

两种四足席夫碱对环境水样中 Fe(III)离子的比色识别

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摘要: 使用季戊四胺与水杨醛、邻香兰素缩合反应得到了两种席夫碱化合物 **1** 和 **2**。化合物 **1** 和 **2** 均可用于不同水样 Fe(II)和 Fe(III)离子的比色识别。通过光谱滴定及液质谱联用等方法研究了化合物 **1** 和 **2** 与 Fe(III)的识别作用, 化合物 **1** 和 **2** 与 Fe(III)离子的配位比为 1:1, 对 Fe(III)铁离子的检出限分别为 0.19 和 0.21 $\mu\text{mol}\cdot\text{L}^{-1}$, 低于世界卫生组织饮用水检出标准(5 $\mu\text{mol}\cdot\text{L}^{-1}$), 具有一定的实用价值。

关键词: 席夫碱; 比色传感器; 铁离子

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Two Tetrapodal Schiff Bases Acting as Colorimetric Sensors for Iron in Environmental Water Samples

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Abstract: Two colorimetric sensors, derived from pentaerythrityltetramine and salicylaldehyde (**1**) or *o*-vanillin (**2**), had been synthesized. Both sensors showed selective colorimetric sensing ability for Fe(II) and Fe(III) by changing color from light yellow to either orange or purple when immersed in water samples. The sensors coordinated to Fe(III) with 1:1 stoichiometry, as has been confirmed from the results of LC-MS spectrometry and UV-Vis spectrum titration. The detection limits of sensors **1** (0.19 $\mu\text{mol}\cdot\text{L}^{-1}$) and **2** (0.21 $\mu\text{mol}\cdot\text{L}^{-1}$) are lower than the WHO guideline (5 $\mu\text{mol}\cdot\text{L}^{-1}$) in drinking water.

Keywords: Schiff base; colorimetric sensor; iron

0 Introduction

According to recent research, the design and production of chemosensors for the detection of metal ions in aqueous solutions is an important area to develop, particularly with regards to sensors for the

detection of heavy and transition metal cations^[1-7]. Along with other transition metal ions, iron is an important element in living systems, as it plays crucial roles in the transport and storage of oxygen^[8-9]. Iron is important because of its redox capacity in living systems, which can have a significant effect on

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homeostasis^[10-11]. Iron can also promote development, increase resistance to disease, regulate tissue respiration, and prevent fatigue^[12-13]. Thus, to design chemosensors for the detection of Fe(II) and Fe(III) in an aqueous medium is of great significance.

Many analytical techniques have been used to determine the content of metal ions, such as plasma atomic emission spectrometry^[14], atomic absorption spectroscopy^[15], and fluorescence^[16-17], electro-chemical^[18], gravimetric^[19-20], and chromatographic^[21] methods. Other analytical techniques are described in^[22-23]. Most of these methods require the use of sophisticated equipment, multi-step sample preparation, and trained operators, all of which lead to high expenses. Colorimetric sensors present the advantage of having a low cost and of being easy to use. No expensive equipment is required and the analyte is detectable by the naked eye.

Schiff bases are good ligands for metal ions, with which they can form coordinate bonds. This characteristic has resulted in their extensive use in the production of sensors. The reported chemosensors for Fe(II) and Fe(III) in aqueous solution are rare^[24-35]. In the present work, two tetrapodal Schiff bases with N and O donor atoms on the four pendant branches have been investigated to determine their ability in detecting the presence of common metal cations. Both **1** and **2** showed selective colorimetric sensing ability for Fe(II) and Fe(III) by changing color from light yellow to either orange or purple when immersed in the water samples. The detection limits of sensor **1** ($0.19 \mu\text{mol} \cdot \text{L}^{-1}$) and **2** ($0.21 \mu\text{mol} \cdot \text{L}^{-1}$) are lower than the WHO guideline ($5 \mu\text{mol} \cdot \text{L}^{-1}$) for drinking water. The determination of the presence of Fe(III) in a variety of environmental water samples was investigated.

