag⁺, Hg²⁺ and Pb²⁺), which arising from a variety of natural processes and human activities, have been a critical issue of concern throughout the world for decades[1-5]. As an example of highly toxic and widespread pollutants, the water-soluble mercury(II) (Hg²⁺), one of the most usual and stable forms of mercury pollution, can damage the brain, nervous system, kidneys, and endocrine system[6, 7]. It is estimated by US Environmental Protection Agency (EPA), the annual total global mercury emissions from all sources, both natural and human-generated, reaches nearly 7500 tons per year. The maximum level of mercury in drinking water permitted by the World Health Organization (WHO) and the U.S. EPA is 30 and 10 nM, respectively [7, 10, 11]. Therefore, it is especially important for studying new method with high sensitivity and selectivity to detect the trace amounts of Hg²⁺ in water[8, 9]. Various methods for detecting Hg²⁺ from nature water and industrial waste have been extensively used, including photoelectrochemical method, atomic absorption spectroscopy (AAS), coupled plasma mass spectrometry (ICP-MS), surface enhanced Raman scattering (SERS), fluorescence spectrophotometer, electro-deposition [12-14]. Among these, fluorescence spectrophotometer is one of the most attractive methods because of its simplicity, low-cost and effectiveness for water treatment. Feng et al. reported a cyclometallated ruthenium complex-modified upconversion nanophosphors for detection of Hg²⁺ ions in water with the detection limit of 8.2ppb [15]. Liu et al. reported a novel ratiometric fluorescent chemodosimeter for reusable detection of Hg²⁺ with the detection limit of 1.0ppb [16].

A amount of studies about the development and application of fluorescent material, such as semiconductor quantum dots, fluorescent dyes, carbon quantum dots and graphene quantum dots, have been explored to detect heavy metal ions [17-20]. Semiconducting polymer quantum dots (Pdots) have emerged as a new class of promising fluorescent nanomaterials with high emission rates, extraordinary fluorescence brightness, excellent photostability, high quantum yields, large absorption cross-sections. [21-26]. Compared with ordinary fluorescent material, the Pdots are prepared easily, low cost, low

cytotoxicity, lack of heavy metal ions. These superior properties make them well-suited for widespread fields such as biological detection and imaging, various biosensing platforms and so on [23, 27-29]. Chiu et al. reported various Pdots with controllable PL properties and applied them to cellular imaging and heavy metal ions analysis[30-32].

The thiol group (-SH) is an excellent ligand because of its strong binding ability for various heavy metal ions, such as Hg^{2+} , Pd^{2+} , Mn^{2+} and Fe^{3+} [33-35]. The low-molecular-weight thiols, such as L-cysteine (L-Cys), homocysteine (Hcy), and glutathione (GSH), which play important roles in many physiological and biochemical application [36]. L-Cys molecule contains a -SH which makes it unique among the amino acids [37]. So we want to synthesize a material containing -SH for detection of metal ions based on above reasons. Though they have been widely researched, it is still a challenge to develop new materials with conjugated structures, which are applied in detection of heavy metal ions.

Herein, o-phenylenediamine-cysteine copolymer dots (O-Cys) was successfully fabricated via a simple hydrothermal approach. This O-Cys showed high fluorescence response for detection of Hg^{2+} . As the concentrations of Hg^{2+} were increased from 2×10^{-11} M to 9×10^{-11} M, O-Cys showed excellent linear relationships and the detection limits was 1.0×10^{-11} M. What's more, it showed high selectivity for Hg^{2+} among most of anion and cation, so it could be as a sensitive fluorescence probe for detection of Hg^{2+} ion. In addition, we also explored further the working mechanism of Hg^{2+} detection. A schematic diagram of the mechanism of O-Cys for Hg^{2+} detection was shown in Scheme 1. Condensation reaction generated between the two amine groups of o-phenylenediamine and the carboxy of cysteine. After the condensation reaction, the surface of copolymer quantum dots riched in active amino and thiol groups. The $-\text{NH}_2$ and $-\text{SH}$ on the surface of the O-Cys has strong affinity for Hg^{2+} to generate insoluble metal chelates, electron transfer occurs between the $-\text{NH}_2$ and $-\text{SH}$ on the surface of the O-Cys and Hg^{2+} , resulting in fluorescence quenching.



Scheme 1. A schematic diagram of the mechanism of O-Cys for Hg^{2+} detection.

