Research Article

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Construction of mercury ion fluorescence system in water samples and art materials and fluorescence detection method for rhodamine B derivatives

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Abstract: At present, the research on fluorescent molecular probe has become a hot topic in the field of environmental science, chemical materials, medicine, and other fields. Therefore, the detection of industrial mercury-containing wastewater (Hg^{2+}) is of great significance. In this article, the fluorescent probe is used to detect mercury ions, and when compared with the traditional detection method, the fluorescent probe has the advantage of operation such as the effect of simplicity is evident. The experiments first synthesized rhodamine B derivatives and then the synthesized rhodamine B derivative fluorescent molecular probes were constructed and used to detect the mercury ions in water sample and oil paints. It was demonstrated that rhodamine B-derived probes have been constructed by UV and fluorescence spectroscopy. The different metal ions and rhodamine B-derived fluorescent molecular probes were compounded, resulting in the appearance of fluorescence peak centered at 583 nm only after the addition of metallic mercury ions with almost no response from other ions. The mercury ion rhodamine B derivative is more responsive to metallic mercury ions.

Keywords: rhodamine B derivatives, fluorescent probe, mercury ion, water environment, oil paints

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1 Introduction

Compared to other metal detection methods, fluorescent molecular type probes are more sensitive because of their good selectivity, no reference term is required, and they have a higher sensitivity, relatively simple operation, low cost of preparation, not easily affected by magnetic and electric fields, and obvious reaction to other characteristics. Therefore, a new fluorescent molecular probe is synthesized [1–4]. Rhodamine has good fluorescence properties, such as large molar absorbance, long excitation and emission wavelengths, strong light stability, and high fluorescence quantum yield. So, this experiment chose to use rhodamine derivatives as probes for detection of mercury ions [5–7]. The main sources of mercury ions are natural environmental and industrial wastewater discharges, which can enter the body by accumulating in bacteria or the food chain and converting to organic mercury. In humans, it can cause irreversible damage to the kidneys, nervous system, and brain function [8–10]. Therefore, it is of great interest to develop new fluorescent probes that respond to mercury ions [11]. There are strict standards for the detection of mercury ions around the world, such as the U.S. EPA's limit of Hg^{2+} in drinking water is $2\,\mu g{\cdot}L^{-1}$. Limit standard for Hg^{2+} in drinking water in China is $1\,\mu g{\cdot}L^{-1}$, and the limit standard for industrial wastewater is $0.25\,mmol{\cdot}L^{-1}$. Therefore, high sensitivity is required for mercury ion fluorescence probe [12–15].

Dhaka et al. developed a novel thioether spiro rhodamine B fluorescent probe [16]. By using a simple thioether spirocycle instead of typical spirolactam as the Hg^{2+} recognition unit, the proposed probe is sensitive to Hg^{2+} and exhibited an independent ultrasensitive response, and showed that the free probe maintained its spirocyclic form in living cells. The probes are responsive and highly selective for Hg^{2+} [17]. In the presence of other metal ions, the fluorescence changes of the probe are very pronounced and are particularly suitable for the rapid response of Hg^{2+} [18,19]. Tian et al. from Hainan Normal University combined rhodamine 6G with hydrazine hydrate and synthesized fluorescent probes. When there was no Hg^{2+} in solution, the R6GH was non-fluorescent and mercury ions were gradually added to 10 μM-R6GH in ethanol/HEPES buffer solution at room temperature. The excitation wavelength of R6GH is 500 nm and an emission peak appears at 554 nm. In ethanol/water buffer solution, R6GH can specifically recognize mercury ions and emit yellow-green fluorescence, and mercury ions can also make R6GH fluorescence. The solution changes from colorless to pink, so R6GH can also be used for colorimetric detection of mercury ions. Mercury ion is the only ion that causes an increase in R6GH fluorescence, and the addition of other metal ions has no effect on the fluorescence spectrum of R6GH. This fluorescent probe is highly selective and can be successfully used for fluorescence imaging of mercury ions in the living cells [20–22]. These experiments have contributed to the development of rhodamine-derived probe technology, thus making rhodamine an ideal material for fluorescent probes to be used for mercury ions.

