Highly Sensitive Fluorescence Detection of Hg^{2+} Based on a Water-soluble Conjugated Polymer with Carboxylate Groups

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A label-free, highly selective, and highly sensitive fluorescent sensor to detect Hg^{2+} was developed using a water-soluble conjugated polymer with carboxylate groups (poly(2,5-bis(sodium 4-oxybutyrate)-1,4-phenylethynylene-*alt*-1,4-phenyleneethynylene, PPE-OBS) in this work. The fluorescence of PPE-OBS would be quenched because of the effect among the unique coordination-induced aggregation and electron transfers of PPE-OBS toward Hg^{2+} . The linear relationship between the fluorescence intensity and concentration of Hg^{2+} was observed within the range from 6×10^{-8} to $8 \times 10^{-5} \text{ mol L}^{-1}$ ($R^2 = 0.9985$), and the limit of detection was $2.10 \times 10^{-9} \text{ mol L}^{-1}$. The proposed method was applied to detect Hg^{2+} in environmental water samples, and satisfactory results were obtained.

Keywords Water-soluble conjugated polymer, Hg^{2+} , fluorescence sensor, environmental water samples

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Introduction

Mercury is derived from various anthropogenic and natural sources, such as coal and gold mining, solid waste incineration, wood pulping, fossil fuel combustion, and chemical manufacturing.¹ Emitted elementary mercury vapors are easily transported into the atmosphere, frequently across continents and oceans, and are eventually oxidized to Hg^{2+} in the environment.^{2,3} Inorganic mercury ions in water can be turned into highly poisonous methyl mercury through the participation of microorganisms. Methyl mercury is lipophilic, readily absorbed, and poorly excreted.⁴ It can be transferred to humans through the food chain.⁵ As toxic heavy metal ions, mercury ions have serious detrimental effects on the human body.^{6,7} The enrichment of excessive amounts of mercury ions can cause many health problems, such as DNA damage, kidney damage, liver damage, brain damage, and increased risk of myocardial infarction.⁸

The deleterious effects of mercury ions have prompted researchers to develop detection methods for Hg^{2+} , such as atom absorption spectroscopy,⁹ infrared spectroscopy,^{10,11} X-ray fluorescence spectrometry,¹² electrochemical methods,¹³ and colorimetric methods.¹⁴ However, these methods are time-consuming and require complicated instruments.^{15,16} In recent years, numerous efforts have been exerted to design various specialty chemosensors for Hg^{2+} detection.^{17–20} Fluorescence spectrometry has many advantages, including high sensitivity, good selectivity, low cost, operator simplicity, and good repeatability; and thus, it has attracted considerable attention.²¹ One attractive approach focuses on fluorescent Hg^{2+} sensors

based on conjugated polymers (CPs).²² Unlike that of their small molecule counterparts, the unique π - π^* conjugated electronic structure of CPs allows for rapid transfer of excitation along the entire backbone to energy/electron receptors, thereby resulting in a remarkable amplification of optical response.²³ Studies that detect metal ions with CPs in organic solvents have been proposed in the past 10 years.^{24–26} However, toxic heavy metal ions mainly exist in aqueous solutions, and the quenching process of CPs and metal ions in aqueous solutions is rarely studied.^{27,28} The lack of high selectivity against other competing analytes or the non-aqueous assay requirement for the majority of these systems prevents their application.²⁹ Therefore, carboxylic-functionalized water soluble CPs were synthesized *via* Heck-Cassar-Sonogashira-Hagihara coupling reaction.³⁰ These CPs were also successfully developed to detect analytes with high selectivity, high sensitivity, and good water solubility. Several research groups developed sensor systems applying the emissive property of carboxylic-functionalized water soluble CPs. For example, Fan *et al.* reported the synthetic route, optical properties, pH responses, and subsequent studies on the interaction and stabilization of poly(2,5-bis(sodium 4-oxybutyrate)-1,4-phenylethynylene-*alt*-1,4-phenyleneethynylene (PPE-OBS) with various surfactants.²³ Pei *et al.* investigated an antioxidant probe based on a bimodal PPE-OBS- SO_3 .³¹ A high-selectivity and high-sensitivity fluorescent sensor for detecting highly toxic Hg^{2+} was developed using PPE-OBS because of the good water solubility and considerable potential applications of PPE-OBS. In addition, the majority of fluorescent sensors for ions based on CPs are based on the following prevalent mechanisms: fluorescence resonance energy transfer,^{32,33} electron transfer,^{34,35} and analyte-induced aggregation or conformational changer.³⁶ Among these mechanisms, analyte-induced aggregation results in red shift and comparatively low quantum yield. However, only a few studies³⁷ have been