2 Materials and methods

2.1 Materials

o-phenylenediamine (oPD), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS), L-cysteine (L-Cys), NaCl, KCl, MgCl_2 , CaCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, HgCl_2 , AlCl_3 , $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, CuSO_4 , AgNO_3 , NiSO_4 , NaNO_2 , NiNO_3 , $\text{Co}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, KH_2PO_4 and Na_2HPO_4 were purchased from Kelong (Chengdou, China) and used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

2.2 Synthesis of O-Cys

Typically, 1.0 mL, 0.5 mM Cys aqueous solution was added into 19 mL, 50 mM oPD aqueous solution, then 2 mL, 10 mM APS aqueous solution was added to the above solution. The mixed solution was transferred into a 25 mL Teflon-lined autoclave and heated to 160 °C and maintained at that temperature for 72 h before being allowed to cool naturally to room temperature. The product was centrifuged to remove large

dots and a yellow transparent supernate solution. The black precipitates were washed with water by centrifugation twice, and the resulting precipitate are dried at 60°C for 12h in vacuum for further use. The yield was about 71%.

2.3 Detection of Hg²⁺

First, we prepared the stock solution of Hg²⁺ with the concentration of 1×10^{-9} M at room temperature. In the experiment, a series of Hg²⁺ concentration were obtained by dilute stock solution. In brief, 2 ml dots solution were added in 16 bottles, then numbered from 1 to 16. Adding different volume stock solution of Hg²⁺ from 0.2 ml to 0.9 ml to 16 bottles using pipette, then 16 bottles were constant volume to 10 ml with distilled water. Mixing above solution separately, then measuring fluorescence spectrum after standing a few minutes with an emission wavelength of 560 nm at 25°C.

2.4 Characterization methods

Transmission electron microscopy (TEM) measurements were made on a H-8100 EM (Hitachi, Tokyo, Japan) operated at an accelerating voltage of 20 kV. UV-vis spectra were obtained on a UV-7502PC Spectrophotometer. Fourier transform infrared (FTIR) was performed on a Thermo Scientific Nicolet 6700 Spectrometer and samples were dispersed in potassium bromide. Fluorescent emission and excitation spectra were recorded on a FL0912μ000 Cary Eclipse at room temperature (25 °C) in aqueous solution. The stability of these products was determined via contrast the fluorescent emission intensity of products aqueous solution under different conservative time at room temperature (25 °C). The optical densities measured on the UV-vis spectrum were obtained on a UV-7502PC Spectrophotometer.

2.5 The quantum yield (ϕ) measurement

Quantum yield (ϕ) was calculated by the following equation:

$$\phi = \phi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2} \quad (1)$$

where I represented the measured integrated emission intensity (emission wavelength of 560 nm), η was the refractive index of the solvent, A was the optical density measured on a UV-vis spectrophotometer, which was limited to less than 0.1. The subscript R refers to the reference standard with a known ϕ [38]. Absolute values were calculated using the standard reference sample that had a fixed and known fluorescence quantum yield value. Here, we chose RhB dissolved in ethanol solution, which ϕ_R was 0.68. In order to minimize reabsorption effects, absorbency was kept under 0.1 at the excitation wavelength in the 10 mm fluorescence cuvette.

3 Results and discussion

3.1 Characterization of O-Cys

The typical TEM images of O-Cys thus formed were shown in Fig. 1a. The corresponding size distribution of O-Cys was shown in Fig. 1b. It can be seen from the Fig. 1b that the quantum dot size of O-Cys were in the range of 1 nm- 4nm and with an average diameter was approximately 1.9 nm.

The UV-vis spectra and FT-IR spectrometer were carried out to investigate the structure properties of O-Cys. Fig. 1c showed the UV-vis absorption spectrum of O-Cys. It had two typical UV-vis absorption peaks at ~450 and ~400 nm, respectively. The absorption peaks centered at approximately 450 nm and ~400 nm can be assigned to the π - π^* and n - π^* transition of the benzenoid rings [39, 40].

The FT-IR spectrum of O-Cys, mixture O-Cys and Hg²⁺ were shown in Fig. 1d. It is clear that the adsorption peaks at 3240 cm^{-1} corresponding to the N-H stretching mode, and implying the presence of secondary amino groups. The peaks at 2920 and 2850 cm^{-1} can be assigned to the C-H stretching mode

and C–H out-of-plane bending mode. The peak at 2550–2580 cm^{-1} areas signed to –SH stretching mode. However the reaction between –SH and Hg^{2+} were happened, the absorption peak of the –SH was obviously decreased. The peaks at 1239 and 1370 cm^{-1} were associated with the C–N stretching in the benzenoid and quinoid imine units, aromatic C=N heterocycles stretching vibrations are at 1309–1650 cm^{-1} [41, 42]. All the above observations indicate the successful formation of O-Cys including –SH.

