Novel Colorimetric Method for Simultaneous Detection and Identification of Multimetal Ions in Water: Sensitivity, Selectivity, and Recognition Mechanism

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Supporting Information

ABSTRACT: Accurate recognition and speciation analysis of heavy-metal ions in complex hydrological environments is always a serious challenge. In this work, we proposed a small-molecule-based ultrasensitive colorimetric detection strategy and successfully applied it to the accurate detection of Fe²⁺, Fe³⁺, Co²⁺, and Hg²⁺ in groundwater through the specific recognition of multiple ligands of different metal ions. The detection limits for Hg²⁺, Co²⁺, Fe²⁺, and Fe³⁺ are calculated to be 6.51, 0.34, 0.49, and 1.01 ppb, respectively, which are far below the drinking water standards and superior to most of the reported colorimetric sensors. Remarkably, the speciation analysis of Fe²⁺/Fe³⁺ also has been successfully realized by a one-step method without complex pretreatment. The speciation and concentration of Fe²⁺ and Fe³⁺ in actual water samples can be accurately identified and monitored. In addition, as an attempt of visual onsite detection, we have developed a simple test strip, which has been applied to visual monitoring of four metal ions with the detection limit estimated by the naked eye to be as low as ppb level. This proposed colorimetric method realizes the rapid, sensitive, and portable multiple metal ions recognition and Fe²⁺/Fe³⁺ speciation analysis, displaying great potential for onsite rapid water quality analysis.

1. INTRODUCTION

Large amounts of toxic and carcinogenic heavy metal ions have been released into the environment in recent years due to the accelerated industrial and agricultural development.¹⁻³ The cross-contamination of heavy metals, which contains multiple or even different speciations of toxic heavy metal ions, is also increasingly common in the hydrological environments,⁴⁻⁵ posing a serious threat to ecological environments and organisms.⁶⁻⁷ Therefore, accurate identification and determination of heavy metal ions and their speciations are crucial. However, the complex hydrological environment makes it a big challenge to accurately detect and assess the contamination of groundwater.⁵⁻⁹

The existing analysis techniques such as atomic absorption, emission, and mass spectrosopies are based on field sampling and laboratory testing modes,¹⁰⁻¹² which are complicated and time consuming, and impose strict demands on the preservation and transportation of sensitive water samples. Moreover, most of the detection techniques can only realize the measurement of the total content of metal ions, whereas speciation analysis requires verbose pretreatments such as oxidation, reduction, or addition of additives.¹³⁻¹⁶ To develop a novel detection technology for rapid, simple, and portable onsite multiple metal ions recognition and polyvalent metal speciation analysis is urgently needed. In this context, colorimetric methods have emerged as an alternative to spectroscopy-based methods because of the convenient operation, low cost, and quick responses.¹⁷⁻²⁰ The colorimetric detection of metal ions can be clearly observed by naked eyes or monitored using a portable UV–vis spectrophotometer, without resorting to cumbersome instrumental analysis.²¹⁻²⁳ In particular, the colorimetric probe of small molecules aroused more interest because it contains multiple recognition sites and has the potential to recognize multimetal ions simultaneously.

Herein, we proposed a small-molecule-based ultrasensitive colorimetric detection strategy and successfully realized the accurate detection of Fe²⁺, Fe³⁺, Co²⁺, and Hg²⁺ in groundwater through the specific recognition of multiple ligands for different metal ions. The obtained chemosensors showed excellent stability in 100% aqueous solution and displayed different absorption spectral signals and significant color differences for four hard-to-distinguish metal ions. The detection limits for Hg²⁺, Co²⁺, Fe²⁺, and Fe³⁺ are calculated...
to be 6.51, 0.34, 0.49, and 1.01 ppb, respectively, which are far below the standards in drinking water recommended by World Health Organization (WHO) and superior to most of the reported colorimetric sensors. Remarkably, the colorimetric sensors have been successfully applied to the speciation analysis of Fe²⁺/Fe³⁺ through a one-step method without complex pretreatment, which can accurately identify and monitor the speciation and concentration of Fe²⁺ and Fe³⁺ in actual water samples. In addition, as an attempt of visual field detection, we have developed a simple test strip, which has been successfully applied to visual monitoring of four metal ions with the detection limit estimated by the naked eye to be as low as ppb level. This proposed colorimetric method realizes the rapid, sensitive, and portable multiple metal ions recognition and Fe²⁺/Fe³⁺ speciation analysis, displaying great potential for onsite rapid water quality analysis.