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performed on the exact mechanism and that how the intramolecular and intermolecular interactions influence the fluorescence properties remains unclear. Nevertheless, the molecular mechanism of the specific ion is necessary.

In the present work, PPE-OBS, which could be used to detect Hg^{2+} in water samples, was synthesized according to a previous report.²³ When Hg^{2+} is added, the coordination-induced aggregation and electron transfer between Hg^{2+} and PPE-OBS results in the significant quenching of fluorescence and in a slight red shift. In particular, PPE-OBS exhibits better linear range, higher sensitivity, and higher selectivity for Hg^{2+} than other metal ions used in other fluorescent sensing methods. PPE-OBS for Hg^{2+} detection was applied in environmental water samples. The experimental results are highly satisfactory.

Experimental

Reagents and chemicals

1,4-Diethynylbenzene (96%), $(\text{PPh}_3)_4\text{Pd}$ (99%), ethyl 4-bromobutyrate (98%) were purchased from J&K Scientific Ltd. (Beijing, China). Hydroquinone (99.5%) and KIO_3 were purchased from Shantou West Long Chemical Co., Ltd. (Shantou, China). I_2 was purchased from Tianjin Fu Chen Chemical Reagent Factory (Tianjin, China). NaCl , KOH , NaOH , $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ were purchased from Beijing Chemical Works (Beijing, China). Triethylamine and diisopropylamine were purchased from Tianjin Fu Yu Chemical Co., Ltd. (Tianjin, China). Dichloromethane, petroleum ether, dimethyl sulfoxide, methyl alcohol, ethyl alcohol, tetrahydrofuran, acetone and acetic ether were purchased from Tianjin Tiantai Fine Chemical Co., Ltd. (Tianjin, China). Anhydrous magnesium sulfate was purchased from Tianjin Dong Li Big Chemical Reagent Factory (Tianjin, China). All chemicals were used without further treatment. Thin layer chromatography (TLC) was carried out using silica gel 60 F254, and column chromatography was conducted over silica gel (300 – 400 mesh), both of which were obtained from the Qingdao Ocean Chemicals (Qingdao, China). Twice-distilled water was used throughout all experiments. All metal ion solutions were diluted from stock solutions.

Apparatus

The nuclear magnetic resonance spectroscopy (NMR) of compounds were identified by ^1H NMR and ^{13}C NMR (Varian Mercury YH-400 NMR spectrometer), using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are given in parts per million and coupling constants are given as absolute values expressed in Hertz. Infrared spectroscopy (IR) spectra were recorded using SpectrometerOne (Perkin-Elmer Corporation, MA). Thermogravimetric analysis (TGA) of the synthesized conjugated polymers was carried out at a heating rate of $10^\circ\text{C}/\text{min}$ within the temperature range of 40 to 600°C at a nitrogen flow rate of 80 ml/min using a synchronous-infrared thermal analysis-mass spectrometry coupled apparatus (NETZSCH, Bruker). Molecular weight and polydispersity of the polymer were determined by a 1260 series HPLC (Agilent Technologies Inc., CA) equipped with PLgel MIXED-B columns ($10\ \mu\text{m}$, $7.8 \times 300\ \text{mm}$, Agilent Technologies Inc.) and a refractive index detector using polystyrene as standard and THF as eluant. All fluorescence measurements were carried out with a Shimadzu RF-5301 spectrometer (Shimadzu Corporation, Japan). Fluorescence quantum yields and fluorescence lifetime were carried out with a FLS920 steady state and transient state fluorescence spectrometer (Edinburgh