Large amount of mercury containing wastewater is produced in non-ferrous metal smelting, chlor-alkali industry, electronic industry production, and other processes. The detection of industrial mercury containing wastewater (Hg^{2+}) is of great significance. If the wastewater containing mercury (Hg^{2+}) is directly discharged into the water, mercury and its compounds can form various forms of mercury through physical, chemical, and biological interactions, and even convert into highly toxic methyl compounds, thus seriously polluting the water environment.

According to literature reports, the methods that can be used for mercury ion monitoring include: high performance liquid chromatography, atomic absorption spectrometry, atomic emission spectrometry, and inductively coupled plasma mass spectrum. However, there are problems in these methods. The operation and maintenance cost of the testing instrument is high, and the instrument is cumbersome which cannot meet the needs of a wide range of applications. Fluorescent molecular probe technology, which has the advantages of high selectivity, high sensitivity, simple operation, and wide application range, has been favored in the detection of mercury ions. According to the different response mechanisms of fluorescent probes to Hg^{2+}, the fluorescent probes can be divided into three types: ratio type, “off-on” type, and “on-off” type. Many fluorescent probes for the detection of mercury ions are designed based on these principles.

In addition, the existence of harmful substances in oil paints, such as mercury and lead metal ions, is very harmful to the human body. In this article, rhodamine B RH-DCP probe was designed for the determination of mercury ions in titanium dioxide and zinc white of oil paints. The probe can be used to detect mercury ions in titanium dioxide and zinc white of oil paints in environmental water samples.

2 Materials and methods

2.1 The white of oil paint is common titanium white, zinc white, and lead white

Titanium dioxide (PW6): Currently, all pigment brands divide the raw materials used to make their colours into two types, R-type and anatase, and the performance of these two materials differs considerably. With strong coverage, it is generally used as the main auxiliary color of oil painting harmonic color. The chemical composition of titanium dioxide is mainly titanium dioxide (TiO_2), white powder.

Zinc white (PW4): Transparent white pigment, poor coverage, poor firmness after oxidation, easy to powder. Chemical composition of zinc white is mainly zinc oxide (ZnO), pure zinc white is cold, with slightly blue tendency, is a good oil painting to brighten the auxiliary color. Generally mixed with titanium dioxide to form mixed white, and titanium dioxide ratio is different, mixed white can reflect different physical properties.

Titanium dioxide (PW6) manufacturer, Langfang Lanke Chemical Co., LTD. Zinc white (PW4) manufacturer, Changzhou Yumeng Chemical Co., LTD.

2.2 Construction of mercury ion fluorescence system for rhodamine B derivatives

Add rhodamine, methanol, hydrazine hydrate, and 2,4-dichloroacetophenone to a beaker in turns, stirred, refluxed, and cooled, and then carried out vacuum rotary evaporation, followed by rinsing, vacuum filtration, and drying to obtain new colorless transparent glassy rhodamine B derivatives. The newly obtained rhodamine B derivatives were dissolved in ethanol/water (1:2) and formulated into 0.2×10^{-5} mol·L^{-1} rhodamine B derivative solution, $HgCl_2$ standard formulated into 5×10^{-4} mol·L^{-1} Hg^{2+} standard solution. A certain volume of rhodamine

B-derivative solution and a certain volume of Hg^{2+} reserve solution were added to a 10 mL colorimetric tube. Dilute 10 mL with distilled water, stir, and let stand for 50 min to obtain a mercury ion fluorescent probe system for rhodamine B derivatives.

2.3 Fluorescence spectroscopy detection methods

A mercury ion fluorescent probe system formulated with rhodamine B derivatives was added as a test sample to a 1 cm quartz colorimetric cell. A separate colorimetric tube is taken and under the same conditions, only the fluorescent probe solution of rhodamine class B derivatives is added without metal Hg^{2+}. These solutions were used as blank samples. Use 530 nm as the excitation wavelength. Set the fluorescence parameters with sensitivity set to 2 and slit width set to 5 nm. Fluorescence emission spectrum in the 500–700 nm was scanned by a fluorescence spectrophotometer to determine the fluorescence emission intensity.