An excitation-dependent emission of O-Cys was observed in Fig. 1e. When excitation (λ_{ex}) wavelength was increased from 500 to 560 nm, the PL intensity increased gradually. However, when λ_{ex} was increased from 560 to 580 nm, the PL intensity decreased gradually. This showed that with the increase of excitation wavelength, number of excited state molecules increased gradually, and in the largest excitation wavelength, number of excited state molecules were the most. So we chose 560 nm as excitation wavelength of O-Cys. We also observed that the emission peak did not shift any more than a maximum red shift when λ_{ex} was increased from 500 to 580 nm, which showed the O-Cys have unified chromophores. The maximum emission peak was observed at 623 nm for an excitation of 560 nm. Fig. 1f showed the fluorescence excitation and emission spectra of O-Cys. It is obviously shown that the maximum λ_{ex} and emission (λ_{em}) wavelength of O-Cys are 560 and 623 nm, respectively.

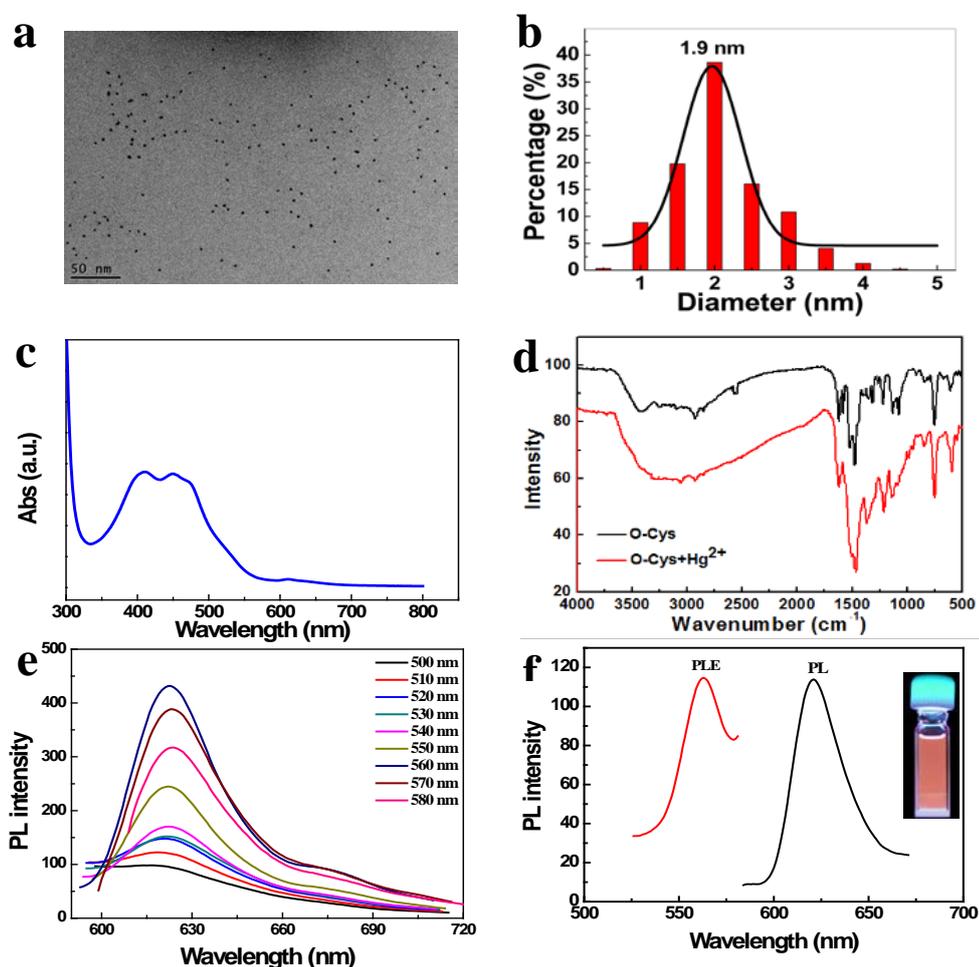


Fig. 1. (a) TEM images of O-Cys. (b) Corresponding size distribution of O-Cys. (c) Normalized UV-vis absorption of O-Cys. (d) The FT-IR spectrum of O-Cys, mixed solution of O-Cys and Hg^{2+} . (e) PL spectrum of the O-Cys at different excitation wavelengths from 500 to 580 nm; both the excitation and emission slit widths were 5 nm. (f) Fluorescence excitation spectra and emission spectra of O-Cys aqueous solution at room temperature (25°C). Inset: photographs of O-Cys aqueous solution.