Scheme 1 Synthetic routes of PPE-OBS. (a) Dimethyl sulfoxide, KOH reflux 24 h, under argon atmosphere, 25°C (83%); (b) ethanol, concentrated sulfuric acid, KIO_3/I_2 , $(\text{PPh}_3)_4\text{Pd}$, reflux 48 h, under argon atmosphere, 60°C (80%); (c) CHCl_3 , triethylamine, diisopropylamine, 1,4-diethynylbenzene, stirring under water bath, 50°C (76%); (d) tetrahydrofuran, methanol, NaOH , reflux 24 h, 50°C (88%).

Instrument). The fluorescence image of the PPE-OBS was taken by an inverted fluorescence microscope (Olympus FV1000 IX71) equipped with a multispectral imaging system (Nuance, CRI, Woburn, MA). All pH measurements were tested with a Sartorius PB-10 digital pH meter. All the optical measurements were carried out at room temperature (298 K) under ambient conditions.

Synthesis of PPE-OBS

Synthesis of water-soluble PPE-OBS was carried out according to the previous report.²³ It showed the synthetic route of PPE-OBS (Scheme 1). There were four steps to synthesize PPE-OBS from hydroquinone and ethyl 4-bromobutyrate. The first step was to synthesize 4-di(ethyl 4-oxybutyrate) benzene (M_1) with hydroquinone and ethyl 4-bromobutyrate under argon atmosphere and refluxed. The second step was to synthesize 1,4-di(ethyl 4-oxybutyrate)-2,5-diiodobenzene (M_2) using KIO_3 and I_2 . The third step was to synthesize PPE-OBE with 4-diethynylbenzene and M_2 . And the last step was to hydrolysis ester into carboxylic acid sodium. The intermediate and final product were characterized by liquid chromatography-mass spectrometry (LC-MS), IR, NMR, GPC, and TGA described in detail (Figs. S1 – S8, Supporting Information).

Preparation of environmental sample solutions

Lake water 1, lake water 2, river water and tap water were obtained from South Lake in Changchun, Peony Garden in Changchun, Yitong River in Changchun section and tap-water. Water samples were filtered by $0.45\ \mu\text{m}$ filter membrane and stored in 100 mL flask, respectively.

Experimental method

A stock solution of PPE-OBS ($100\ \mu\text{mol L}^{-1}$, repeat unit) was diluted to 500 mL with phosphate buffer saline (PBS) buffer solution (pH 7.4, $10\ \text{mmol L}^{-1}$). Then, $90\ \mu\text{L}$ of mercury ion standard solution ($1\ \text{mmol L}^{-1}$) and $1500\ \mu\text{L}$ of PPE-OBS standard solution ($100\ \mu\text{mol L}^{-1}$) were mixed and diluted to 3.0 mL, and the solution was allowed to stand for 40 min before

Fig. 1 (A) The absorption spectra of PPE-OBS and PPE-OBS added Hg^{2+} . (B) a, Excitation spectrum of PPE-OBS; b, emission spectrum of PPE-OBS; c, emission spectrum of PPE-OBS added Hg^{2+} . Concentration of PPE-OBS, $50 \mu\text{mol L}^{-1}$; concentration of Hg^{2+} , $30 \mu\text{mol L}^{-1}$.

fluorescence measurement. The fluorescence emission intensity was measured at 516 nm when the excitation wavelength was 400 nm. A quartz cell of 1 cm path length was used. The excitation and emission slits were set at 10 and 5 nm, respectively.