2. RESULTS AND DISCUSSION

2.1. Synthesis of Tpy-QL and Tpy-BZ. Efficient detection of multiple metal ions means that efficient ligands are required. Terpyridine (Tpy) is considered as a good candidate because it contains three strongly chelating N elements. In addition, terpyridine possesses a typical conjugated system that has great potential to cause fluorescence or absorption spectrum changes and even induce significant color changes when coupling with metal ions, which is of great significance for visual monitoring.

However, the unsatisfactory water solubility limits its further application. We herein introduce hydrophilic groups quinolinium iodide (QL) and benzothiazolium iodide (BZ) to terpyridine backbone to improve hydrophilicity. The synthesis procedures of terpyridine derivatives Tpy-QL and Tpy-BZ are outlined in Scheme 1. All products were purified by column chromatography and then characterized by NMR and high-resolution mass spectrum (HRMS), from which satisfactory data were obtained corresponding to their molecular structures.

Figure 1. Absorption spectra of (a) Tpy-QL and (b) Tpy-BZ (10 μM) in 100% water solution (phosphate buffer solution (PBS) buffer, 10 mM, pH = 7.0) in the presence of different metal ions (3 equiv). Inset: (up) color patterns of the solutions using (a) Tpy-QL and (b) Tpy-BZ for different metal ions and (below) digitalized color pattern corresponding to above.
metal ions were completely different, so were the color changes.

Next, we focused on the changes in absorption spectra of Hg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Fe$^{3+}$ after binding to Tpy-BZ and Tpy-QL. As depicted in Figure 2a, the bands at 282 and 354 nm gradually decreased and finally the band at 282 nm vanished with the addition of Hg$^{2+}$. Meanwhile, the decrease of band at 354 nm was accompanied by a significant red shift from 354 to 409 nm. Accordingly, an obvious color change from colorless to pale yellow was observed. For the titration of Co$^{2+}$, the band at 282 nm was almost unchanged and the band at 354 nm was slightly enhanced, whereas a new band at 520 nm formed and developed, which led to significant color change from colorless to pink. Unlike Co$^{2+}$, this newly emerging absorption band was transferred to 607 nm when Fe$^{2+}$ ions were added and sharply enhanced as the concentration of Fe$^{2+}$ increased. Furthermore, the color quickly turned into blue. Interestingly, when Fe$^{3+}$ was introduced into Tpy-QL solution, the phenomenon was also different from that of Fe$^{2+}$. As shown in Figure 2d, in the presence of Fe$^{3+}$, the band at 607 nm was slightly blue-shifted to 598 nm and the intensity was reduced to half. Meanwhile, an inconspicuous band gradually appeared at 488 nm as the Fe$^{3+}$ concentration increased. Undoubtedly, such a phenomenon that one chemosensor exhibits completely different spectral change and colors than multiple metal ions is extremely rare, which can be used for colorimetric detection of multiple metal ions. Moreover, similar results that exhibited completely different absorption bands and color changes for Hg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Fe$^{3+}$ could be observed when investigating Tpy-BZ (Figure S1). We also carefully studied the stability of Tpy-QL and Tpy-BZ after the addition of excess metal ion. As shown in Figure S2, the absorption intensities of Tpy-QL and Tpy-BZ were quite stable and almost no changes were observed within 150 min. This result indicated that Tpy-QL and Tpy-BZ had good stability in aqueous solution and met the detection requirements.