3.2 Stability experiments

The stability of product was very crucial for practical applications. Here, to confirm the stability of O-Cys, we observed the change of the PL intensities of O-Cys under different influencing factors such as continuous excitation under visible light and different pH values (Fig. 2). As shown in Fig. 2a, only a slight PL intensity change was observed, indicating high stability of the O-Cys after continuous excitation under visible light for more than a week. This also means the O-Cys were stable and had great potential applications. Meanwhile, in Fig. 2b, we also found the PL intensity was stable when the pH value was changed from 4 to 11. This meant that O-Cys had excellent stability and could be used in most biological environments.

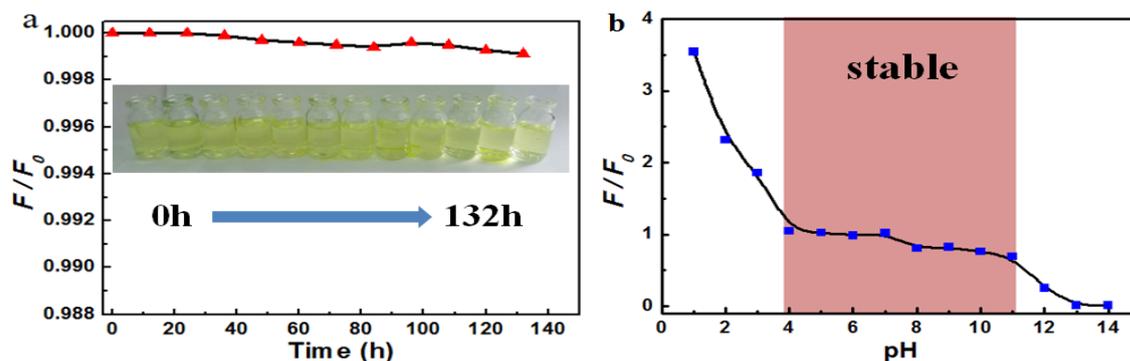


Fig. 2. (a) The PL intensity ($\lambda_{ex} = 560\text{nm}$, $\lambda_{em} = 623\text{nm}$) of the O-Cys in the different time under visible light. F_0 and F are PL intensities in the initial ($t=0$) and specify time, respectively. Inset: the photograph of O-Cys in the different time under visible light. (b) The PL intensity ($\lambda_{ex} = 560\text{nm}$, $\lambda_{em} = 623\text{nm}$) of the O-Cys in the different pH at 25°C . F_0 and F are PL intensities of O-Cys solution and specify pH, respectively.

3.3 Detection of Hg^{2+}

The stability of product was very crucial for practical applications. Here, to confirm the stability of O-Cys, we observed the change of the PL intensities of O-Cys under different influencing factors such as continuous excitation under visible light and different pH values (Fig. 2). As shown in Fig. 2a, only a slight PL intensity change was observed, indicating high stability of the O-Cys after continuous excitation under visible light for more than a week. This also means the O-Cys were stable and had great potential applications. Meanwhile, in Fig. 2b, we also found the PL intensity was stable when the pH value was changed from 4 to 11. This meant that O-Cys had excellent stability and could be used in most biological environments.

We further explored the feasibility of using the O-Cys for detection of Hg^{2+} . For a sensitivity study, PL intensities change was monitored after adding different concentration Hg^{2+} to O-Cys solution for a fixed time of 10 min. As the concentration of Hg^{2+} was increased from 2×10^{-11} to 9×10^{-11} M, the PL peak at 623 nm gradually decreased. It was obvious shown that Hg^{2+} could quench fluorescence of O-Cys. The reason of quenching was presumably via electron transfer. Strong coordination interactions between Hg^{2+} and the surface $-\text{NH}_2$ and $-\text{SH}$ groups of O-Cys resulted in the fluorescence quenching of O-Cys, which was the character of static quenching. Electron transfer could happen between Hg^{2+} and O-Cys. Furthermore, molecular orbital theory was adopted to interpret the quenching mechanism, schematically displayed in Scheme 2. As seen, when O-Cys accepted the energy without the existence of Hg^{2+} and the electron of O-Cys would be excited from the ground state (valence band) to the excited state (conduction band). And the excited electron was not stable, and could return to the ground state. In the returning process, O-Cys could emit fluorescence (Scheme 2 (a)). On the other hand, with the existence of Hg^{2+} , the $-\text{NH}_2$ and $-\text{SH}$ on the surface of the O-Cys had strong affinity for Hg^{2+} . The strong interaction force would lead to electron transfer between O-Cys and Hg^{2+} , so the excited electron could directly jump into the LUMO level layer of the complex. The energy level of the complex was higher than that of O-Cys, so the excited electrons of O-Cys could return back to the ground state without emitting fluorescence, which would lead to the fluorescence quenching of O-Cys (Scheme 2 (b)). The PL intensity of the O-Cys was proportionately decreased upon increasing Hg^{2+} concentration, which could be observed in Fig. 3a. The fluorescence