Results and Discussion

Spectroscopic properties of PPE-OBS

The absorption spectra of PPE-OBS and PPE-OBS- Hg^{2+} in phosphate buffered saline (PBS, pH 7.4) were recorded. The absorption spectrum of PPE-OBS- Hg^{2+} exhibited a slight redshift compared with that of PPE-OBS. The platform of absorbance was observed from 400 to 450 nm (Fig. 1A). Any light that ranged in wavelength from 400 to 450 nm could excite the fluorescent emission of PPE-OBS. The fluorescence excitation and emission spectra of PPE-OBS in PBS (pH 7.4) are shown in Fig. 1B. The fluorescence emission peak was observed at 516 nm with an excitation wavelength of 426 nm. However, the obtained fluorescence emission spectrum was not complete at this excitation wavelength because the emission peak ranged from 430 to 750 nm. Thus, 400 nm was selected as the excitation wavelength for subsequent experiments to maintain the integrality of the fluorescence emission spectrum. The fluorescence quantum yields and fluorescence lifetime of PPE-OBS ($50 \mu\text{mol L}^{-1}$) in PBS (pH 7.4) were measured. The results are presented in Fig. S9 (Supporting Information). The absolute fluorescence quantum yield was 5.83%, and the fluorescence lifetime values were 1.412 and 5.070 ns. Hg^{2+} could quench the fluorescence emission of PPE-OBS and the fluorescence quantum yield values decreased from 5.83 to 1.45%. The crest of the fluorescence emission of PPE-OBS exhibited a slight redshift from 516 to 525 nm when mercury ion was added. The redshift in the absorbance and the fluorescent emission suggested the presence of molecular aggregation in the polymer.

An equilibrium occurs in the absence of Hg^{2+} ions; $\text{R-COONa} \rightleftharpoons \text{R-COO}^- + \text{Na}^+$, which causes the polymer PPE-OBS to carry a negative charge. PPE-OBS exhibits strong fluorescence emission. Hg^{2+} ions function as fluorescence quenchers in this fluorescence sensing system. Upon adding Hg^{2+} , the polymer chains possess a large number of carboxylic acid anchoring units and behave as multidentate ligands to

Fig. 2 (A) Fluorescence sensing schematic diagram of the PPE-OBS and Hg^{2+} reaction process; (B) fluorescence microscope photos of PPE-OBS; (C) fluorescence microscope photos of PPE-OBS with Hg^{2+} taken after 10 min; (D) 20 min; (E) 40 min. Concentration of PPE-OBS, $50 \mu\text{mol L}^{-1}$; concentration of Hg^{2+} , $30 \mu\text{mol L}^{-1}$.

scavenge for Hg^{2+} ions in the solution. The efficient coordination of Hg^{2+} with the carboxylate group pendants along the polymer backbone results in the formation of interpolymer π -stacking

Fig. 3 The quenching efficiency of $50 \mu\text{mol L}^{-1}$ PPE-OBS- $30 \mu\text{mol L}^{-1}$ Hg^{2+} at various pH in the 0.04 mol L^{-1} mixed acid buffer solution.

aggregation among their large aromatic units. The delocalized electrons of PPE-OBS can directly transfer the electron-withdrawing Hg^{2+} , which induces the efficient quenching of PPE-OBS.^{38,39} The diagram and fluorescence images of the procedure of Hg^{2+} that interacts with PPE-OBS are shown in Fig. 2. These pictures can confirm the quench mechanism of PPE-OBS with Hg^{2+} . The PPE-OBS in the aqueous solution emitted bright yellow-green fluorescence before Hg^{2+} was added (Fig. 2A). Figures 2C to 2E show the fluorescence microscope images of PPE-OBS with Hg^{2+} , which were taken after 10, 20, and 40 min, respectively. A remarkable aggregation of PPE-OBS into many rods about $10 \mu\text{m}$ was observed after 10 min. This formation of aggregated rods was also evident from the redshift of their absorption spectrum and fluorescence spectrum. The fluorescence of PPE-OBS significantly darkened after 20 min. The fluorescence of PPE-OBS was completely quenched after 40 min. Therefore, these results indicated that the proposed approach could be used to detect Hg^{2+} .