To measure the strength of the selectivity of the probe to mercury ions, 14 common metal ions such as Pb^{2+}, Zn^{2+}, Ag^{+}, Ca^{2+}, Mn^{2+}, Cu^{2+}, Al^{3+}, and Cr^{3+} were added to the rhodamine class B derivative probe solution, respectively.

3 Results

3.1 Spectra of mercury ion fluorescence systems for rhodamine B derivatives

Figure 1a shows the UV-Vis absorption spectra of the mercury ion fluorescence system of rhodamine B derivatives in the wavelength range of 400–700 nm. As shown in Figure 1, the rhodamine B-derivative probe solution of the blank sample without the addition of metallic mercury ions had no UV absorption in the range of 500–650 nm. The addition of metallic mercury ions to the system resulted in peak centered at 558 nm. It can be inferred that mercury ion class B derivatives have been constructed based on the changes in the UV spectrum.

Figure 1b shows the infrared spectrum of Rh-DCP, a derivative of rhodamine B. Rh-DCP contains absorption peaks of characteristic functional groups of intermediates, and there is an absorption peak at 1,614 cm^{-1}, which

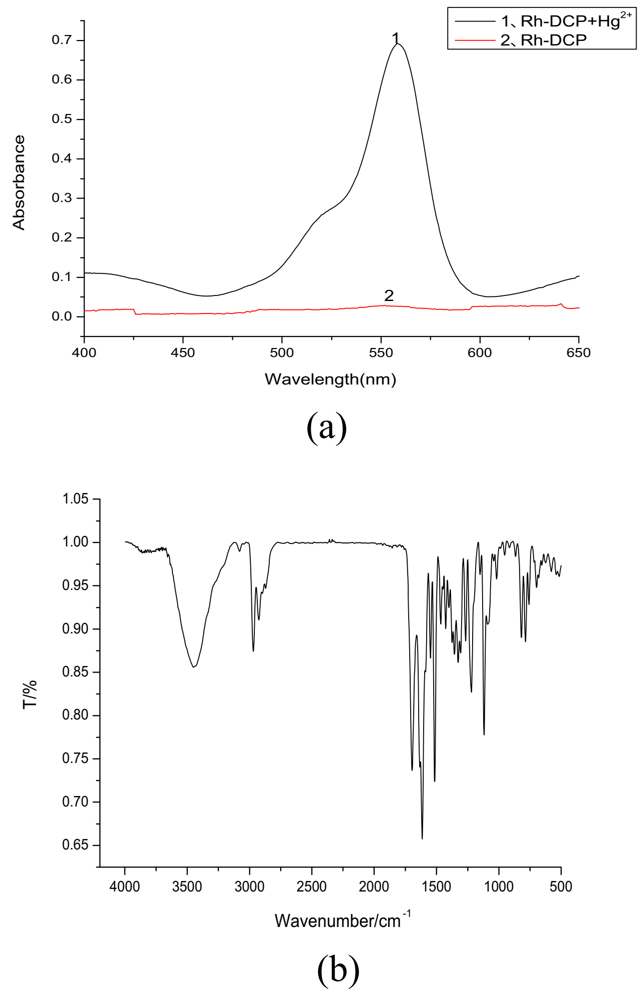

Figure 1: (a) UV-Vis absorption spectra of rhodamine class B derivatives and Hg^{2+} fluorescence systems (CH_3CH_2OH/H_2O [v/v,1/2], probe concentration 10×10^{-5} $mol{\cdot}L^{-1}$, Hg^{2+} concentration 10×10^{-5} $mol{\cdot}L^{-1}$). (b) IR spectrum of Rh-DCP.

is the stretching vibration peak of C═N. Moreover, rh-DCP has a strong absorption peak at this position, indicating that the $-NH_2$ structure of rhodamine B-hydrazide forms a new (C═N) bond with the C═O structure, which can be judged as the successful synthesis of Rh-DCP.