quenching data followed the Stern–Volmer equation, via either a dynamic or a static mechanism:

$$F_0 / F_{-1} = K_{sv}C \quad (2)$$

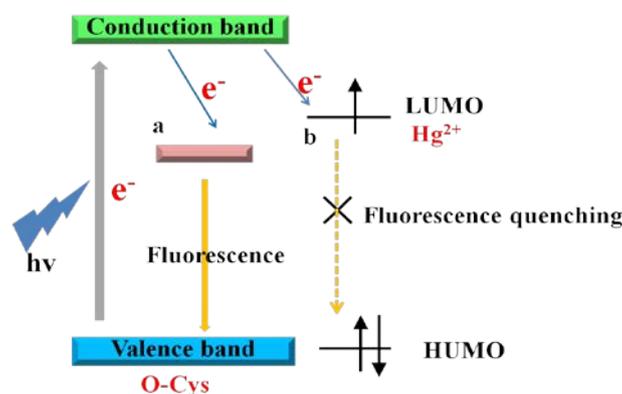
where K_{sv} is the Stern–Volmer quenching constant, c is the analyte (Hg^{2+}) concentration, and F_0 , F are PL intensities of O-Cys at 560 nm in the absence and presence of Hg^{2+} , respectively. A linear Stern–Volmer equation in the concentration range of 2×10^{-11} to 4×10^{-11} M was shown in Fig. 3b. The correlation coefficients (R^2) were 0.9967. The limit of detection (LOD) for Hg^{2+} , at a signal-to-noise ratio of 3, was estimated to be 1×10^{-11} M, which was much lower than the maximum contamination level of Hg^{2+} in drinking water permitted by WHO (30nM) and the limit of the 10nM set by the U.S. EPA. The sensor provided a sensitivity and low LOD for Hg^{2+} that were much better than those previously reported. The method and fluorescent material of detection of Hg^{2+} by other fluorescent probes were shown in Table 1 [2,43–47] and Table 2 [1,3–4,10–12,48–53]. The as-prepared O-Cys had higher LOD, which could be indeed used as impressive fluorescent probes for separately Hg^{2+} with a high degree of accuracy and simplicity.

Table 1. Comparison of different detection method for monitoring Hg^{2+}

Detection method	Detection limit	Ref.
Ratiometric Fluorescence	5×10^{-8} M	[2]
ICP-AES	3.5×10^{-9} M	[43]
Energy Transfer	1.0×10^{-10} M	[44]
Photocatalytic	2.5×10^{-7} M	[45]
FRET-Based Ratiometric Detection	1.0×10^{-7} M	[46]
AAS/sequential injection	4.5×10^{-8} M	[47]

Table 2. Comparison of different fluorescent material for Hg^{2+} detection.

Fluorescent material	Detection limit	Ref.
DNA-Capped Mesoporous Silica Nanoparticles	2×10^{-8} M	[1]
Silver Amalgamation	2.6×10^{-9} M	[3]
Lysine-Promoted Colorimetric Response of Gold Nanoparticles	1×10^{-8} M	[4]
β -Cyclodextrin	2×10^{-9} M	[10]
T- Hg^{2+} -T/AuNPs	5×10^{-8} M	[11]
Graphene Aptasensor	5×10^{-5} M	[12]
Gold Nanorods	1.5×10^{-11} M	[48]
Ammonium Group-Capped Gold Nanoparticles	3×10^{-8} M	[49]
DNA-Functionalized Monolithic Hydrogels	5×10^{-9} M	[50]
Silver Nanoparticle-Embedded Polymer	1.7×10^{-9} M	[51]
Functionalized Carbon Nanodots	5×10^{-8} M	[52]
Graphene Quantum Dots	1.2×10^{-7} M	[53]
O-Cys	1×10^{-11} M	This work



Scheme 2. Schematic for the fluorescence quenching mechanism according to molecular orbital theory in the absence (a) and presence (b) of Hg^{2+} .