Effects of different pH values on fluorescence response

The effects of different pH values of the PPE-OBS solution on Hg^{2+} sensing were explored. Figure S10 (Supporting Information) shows that the fluorescence intensity (excited at 400 nm) of PPE-OBS is non-luminescent, and no significant change is observed in the presence of Hg^{2+} within the pH range from 4 to 6. This phenomenon indicates that PPE-OBS, whose pendant group is $-\text{COOH}$ instead of $-\text{COO}^-$, tends to become hydrophobic; this PPE-OBS forms considerably tight aggregates²³ at pH lower than 6, and the interaction between Hg^{2+} and PPE-OBS is extremely weak. When pH was changed from 6 to 7, quench efficiency exhibited a significant change because the carboxylate group pendants along the polymer backbone hydrolyzed in strongly hydrophilic $-\text{COONa}$. Moreover, the aggregation of PPE-OBS was reduced, and its luminosity was increased. Thus, an obvious fluorescence off-on change of PPE-OBS occurred with different fluorescence enhancement efficiencies within the pH range from 6 to 10.5, and the increased fluorescence intensity of PPE-OBS was low when pH was higher than 7 (Fig. S10 (Supporting Information)). An obvious fluorescence quenching phenomenon occurred in the presence of Hg^{2+} . A pH of 7.4 was chosen for fluorescence intensity determination according to the quenching efficiency of PPE-OBS (Fig. 3).

Fig. 4 (A) The effect of reaction time on fluorescence intensity of the PPE-OBS (black line) and the PPE-OBS mixed with Hg^{2+} (red line). (B) The quenching efficiency of PPE-OBS- Hg^{2+} at various temperatures. Concentration of PPE-OBS, $50 \mu\text{mol L}^{-1}$; concentration of Hg^{2+} , $30 \mu\text{mol L}^{-1}$.

Effect of reaction parameters on the fluorescence response of PPE-OBS

The effect of reaction time on the fluorescence intensity of the PPE-OBS- Hg^{2+} complex was studied at room temperature. The investigation showed that the fluorescence intensity of free PPE-OBS was highly stable and approximately 750 (arb. unit) (Fig. 4). In addition, the fluorescence signal of PPE-OBS was quenched sharply in PBS (pH 7.4) when mercury ions were added into the solution. Fluorescence intensity reached a stable value within 40 min and remained nearly constant thereafter. Therefore, a reaction time of 40 min was selected in the subsequent experiments. The effect of reaction temperature was also studied.

The change in fluorescence intensities of PPE-OBS and PPE-OBS- Hg^{2+} followed the change in temperature as shown in Fig. S11 (Supporting Information). Figure 4 shows that the quench efficiency of PPE-OBS continuously decreases with a temperature ranging from 25 to 60°C . This observation illustrates that temperature can seriously affect the quantum yield of CPs. In particular, a high temperature decreases the viscosity of a solution. The kinetic energy of the solvent and PPE-OBS molecules increases, thereby enhancing the collision probability of the PPE-OBS molecules with other molecules. The excited fluorescence molecules transfer their energy through molecular collision or intramolecular energy transfer. The excited molecules return to ground state in the form of radiation, which leads to fluorescence quenching and quantum yield reduction.⁴⁰ Fluorescence measurements were obtained under 25°C for subsequent experiments according to the quench efficiency of PPE-OBS.

Interference of common ions in Hg^{2+} detection

An important feature of the sensor is its high selectivity toward Hg^{2+} over other competitive species. In this section, the

Fig. 5 (A) Images of an aqueous solution of the PPE-OBS in the presence of various ions under the condition of visible light. (B) Images of an aqueous solution of the PPE-OBS in the presence of various ions under a UV-lamp with a light wavelength of 365 nm. (C) I_0/I of PPE-OBS with different metal ions (black bars); the red bars, PPE-OBS with different metal ions in the presence of Hg^{2+} . Concentration of PPE-OBS, $50 \mu\text{mol L}^{-1}$; concentration of metals, $30 \mu\text{mol L}^{-1}$.