Figure 2 shows the fluorescence spectra of the mercury ion fluorescence system obtained at a fixed excitation wavelength of 530 nm with a slit width setting of 5.0 nm. The variation of the fluorescence intensity in 530–680 nm was also recorded. The results are shown in Figure 2. There was no peak in the range of 560–620 nm in the rhodamine class B derivative probe solution. After adding Hg^{2+} to the system and mixing the solution for 50 min before performing the assay, a strong peak centered at 583 nm appeared. It can be inferred that fluorescence spectra has been constructed in this experiment.

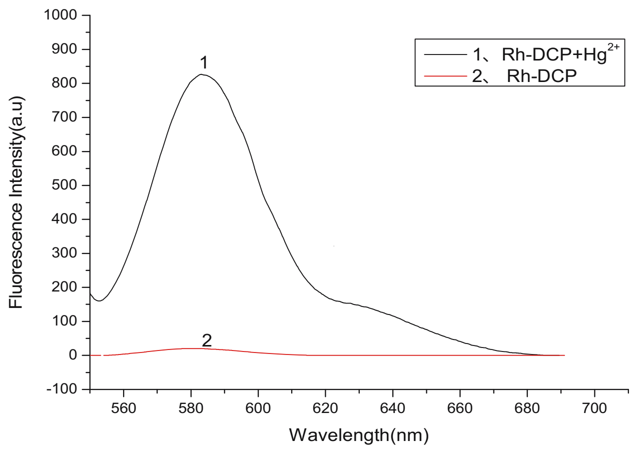

Figure 2: Fluorescence spectrum of rhodamine class B derivatives and Hg^{2+} fluorescence systems (CH_3CH_2OH/H_2O [v/v, 1/2], λ_{ex} = 530 nm, probe concentration 10×10^{-5} mol·L^{-1}, Hg^{2+} concentration 10×10^{-5} mol·L^{-1}).

Figure 3 shows the fluorescence spectra of the binding ratio of rhodamine class B derivatives to the mercury ion fluorescence system. In order to confirm the binding pattern of rhodamine class B derivative probe and mercury ion, the binding ratio of rhodamine B-derived probes to Hg^{2+} was determined by an iso-molar continuous change method (Job-Plot). The molar ratio of Hg^{2+} concentration in the system is from 0.1 to 0.9, and the solution at different ratios was recorded. It can be seen from the graph that the maximum fluorescence intensity is reached when the molar concentration ratio of metal ions to the probe is 1:1, which means that the ratio of mercury ions to the probe is 1:1. The optimal binding ratio of the probe also indicates a 1:1 binding ratio between the mercury ion and the probe.

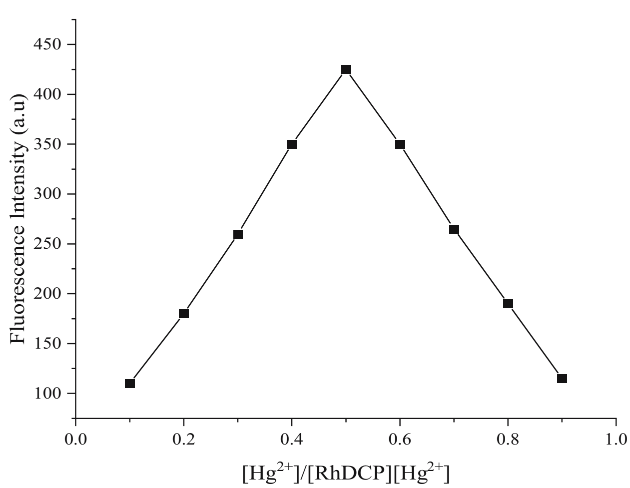

Figure 3: Determination of the binding ratio (CH_3CH_2OH/H_2O [v/v, 1/2], λ_{ex} = 530 nm); the fluorescent system by the equimolar method.