To assess the sensitivity, different concentrations of Hg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Fe$^{3+}$ were added to the Tpy-QL solution (10 μM). As shown in Figure S3, good linear relationships between the absorbance intensity and the specified concentration range were obtained. The corresponding detection limits (LOD = 3σ/s) were also calculated to be 32.56 nM (Hg$^{2+}$), 5.89 nM (Co$^{2+}$), 8.75 nM (Fe$^{2+}$), and 17.89 nM (Fe$^{3+}$), which were much lower than the majority of the reported colorimetric sensor (Tables S1–S4). The detection performance of Tpy-BZ was also analyzed (Figure S4), and the detection limits calculated by the same method were 27.69 nM (Hg$^{2+}$), 4.81 nM (Co$^{2+}$), 5.58 nM (Fe$^{2+}$), and 24.73 nM (Fe$^{3+}$), which were basically consistent with that for Tpy-QL. Such low detection limits and distinct color changes promise their practical application for detecting Hg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Fe$^{3+}$ in water.

The colorimetric sensors not only exhibited excellent sensitivity to Hg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Fe$^{3+}$ but also displayed good selectivity. Take Tpy-QL as an example, as shown in Figure 3, it only showed distinct differential absorption signal for Hg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Fe$^{3+}$ but no change for other metal ions, showing good selectivity. The interference tests were subsequently operated by adding corresponding ions to the probe solution containing the interference cations. The results indicated that signal recovery of Hg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, or Fe$^{3+}$ was not affected by the coexisting metal ions or anions.

The Job’s plot analysis was executed to investigate the reaction ratio between sensors and metal ions. The measured absorbance intensity reached a maximum when the molar fraction of ([M$^{n+}$]/([M$^{n+}$] + [Tpy-QL])) was approximately 0.33, suggesting that Tpy-QL reacted with Hg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Fe$^{3+}$ in 2:1 stoichiometry (Figure S5). Further, the binding affinity of Tpy-QL and Tpy-BZ for Hg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Fe$^{3+}$ was estimated from the Benesi–Hildebrand plots. By using the linear fitting of absorbance titration data with 1:2 binding model (Figure S6), the association constants ($K_a$) of Tpy-QL for four metal ions were estimated to be 2.89 × 10$^7$ M$^{-1/2}$ (Hg$^{2+}$), 3.12 × 10$^5$ M$^{-1/2}$ (Co$^{2+}$), 3.31 × 10$^4$ M$^{-1/2}$ (Fe$^{3+}$), and

Figure 2. UV−vis titrations spectra of Tpy-QL (10 μM) in water (PBS buffer, 10 mM, pH = 7.0) in the presence of various concentrations of (a) Hg$^{2+}$, (b) Co$^{2+}$, (c) Fe$^{2+}$, and (d) Fe$^{3+}$. The red line represents the spectrum of free Tpy-QL in water and blue line represents the spectrum after reaction saturation. The inset photographs were taken after the Tpy-QL and metal ions were completely reacted.
Interestingly, simultaneously detecting Fe²⁺ and Fe³⁺ in samples are rarely reported and only total concentration or speciation analysis of Fe²⁺/Fe³⁺ can be ascertained by S₉₉₈/S₄₈₈, thus realizing the speciation analysis of Fe²⁺/Fe³⁺.

2.4. Mechanism Studies. We monitored the reactions of Tpy-QL and Tpy-BZ with metal ions by ¹H NMR titration experiments in DMSO-d₆. However, we failed to obtain the ¹H NMR spectra of Tpy-QL-Fe²⁺, Tpy-QL-Fe³⁺, and Tpy-QL-Co²⁺ due to the strong interference of lone electron in Fe²⁺, Fe³⁺, and Co²⁺ compounds, and only the ¹H NMR spectra of Tpy-QL-Hg²⁺ was available. As shown in Figure 6, all pyridine protons on Tpy-CHO, Tpy-BZ, and Tpy-QL exhibited varying degrees of up-shift after reaction with 5 equiv of Hg²⁺, whereas the aldehyde proton or quinoline ring protons remained unchanged. This result indicated the electron density on the pyridine rings was reduced after reaction, implying all pyridine rings were involved in the reaction and the electrons may flow to the metal moiety.