effect of common metal ions on Hg^{2+} detection using PPE-OBS was investigated. Figure 5A shows that the color of the metal ion solution did not obviously change in PBS (pH 7.4). However, among the metal ions tested (*i.e.*, Hg^{2+} , Al^{3+} , Co^{2+} , Cr^{6+} , Cu^{2+} , Ba^{2+} , K^+ , Mg^{2+} , Ca^{2+} , Ni^{2+} , Mn^{2+} , Fe^{3+} , Pt^{2+} , Sr^{2+} , Cd^{2+} , As^{3+} , Mo^{6+} , Zn^{2+} , Li^+ , Na^+ , and Pb^{2+}), only Hg^{2+} could quench the green fluorescence of PPE-OBS (Fig. 5B). Although the metal ions Zn^{2+} , Cd^{2+} , and Hg^{2+} were under the same group of elements and possessed filled d^{10} -configuration; the polymer was selective toward Hg^{2+} ions. The high selectivity of PPE-OBS to Hg^{2+} resulted from the efficient coordination of Hg^{2+} with carboxylic acid pendants.^{38,39} The interference of common metal ions during Hg^{2+} detection was also investigated. Figure 5C illustrates the fluorescence response of PPE-OBS in the presence of different metal ions (blue bar portion). No obvious fluorescence quenching was observed in the presence of contaminating metal ions. This observation indicates that other metal ions cannot change the status of PPE-OBS. Thus, water-soluble CPs exhibit high selectivity toward Hg^{2+} .

Competition experiments were also conducted to test the practical applicability of our fluorescence chemosensor for Hg^{2+} . A sample solution containing the aforementioned metal ions ($30 \mu\text{mol L}^{-1}$) was added to $30 \mu\text{mol L}^{-1}$ Hg^{2+} in PBS (pH 7.4), and the fluorescence response of the chemosensor was detected and then compared with the solution that contained only $30 \mu\text{mol L}^{-1}$ Hg^{2+} . The results are also shown in Fig. 5C (red bar portion). The experimental results show that the response of the sensor to Hg^{2+} is unaffected by other potentially contaminating metal ions. This observation indicates that PPE-OBS is a viable selective chromogenic sensor for Hg^{2+} .

Fig. 6 Fluorescence spectra of PPE-OBS ($50 \mu\text{mol L}^{-1}$) in different concentrations of Hg^{2+} (0.06, 0.1, 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 20.0, 40.0, 60.0, 80.0, 100.0 $\mu\text{mol L}^{-1}$); the insert figure show the linear relationship between (I_0/I) and the concentrations of Hg^{2+} .

Analytical characteristics

Under the optimized conditions, the fluorescence response of PPE-OBS quenched with Hg^{2+} concentration increased from 6×10^{-8} to $8 \times 10^{-5} \text{ mol L}^{-1}$ (Fig. 6). The quenched fluorescence intensity of PPE-OBS is directly proportional to the Hg^{2+} concentration, which can be described best using a Stern-Volmer equation:

Table 1 Comparison of different fluorescent sensors for detection of Hg^{2+}

No.	Fluorescent sensor type	Range of linearity/mol L ⁻¹	LOD/mol L ⁻¹	Ref.
1	Based on chemical bond	$4.99 \times 10^{-9} - 2.49 \times 10^{-8}$	4.99×10^{-9}	41
2	Based on hydrogen-bonding interactions	$0 - 1.00 \times 10^{-7}$	1.00×10^{-9}	42
3	Based on nanomaterials	$1.60 \times 10^{-6} - 1.60 \times 10^{-5}$	4.00×10^{-8}	43
4	Based on the process between molecules and nanomaterials	$8.00 \times 10^{-7} - 9.00 \times 10^{-6}$	1.00×10^{-7}	44
5	Based on micelles	$0 - 1.00 \times 10^{-6}$	7.50×10^{-8}	45
6	Based on strip and chip	$8.60 \times 10^{-9} - 1.00 \times 10^{-4}$	1.00×10^{-7}	46
7	Based on metal complexes	$0 - 1.00 \times 10^{-4}$	—	47
8	Based on conjugated polymer	$0 - 1.00 \times 10^{-4}$	1.00×10^{-7}	22
9	Based on conjugated polymer	$6.00 \times 10^{-8} - 8.00 \times 10^{-5}$	2.10×10^{-9}	This work