3.2 Response of rhodamine B derivatives to metal ion fluorescent probes for mercury ions

Figure 4 shows the effect of rhodamine class B derivative probes on Pb^{2+}, Zn^{2+}, Ag^{+}, Ca^{2+}, Mn^{2+}, and Cu^{2+} and the fluorescence spectra of the selective responses of 14 common metal ions. From Figure 4, it can be seen that the only significant response to the fluorescence intensity is the metal mercury ion solution. In the range of 400–600 nm, the fluorescence emission spectra are shown by the absence of significant fluorescence before the addition of metal. After metallic mercury ions, a peak centered at 583 nm appeared. Except for Hg^{2+}, the fluorescence intensity of Al^{3+} is also slightly enhanced, while the other ions have almost no response and do not affect the detection of mercury ions. The results showed that the mercury ion rhodamine B derivative probe molecule was selective only for metallic mercury ions. In order to ensure the safety of RH-DCP in daily application, the *in vitro* toxicity of RH-DCP was measured by MTT cell survival test. The cell survival rate was higher than 76% at all concentrations, indicating that RH-DCP is safe enough for routine use.

The synthesis of rhodamine B derivative Rh-DCP is shown in Figure 5. Figure 6 shows possible binding mechanism of probe Rh-DCP to Hg^{2+}. According to the above experiment, the binding ratio of probe RH-DCP to Hg^{2+} was 1:1. When the RH-DCP fluorescent probe was

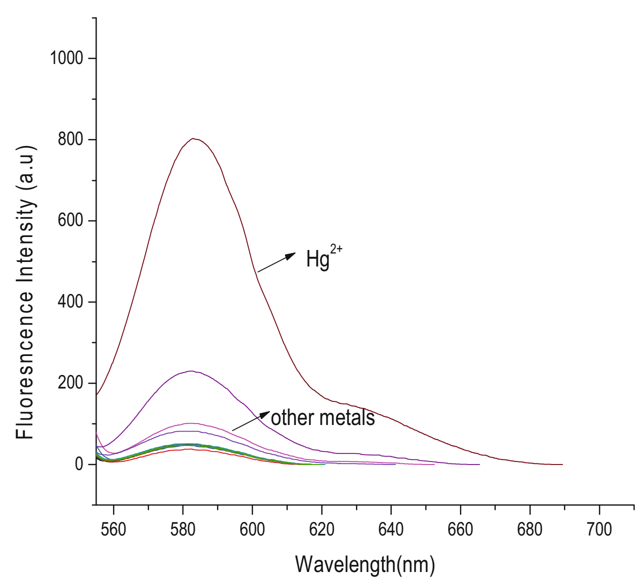

Figure 4: Fluorescence spectrum of different metal ions and rhodamine class B derivatives response (CH_3CH_2OH/H_2O [v/v, 1/2], λ_{ex} = 530 nm, probe concentration 10×10^{-5} mol·L^{-1}, metal ions concentration 10×10^{-5} mol·L^{-1}).

alone, the spirolactam ring in the structure was in a closed loop state and hardly produced fluorescence. After the addition of Hg^{2+} ions, Hg^{2+} coordinates with oxygen and nitrogen on amide, and electron rearrangement occurs in the molecule. Therefore, the spirolactam ring of the probe molecule breaks, and rH-DCP in the ring-open state will cause changes in fluorescence intensity and color.

Compared with the reported methods, the fluorescence molecular probe technology has the advantages of high selectivity, high sensitivity, simple operation, and wide application range, and has been favored in the study and detection of mercury ions.

3.3 Determination of the sample

3.3.1 Determination of Hg(II) in water samples

Table 1 is the water sample determination experiment. The river water and tap water are filtered through the filter membrane to remove impurities in the water. Mercury ion content was measured by fluorescence probe, and no response indicated that there was no Hg^{2+}. The addition scalar of Hg^{2+} at high and low levels is consistent with the measured data. The experimental results show that the synthesized probe can be applied to the analysis and determination of Hg^{2+} in tap water and lake water and has high practical value.

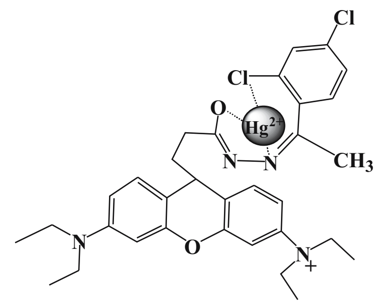

Figure 6: Possible binding mechanism of probe Rh-DCP to Hg^{2+}.