To get a deep insight into the binding mode, the geometry optimizations and electronic calculations for several possible complex structures of Tpy-QL and metal ions with a 2:1 stoichiometry were performed using the B3LYP functional and Gaussian 09 package. The calculated optimized structures indicated that the binding sites of Tpy-QL with metal ions were the pyridine nitrogen. As depicted in Figure 7a, each Hg²⁺ ion chelated with six pyridine nitrogen of two Tpy-QL molecules to form a stable six-coordinate structure. The two Tpy-QL molecules were almost perpendicular to each other, with an angle of 91.28°, the length of the Hg–N bonds was 1.97 Å, and the angle of the coordinate bond was 81.55°. Similar calculated results could be obtained from Tpy-QL-Fe²⁺, Tpy-QL-Fe³⁺, and Tpy-QL-Co²⁺ (Figure S8), and the structural parameters were all within the reasonable range of stable structures (Table S5). These results implied the difference in absorption spectra result in diverse chemical properties of the metal ions, rather than the differences in the chelating mode.

The electron transformations of Tpy-QL before and after reaction with Hg²⁺, Co²⁺, Fe²⁺, and Fe³⁺ were investigated using Multiwfn package. As displayed in Figure 7b, the blue region indicated a decrease in electron density after the reaction, meaning that electrons were contributed. The purple area indicated an increase in electron density, implying an
inflow of electrons. Obviously, the electrons on the pyridine ring, especially on the N atom, significantly flowed to the metal center during the reaction, whereas the electron density on the quinoline moiety was almost unchanged, being highly consistent with the $^1$H NMR experimental phenomenon. In addition, the two-dimensional electron density color-filled maps of Tpy-QL-Hg$^{2+}$ could provide more evidence that the electron density of terpyridine moiety decreased significantly after binding to mercury ions (Figure 8).

### 2.5. Analytical Applications in Real Water Samples.

Considering the excellent stability, selectivity, and sensitivity of Tpy-QL and Tpy-BZ to Hg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Fe$^{3+}$, their detection performances in the natural water samples are expected. Herein, the analysis of natural water samples and standard addition recovery experiments were carried out to verify the practicability of the proposed method. As depicted in Table 1, the found values of four metal ions were consistent with the spiked values and agreed with the inductively coupled plasma-optical emission spectroscopy (ICP-AES) results, demonstrating the validity of the sensors to the natural water samples. Next, we carefully investigated the feasibility of the sensors for the speciation analysis of Fe$^{2+}$/Fe$^{3+}$ by adding different molar ratios of Fe$^{2+}$ and Fe$^{3+}$ (total concentration was 100 ppb) into different natural water samples. As shown in Table 2, the found values were all consistent with the added values in tap water, Yangtze River water, and Jianghan Plain groundwater samples. The sum of Fe$^{2+}$ and Fe$^{3+}$ concentrations measured by the proposed colorimetric method was in good agreement with the ICP-AES results, and the standard deviation was within the error tolerance. This result showed that the presented method had the ability to simultaneously recognize Fe$^{3+}$ and Fe$^{2+}$ in Fe$^{3+}$/Fe$^{2+}$ mixtures, displaying the potential for speciation analysis of Fe$^{2+}$/Fe$^{3+}$ in actual samples.

![Figure 5](image_url)

Figure 5. (a) Plot of $S_{598} + S_{488}$ vs the total iron concentrations ([Fe$^{2+}$] + [Fe$^{3+}$]). Inset: linear fitting curve of $S_{598} + S_{488}$ with respect to the total iron concentrations in the range of 0–8 μM. (b) Plot of peak area ratio $S_{598}/S_{488}$ as a function of the Fe$^{2+}$ percentage content.

![Figure 6](image_url)

Figure 6. $^1$H NMR spectra of Tpy-CHO, Tpy-BZ, and Tpy-QL in DMSO-d$_6$ before (a, c, e) and after (b, d, f) the addition of 5 equiv of Hg$^{2+}$.

![Figure 7](image_url)