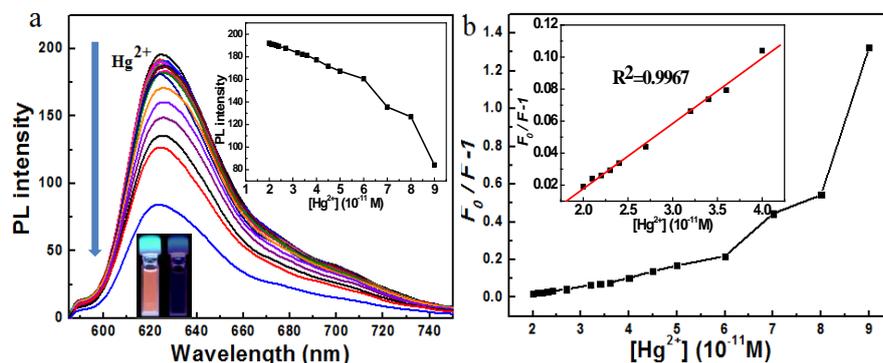


Fig. 3. (a) PL spectra of O-Cys in the presence of different concentrations of Hg^{2+} (2×10^{-11} M to 9×10^{-11} M) with an emission wavelength of 623nm at 25°C. Inset: The intensity of PL peak at excitation wavelength 560nm in the presence of different concentrations of Hg^{2+} (2×10^{-11} M to 9×10^{-11} M) and photographs of O-Cys aqueous solution in the absence (left) and presence (right) of Hg^{2+} . (b) The Stern-Volmer plot of the PL peak at emission wavelength of 623 nm in the presence of different concentrations of Hg^{2+} . Inset: Linear fitting of the Stern-Volmer plot of the PL peak at 623nm in the presence of different concentrations of Hg^{2+} (2×10^{-11} M to 4×10^{-11} M). F_0 , F are PL intensities of O-Cys in the absence of Hg^{2+} and in the presence of different Hg^{2+} concentration, respectively.

Further, to confirm O-Cys can strongly interact with Hg^{2+} , we considered that the change of PL intensity of the O-Cys in the presence of Hg^{2+} in Fig. 4. It was seen that the O-Cys solution in the absence of Hg^{2+} exhibited a strong PL peak at 623 nm (Fig. 4a, black curve). In contrast, the PL intensity of O-Cys obviously decreased in the presence of Hg^{2+} , indicating that Hg^{2+} could effectively quench the PL of O-Cys (Fig. 4a, red curve). The most probable explanation for the quenching of PL of O-Cys in the presence of Hg^{2+} was based on the electron transfer mechanism. That is, Hg^{2+} is an acid of borderline hardness (according to the hard and soft acids and bases principle) and had strong affinity for sulfur donor atoms than the nitrogen atom, as result of forming the stable metal complexes[42]. Moreover, when adding a strong Hg^{2+} chelator (such as EDTA), Hg^{2+} were removed from the surface of O-Cys by forming metal chelates with EDTA, which resulted in the PL recovery of O-Cys (Fig. 4a, blue line). As increasing EDTA concentration, the PL peak of O-Cys at 623 nm gradually increased were observed in Fig. 4b.

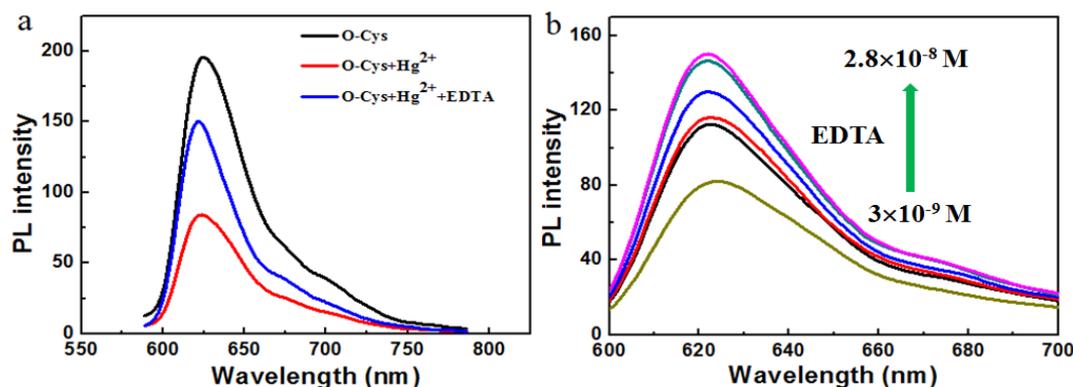
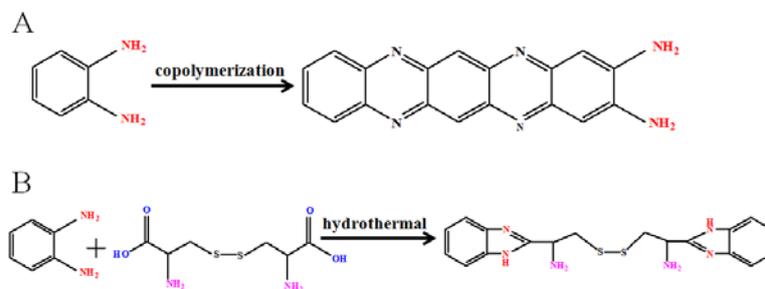