Table 1: Sample determination experiment (n = 6)

Sample	Detection volume ($mol·L^{-1}$)	Add amount ($mol·L^{-1}$)	Recovery rate (%)	RSD (%)
		10×10^{-6}	99.6	1.88
Tap water	—	20×10^{-6}	100.7	2.03
		40×10^{-6}	101.2	1.95
		10×10^{-6}	98.5	2.11
Songhua river water	—	20×10^{-6}	100.6	1.95
		40×10^{-6}	101.6	1.83

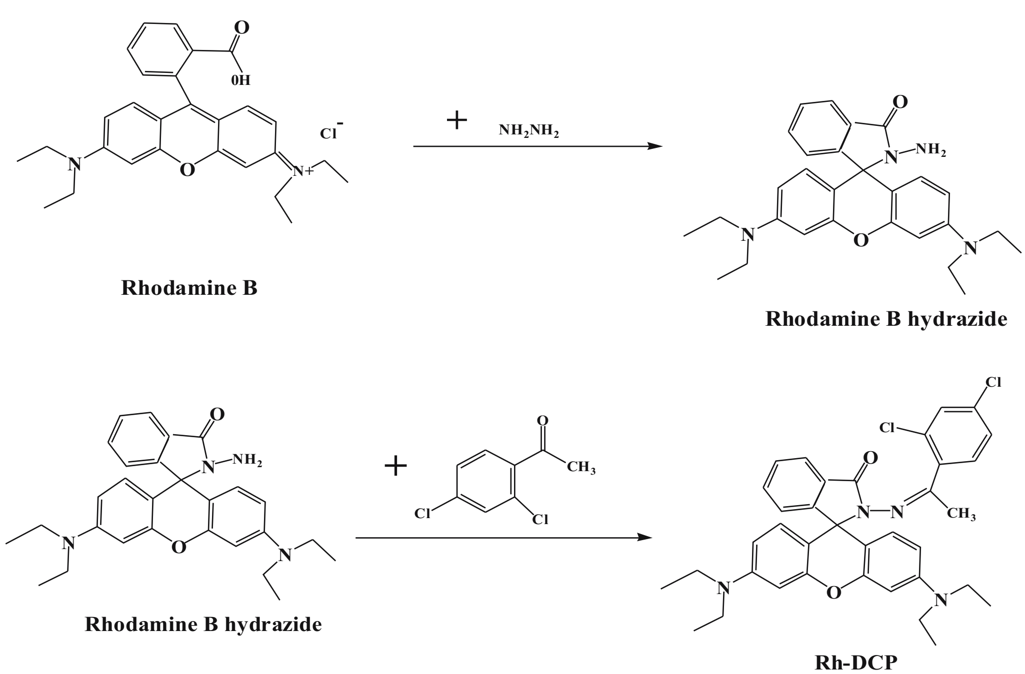

Figure 5: Synthesis of rhodamine B derivative Rh-DCP.

3.3.2 Determination of Hg(II) in titanium dioxide and zinc white samples

Table 2 shows the determination experiment of titanium dioxide and zinc white samples of oil paint. First, the sample solution of titanium dioxide and zinc white of oil paint was prepared. An appropriate amount of mercury ions was added to the prepared fluorescent probe, and the mercury content in the two samples was measured by fluorescence analysis. The reaction showed no response, indicating that there was no Hg^{2+}. As can be seen from Table 1, three different high and low levels of Hg^{2+} were added to the markers. The results show that the probe RH-DCP can be effectively applied to the determination of Hg^{2+} in zinc white and titanium white solution of oil paint samples. Avoid painting workers, contact with paint containing toxic metals, has high practical application value.