Figure 7. (a) Different observation view of density functional theory (DFT) calculated optimization Tpy-QL-Hg$^{2+}$ structure. (b) Corresponding electron density changes before and after the reaction of Tpy-QL with Hg$^{2+}$. The blue area indicates decrease in electron density after the reaction, whereas the purple area indicates increase in electron density.
Onsite visual monitoring is of great significance for water quality analysis. Here, as an attempt, we developed a simple test strip for visual detection of metal ions by immersing ordinary filter paper into the water mixtures of poly(vinyl alcohol) and Tpy-QL. As shown in Figure 9, the test strips displayed different colors for Hg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Fe$^{3+}$, and the color deepened as the concentration increases. It should be noted that this test strip is very stable and can be stable for at least 2 weeks. The detection limits observed by the naked eye were estimated to be 10, 25, 10, and 200 ppb for Fe$^{2+}$, Fe$^{3+}$, ...
Co²⁺, and Hg²⁺ with a stoichiometric ratio of 2:1, exhibiting Fe³⁺, Co²⁺, and Hg²⁺ detection in groundwater. Tpy-QL and detection limits for Hg²⁺, Co²⁺, Fe²⁺, and Fe³⁺ were calculated from Perkin Elmer Lambda 35 spectrophotometer. The absorbance spectra of Tpy-QL and Tpy-BZ were collected and 1H NMR (Bruker Avance 400 MHz NMR spectrometer).

The structure of obtained organic products was characterized by HRMS (GCT premier CAB048 mass spectrometer) and 1H NMR (Bruker Avance 400 MHz NMR spectrometer). The absorbance spectra of Tpy-QL and Tpy-BZ were collected by silica gel column chromatography to get faint yellow Tpy-BZ (66.8 mg, yield 61%). Tpy-QL was obtained by a similar synthetic procedure with a yield of 56% (60.7 mg). The characterization data are provided in Figures S9–S16.

4.4. Application in Natural Water Samples. The detection effect of the proposed colorimetric method for Fe²⁺, Fe³⁺, Co²⁺, and Hg²⁺ were carefully investigated in natural water by spiked different amounts of standard sample. The natural water samples were collected from tap water, Yangtze River water, and Jianghan Plain groundwater. The obtained samples were first filtered to remove solid impurities and then neutralized with PBS buffer solvent (pH = 7.0). For analysis, the blank natural water samples were first analyzed by the proposed colorimetric method. Then, different amounts of Fe²⁺, Fe³⁺, Co²⁺, and Hg²⁺ were added into three natural water samples, making the metal ion concentration in the water samples to be 30, 100, and 300 ppb, respectively. The prepared samples were tested immediately at room temperature using the proposed colorimetric method, and each concentration was done in triplicate. The obtained results were compared with the ICP-AES results.

The spectrall analysis of Fe²⁺/Fe³⁺ was operated in natural water samples. For analysis, different concentrations of Fe²⁺ and Fe³⁺ (20/80, 50/50, 80/20 ppb) were first added to the actual water samples, the total concentration of Fe²⁺ + Fe³⁺ was kept at 100 ppb, and then tested by the proposed method. Each concentration was measured in triplicate and verified by ICP-AES.

4.5. Preparation of Test Strips for Visual Detection. The test strips for Fe²⁺, Fe³⁺, Co²⁺, and Hg²⁺ were prepared based on the reported method with minor modifications. One gram of PVA was first introduced into 20 mL of water and then stirred vigorously under heating until completely dissolved. After cooling to room temperature, 1 mL of Tpy-QL water solution (5 mM) was added into 5 mL of PVA solution and stirred until it a clear solution was obtained. Finally, the mixtures of Tpy-QL and PVA were evenly smeared on the surface of the common filter paper and dried at room temperature. For the visual detection of metal ions, different concentrations of Fe²⁺, Fe³⁺, Co²⁺, and Hg²⁺ were prepared in 10 mL beaker and then the obtained strips were immersed in different metal ion solutions for 30 seconds.

4.6. Theoretical Calculation. All of the theoretical calculations were carried out using the Gaussian 09 package. The C, N, and H atoms were described by the hybrid exchange–correlation functional B3LYP. 6-31G* basis sets, and the metal atoms were described by Lanl2dz basis sets. All
of the electron density analyses were performed using the Multiwfn package.

**ASSOCIATED CONTENT**

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00312.

Titrations spectra of Tpy-BZ, Job’s plot, Benesi-Hildebrand plot, detection limits, DFT calculation, structural parameters of theoretical calculation, $^1$H NMR, and HRMS characterizations (PDF)

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Natural Science Foundation of China (Nos. 41878633) and the Foundation for Innovative Research Groups of the National Natural Science Foundation of China (No. 41521001) and the “Fundamental Research Funds for the Central Universities”.

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