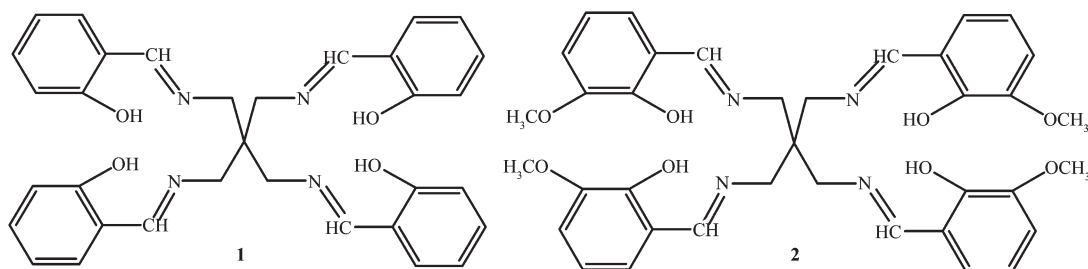


Fig.1 Structures of sensors **1** and **2**

1 Experimental

1.1 Materials and instrumentation

Commercially available metal salts were purchased from Aldrich and Alfa Aesar Chemical Co., Ltd. The solutions of metal ions were prepared from chloride or nitrate salts of Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Mn^{2+} , Cr^{3+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , K^{+} , Ca^{2+} and Mg^{2+} . Crystal structure was determined on a Bruker Apex 2 diffractometer. ^1H NMR and ^{13}C NMR (solvent CDCl_3 or DMSO-d_6) spectral analyses were performed on a JEOL-ECX 500 NMR spectrometer at room temperature using TMS as an internal standard. LC-MS was determined on an Agilent LC/MSD Trap based on infusion methods. UV-Vis absorption spectra were recorded on a UV-1800 spectrophotometer (Beijing General Instrument Co., China) in a 1 cm quartz cell.

1.2 Preparation of Schiff base

The Schiff bases **1** and **2** were prepared according to our previously described procedure^[36-37].

1.3 Visual sensing of metal ions and UV-Vis study

Either sensor **1** or **2** (0.005 mmol) was dissolved in DMSO (Dimethyl sulfoxide; 50 mL). Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Mn^{2+} , Cr^{3+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , K^{+} , Ca^{2+} and Mg^{2+} (0.05 mmol) were dissolved in double-distilled water (50 mL), containing 1 mL of solution of either sensor **1** or **2**; 0.5 mL of each metal salt solution were transferred to a 10 mL volumetric flask and diluted to the final volume of 10 mL with DMSO and double-distilled water to make the final solution ($1:5$, $n_{\text{sensor}}/n_{\text{metal}}$ cations and $1:9$, $V_{\text{DMSO}}/V_{\text{H}_2\text{O}}$). Significant color changes (from light yellow to orange for **1**, to purple for **2**) could be observed by the naked eye. After mixing for a few minutes, UV-Vis spectra were taken

at room temperature.

1.4 Molar ratio method measurement of sensor 1 or 2 with Fe³⁺

Either sensor **1** or **2** (0.05 mmol) was dissolved in DMSO (50 mL), Fe(NO₃)₃·9H₂O (20.2 mg, 0.05 mmol) was dissolved in double-distilled water (50 mL); 0.1~2.0 mL of Fe(NO₃)₃ solution were transferred to a 10 mL volumetric flask, 1 mL of the solution of either sensor **1** or **2** was added subsequently, and diluted to 10 mL with DMSO and double-distilled water to make the final solution (1:9, $V_{\text{DMSO}}/V_{\text{H}_2\text{O}}$). After mixing for a few minutes, UV-Vis spectra were taken at room temperature.