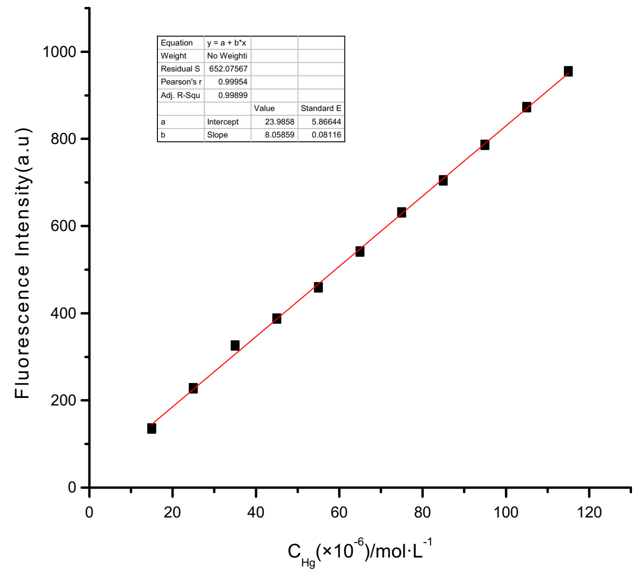

Figure 7: Standard curve of Rh-DCP detection of Hg^{2+}.

3.4 Standard curve drawing

Figure 7 shows the standard curve of RH-DCP for mercury ion detection. According to the analysis of detection system, the fluorescence intensity of the fluorescence system increased with the increase of the concentration of Hg^{2+} added. In a certain range, the relative fluorescence intensity of the system has a good linear relationship with the concentration, and the regression curve is $y = 8.059X + 23.986$, $R^2 = 0.9989$. Therefore, the fluorescence system can be used as a probe to determine the content of Hg^{2+} in water.

3.5 Linear detection range and detection limit

Figure 8 shows the fluorescence spectra of blank samples. By measuring the blank solution 11 times in parallel and then calculating the three times standard deviation, $\delta = 0.525$ was calculated. The detection limit of the probe molecule detected by this method was calculated to be 0.2×10^{-6} mol·L^{-1}. When Hg^{2+} was in the range of 10.0×10^{-6}–12.8×10^{-5} mol·L^{-1}, the relative fluorescence intensity of the system had a good linear relationship with the concentration, and the linear correlation coefficient was 0.9993.

3.6 The graph results of the MTT cytotoxicity test

The results of MTT cytotoxicity test were as follows (Figure 9): the fluorescence of rH-DCP-treated cells was weak, and the HeLa cells showed strong green fluorescence when Hg^{2+} and probe were added, indicating that the RH-DCP probe had good membrane permeability and could be used for the detection of Hg^{2+} in HeLa cells. In the follow-up experiments, our research group will carry

Table 2: Sample determination experiment ($n = 6$)

Sample	Detection volume	Add amount (mol·L^{-1})	Recover amount (mol·L^{-1})	Recovery rate (%)	RSD (%)
		50×10^{-6}	49.81×10^{-6}	99.7	1.86
Titanium white	—	80×10^{-6}	81.02×10^{-6}	101.1	2.21
		100×10^{-6}	100.8×10^{-6}	100.8	1.95
		50×10^{-6}	50.86×10^{-6}	101.7	2.12
Chinese white	—	80×10^{-6}	80.61×10^{-6}	100.8	2.02
		100×10^{-6}	102.5×10^{-6}	102.3	1.78

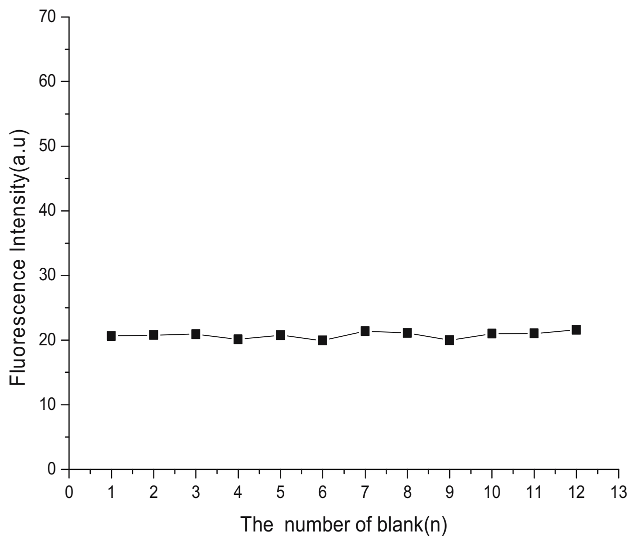

Figure 8: Spectral detection limit of blank sample (n = 11).

out relevant work according to the experimental ideas of literature [23,24].