Fig. 4. (a) The PL spectra of O-Cys (black line), O-Cys and Hg^{2+} (concentration of Hg^{2+} was 9×10^{-11} M, red line), mixture of O-Cys, Hg^{2+} and EDTA (concentration of Hg^{2+} was 9×10^{-11} M, concentration of EDTA was 2.8×10^{-8} M, blue line). (b) PL emission spectrum ($\lambda_{ex} = 560$ nm) of O-Cys in the presence of Hg^{2+} (9×10^{-11} M) with different concentrations of EDTA (3×10^{-9} - 2.8×10^{-8} M) at 25°C.

To confirm our suspect that Hg^{2+} had higher fluorescent quenching ability for as-prepared O-Cys was due to $-\text{NH}_2$ and $-\text{SH}$ work together, we synthesized other two kind of polymer containing $-\text{NH}_2$ and in the

absent of $-SH$ via the same method, one was poly(o-phenylenediamine) (PoPD), other was o-phenylenediamine-cystine copolymer (ocyCP). A schematic diagram of the structure of PoPD and ocyCP were shown in Scheme 3. It is obviously shown that PoPD and ocyCP for the detection ability of Hg^{2+} were worse than O-Cys with detection limit 1.0×10^{-11} M (Fig. 5.). The detection limits for Hg^{2+} were 1.0×10^{-7} and 2.0×10^{-7} , respectively. These results further confirmed that $-NH_2$ and $-SH$ work together in the detection of mercury ion, most important, these results also confirmed the $-SH$ enhance detection ability of O-Cys for Hg^{2+} .



Scheme 3. A schematic diagram of the structure of PoPD and ocyCP.