$$I_0/I = 1 + K_{SV}[\text{Hg}^{2+}], \quad (1)$$

where I_0 is the fluorescence intensity of PPE-OBS, I is the fluorescence intensity of the PPE-OBS in the presence of Hg^{2+} , and K_{SV} stands for the Stern-Volmer quenching constant. The formula shows that the fluorescence intensity ratio (I_0/I) exhibits a good linear relationship with Hg^{2+} concentration within the range of 6×10^{-8} to 8×10^{-5} mol L⁻¹. From the Stern-Volmer plot, $K_{SV} = 1.405 \times 10^5$ L mol⁻¹ suggests fluorescence quenching in the present sensing event and a highly sensitive Hg^{2+} detection based on this CP. The limit of detection (LOD) for Hg^{2+} is 2.10×10^{-9} mol L⁻¹ (based on $S/N = 3$). Thus, the CP sensor of Hg^{2+} can provide a highly sensitive fluorescence probe to detect Hg^{2+} in water or biological samples.

A comparison between this method and the use of other reported fluorescent sensors in the past 5 years for Hg^{2+} detection is provided in Table 1. The sensitivity and linear response range of our fluorescence sensor are better than those of the majority of the reported methods. Moreover, compared with other Hg^{2+} sensors, our sensor has the advantages of being non-toxic, label-free, easy to prepare, and low cost.

Hg^{2+} detection in water samples

The practical application of a CP chemosensor was evaluated by using this chemosensor to detect Hg^{2+} in four environmental water samples. Then, 2.5 mL PBS with PPE-OBS was added to 0.5 mL of the sample to reduce pH influence on the detection by maintaining the pH value at 7.4, and the fluorescence intensity change of the sample was measured. The Hg^{2+} concentrations of the samples were determined using an optimized fluorimetric procedure. The results obtained are summarized in Table 2. Hg^{2+} was not detected in the water samples, and recovery experiments for varying added amounts of Hg^{2+} were conducted. The experimental results are also shown in Table 2. The recovery of Hg^{2+} ranged from 97.5 to 103.5%, and the relative standard deviation was less than 1%. These results confirmed the validity of the proposed method.

Conclusions

In summary, we demonstrated that as a novel fluorescent probe for Hg^{2+} detection, PPE-OBS exhibited high sensitivity. Moreover, fluorescence intensity was quenched quantitatively with an increase in Hg^{2+} concentration and an LOD of 2.10×10^{-9} mol L⁻¹ under optimized conditions. PPE-OBS has higher selectivity for Hg^{2+} than other metal ions. No obvious influence occurred on the detection of mercury when the other metal ions coexisted with Hg^{2+} . The concentrations of mercury ion in the actual water samples were determined, and the results obtained were satisfactory.

Table 2 Recovery study of Hg^{2+} in real samples

Sample	Hg^{2+} added/ mol L ⁻¹	Hg^{2+} found/ mol L ⁻¹	Recovery ^a , %	RSD ^b , %
Tap water	0.00	0.00	—	—
	6.00×10^{-8}	5.85×10^{-8}	97.5	0.35
	1.80×10^{-7}	1.76×10^{-7}	98.0	0.32
	3.00×10^{-7}	3.11×10^{-7}	103.5	0.94
Lake water 1	0.00	0.00	—	—
	6.00×10^{-8}	6.07×10^{-8}	101.5	0.26
	1.80×10^{-7}	1.86×10^{-7}	103.2	0.40
	3.00×10^{-7}	2.96×10^{-7}	98.6	0.46
Lake water 2	0.00	0.00	—	—
	6.00×10^{-8}	6.07×10^{-8}	101.2	0.86
	1.80×10^{-7}	1.78×10^{-7}	99.0	0.42
	3.00×10^{-7}	3.02×10^{-7}	100.5	0.62
River water	0.00	0.00	—	—
	6.00×10^{-8}	5.95×10^{-8}	99.2	0.45
	1.80×10^{-7}	1.95×10^{-7}	102.5	0.32
	3.00×10^{-7}	2.95×10^{-7}	98.2	0.51

a. Recovery is amount of Hg^{2+} found except amount of Hg^{2+} added.

b. RSD is the ratio of standard deviation except the arithmetic average of five times measurement.

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Supporting Information

The Supporting Information provides synthesis and characterization data of the intermediate and final product and supplementary spectral data (PDF). This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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