4 Discussion

In recent years, fluorescent molecular probes have attracted extensive attention because of their advantages such as good selectivity, no reference term, high sensitivity, relatively simple operation, low preparation cost, and not easily affected by magnetic and electric fields. In the design of fluorescent probes, fluorophores commonly used are rhodamine, coumarin, and so on. In the selection of these types of materials, rhodamine has the highest fluorescence quantum yield, which is cheap and easy to obtain, and can even be seen by the naked eye, and has unique advantages such as obvious color change of the target detection object. Therefore, rhodamine was selected as fluorophore in this article to prepare the fluorescence probe for detecting metal ions in the environment. In this article, the mercury ion fluorescence system of rhodamine B derivatives was first constructed and then based on its UV and fluorescence absorption in the addition of metallic mercury. An absorption peak centered at 558 nm is obtained in the UV-Vis absorption spectrum. Peak centered at 583 nm is obtained in the fluorescence spectrum, and all of the above indicate that the mercury ion fluorescence system of rhodamine B derivatives has been constructed. Detection of the response of rhodamine B derivatives to mercury and other metal ions by fluorescence spectroscopy resulted at 583 nm, while other ions showed little response and did not affect the detection of mercury ions. By changing the concentration of Hg^{2+}, the whole UV-Vis and fluorescence titration spectra of the ligand were changed. It was found that the peak position of the spectra did not change, but the peak intensity changed. The results show that the rhodamine B derivative probe molecule has a good selectivity only for metallic mercury ions and that metallic mercury ions have a good selectivity. The maximum fluorescence intensity is reached at the molar concentration ratio of 1:1, which is the best binding ratio of mercury ions to the probe.

Therefore, the treatment methods of mercury-containing wastewater mainly include chemical precipitation, adsorption, ion exchange, and ultrafiltration. At present, chemical precipitation method is mostly used to treat mercury-containing wastewater in industry, while other methods are still in the stage of experimental research, or the treatment cost is high, so it is difficult to popularize and apply. Therefore, adsorption, ion exchange, and ultrafiltration methods should be used.

5 Conclusions

In addition, the existence of harmful substances in oil paints, such as mercury and lead metal ions, is very

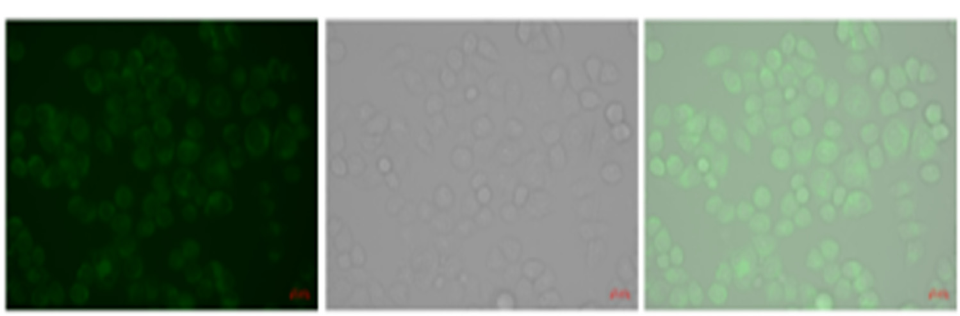

Figure 9: Cell fluorescence imaging of the probe.

harmful to the human body. In this article, rhodamine B RH-DCP probe was designed for the determination of mercury ions in titanium dioxide and zinc white of oil paints. The probe can be used to detect mercury ions in titanium dioxide and zinc white of oil paints in environmental water samples.

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Author contributions: Zhankun Wang: writing – original draft, writing – review and editing, methodology, formal analysis; Yanqiu Hu: writing – original draft, formal analysis, visualization, project administration; Xiaoxuan Zhou: data analysis; and Yuguang Lv: resources.

Conflict of interest: Authors state no conflict of interest

Data availability statement: The datasets generated during and analyzed during the current study are available from the corresponding author on reasonable request.

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