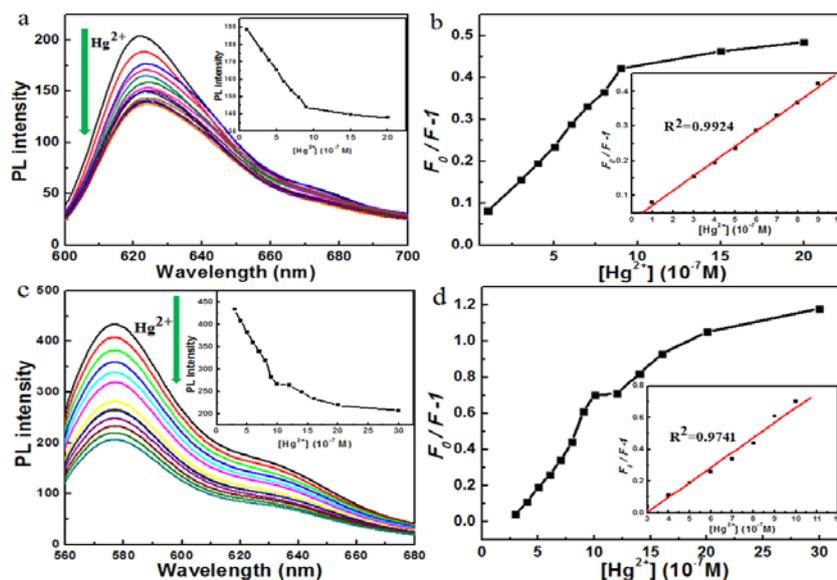


Fig. 5. (a) PL emission spectrum (λ_{ex} = 560 nm, λ_{em} = 623 nm) of PoPD in the presence of Hg^{2+} with different concentrations (1×10^{-7} M– 2×10^{-6} M) at 25 °C. Inset: the intensity of PL peak at excitation wavelength 560 nm in the presence of different concentrations Hg^{2+} (1×10^{-7} M– 2×10^{-6} M). (b) The Stern-Volmer plot of the PL peak at emission wavelength of 623 nm in the presence of different concentrations of Hg^{2+} . F_0 and F are PL intensities of PoPD without and with the presence of Hg^{2+} (1×10^{-7} M– 2×10^{-6} M) at 25 °C, respectively. Inset: linear fitting of the Stern-Volmer plot of the PL peak at 623 nm in the presence of different concentrations of Hg^{2+} ion (1×10^{-7} M– 9×10^{-7} M). (c) PL emission spectrum (λ_{ex} = 530 nm, λ_{em} = 577 nm) of ocyCP in the presence of Hg^{2+} ions with different concentrations (3×10^{-7} M– 3×10^{-6} M) at 25 °C. Inset: the intensity of PL peak at excitation wavelength 530 nm in the presence of different concentrations Hg^{2+} (3×10^{-7} M– 3×10^{-6} M). (d) The Stern-Volmer plot of the PL peak in the presence of different concentrations of Hg^{2+} ions. F_0 and F are PL intensities of ocyCP without and with the presence of Hg^{2+} (3×10^{-7} M– 3×10^{-6} M) at 25 °C, respectively. Inset: linear fitting of the Stern-Volmer plot of the PL peak at 577 nm in the presence of different concentrations of Hg^{2+} (3×10^{-7} M– 1×10^{-6} M).

3.4 Selectivity experiments

As fluorescence probe, in addition to its high sensitivity, selectivity was also another important parameter

to evaluate the performance of the sensing system. Under the experiment optimal conditions, we tested the PL intensity changes of the O-Cys in the presence of competitive metal ions and other ions under the same conditions, respectively, including Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , Cu^{2+} , Hg^{2+} , Cd^{2+} , Pb^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cl^- , SO_4^{2-} , NO_3^- , NO_2^- , H_2PO_4^- , HPO_4^{2-} , and as shown in Fig. 6. The PL intensities of the O-Cys with and without the present of other ions were denoted by F and F_0 , respectively. It was obviously seen that a much higher PL intensity respond was observed for O-Cys upon addition of Hg^{2+} . In contrast, no tremendous decrease was observed by adding other ions into the O-Cys solution. All these results suggested that as-prepared O-Cys showed excellent selectivity and sensitivity for Hg^{2+} ion in biological and water environmental fields, which had high practical applications.

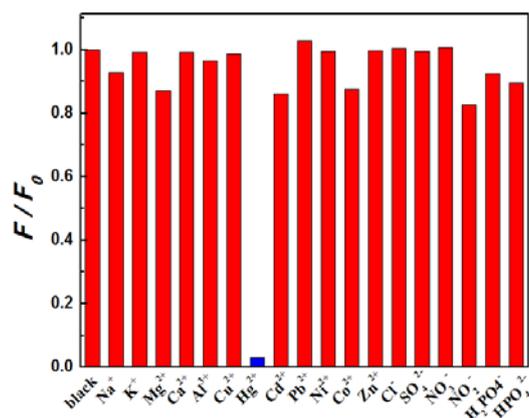


Fig. 6. Fluorescence response of O-Cys in the presence of different ions at 25°C. F_0 and F are PL intensities O-Cys without and with the presence of other ions. The concentrations of all ions is 5×10^{-5} M. The ions are black, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , Cu^{2+} , Hg^{2+} , Cd^{2+} , Pb^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cl^- , SO_4^{2-} , NO_3^- , NO_2^- , H_2PO_4^- , HPO_4^{2-} .

4 Conclusions

In summary, low-cost, high-stability fluorescent O-Cys was synthesized by a facile and one step hydrothermal method. The O-Cys could be used as a sensitive fluorescent probe for the detection of Hg^{2+} with detection limit of 1×10^{-11} M, which was superior to most current methods and fluorescent materials for Hg^{2+} analysis. On the other hand, we also discussed the working mechanism of Hg^{2+} detection. We found $-\text{SH}$ in the O-Cys can largely enhance the ability of Hg^{2+} detection compared with polymer without $-\text{SH}$, which were PoPD and ocyCP, respectively. The O-Cys was comparatively stable in a wide range of pH values and continuous illumination, which meant it could be applied in gentle condition. The fluorescent O-Cys provided a good exponent of detection Hg^{2+} with low detection limit. We supposed that the O-Cys will have many potential applications in environmental detection and health care.

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