1.5 Job plot measurement

Either sensor **1** or **2** (0.05 mmol) was dissolved in DMSO (50 mL); 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 mL of the solution of either sensor **1** or **2** were transferred to a 10 mL volumetric flask. Fe(NO₃)₃·9H₂O (20.2 mg, 0.05 mmol) was dissolved in double-distilled water (50 mL); 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1 mL of the Fe(NO₃)₃ solution were added to each 10 mL volumetric flasks and diluted to 10 mL with DMSO and double-distilled water to make the final solution (1:9, $V_{\text{DMSO}}/V_{\text{H}_2\text{O}}$). After mixing for a few minutes, UV-Vis spectra were taken at room temperature.

1.6 Competitive experiments

Sensor **1** or **2** (0.05 mmol) was dissolved in DMSO (50 mL), and all the metal ions (0.05 mmol) were dissolved in double-distilled water (50 mL); 1.0 mL of the solution of either sensor **1** or **2** solution was transferred to a 10 mL volumetric flask; 1.0 mL of Fe(NO₃)₃ solution and 1.0 mL of each other metal solution were added, then diluted to 10 mL with DMSO and double-distilled water to make the final solution (1:1:1, $n_{\text{sensor}}:n_{\text{Fe}^{3+}}:n_{\text{other metal cations}}$; 1:9, $V_{\text{DMSO}}/V_{\text{H}_2\text{O}}$). After mixing for a few minutes, UV-Vis spectra were taken at room temperature.

1.7 Determination of Fe³⁺ in environmental water samples

Environmental water samples were collected from a nearby river, water company, and spring water

company. One milliliter of 1.0 mmol·L⁻¹ Fe(NO₃)₃ solution was added to 8 mL of each environmental water sample using 10 mL volumetric flasks. Following this step, 1 mL of the 1.0 mmol·L⁻¹ DMSO solution of either sensor **1** or **2** was added in each sample; 9 mL of each environmental water sample was mixed with 1 mL of the 1.0 mmol·L⁻¹ DMSO solution of sensor **1** or **2** to carry out contrast experiments. The color changes of the artificial Fe(III) containing environmental water samples could be observed easily.

2 Results and discussion

2.1 Detection properties of sensor 1 and 2 toward Fe²⁺ and Fe³⁺

We examined the detection abilities of sensors **1** and **2** in a series of metal ions such as Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Mn²⁺, Cr³⁺, Cd²⁺, Pb²⁺, Hg²⁺, K⁺, Ca²⁺ and Mg²⁺ in a DMSO/H₂O (1:9, V/V) solution. Sensor **1** showed a significant color change, from light yellow to orange, in the presence of Fe²⁺ or Fe³⁺, while other metals caused no color change under identical conditions (Fig.2a). Sensor **2** also showed a significant color change, from light yellow to purple, for Fe²⁺ or Fe³⁺ (Fig.2b). Fig.2c shows new absorption peaks at 482 nm and 488 nm in the presence of Fe²⁺ and Fe³⁺, respectively, for sensor **1**; Fig.2d shows new absorption peaks at 514 and 519 nm in the presence of Fe²⁺ and Fe³⁺, respectively, for sensor **2**. These results are consistent with the changes of color in the Fe²⁺ and Fe³⁺ solution.

The binding properties of sensors **1** and **2** with Fe³⁺ were studied by UV-Vis titration. Upon the gradual addition of Fe³⁺ (0.0~1.0 equiv) to a solution of either sensor **1** or **2**, new absorbance peaks appeared. For sensor **1**, the new peak formed at 488 nm and kept increasing with a clear isosbestic point at 338 nm (Fig.3a); for sensor **2**, the new peak appeared at 519 nm and kept increasing with a clear isosbestic point at 345 nm (Fig.3b). These changes in the UV-Vis spectra clearly indicated that new species formed during the titration of sensor **1** or **2** with Fe³⁺. The new peaks at 488 and 519 nm with molar extinction coefficients of 6.1×10^3 and 4.4×10^3 L·mol⁻¹·cm⁻¹,

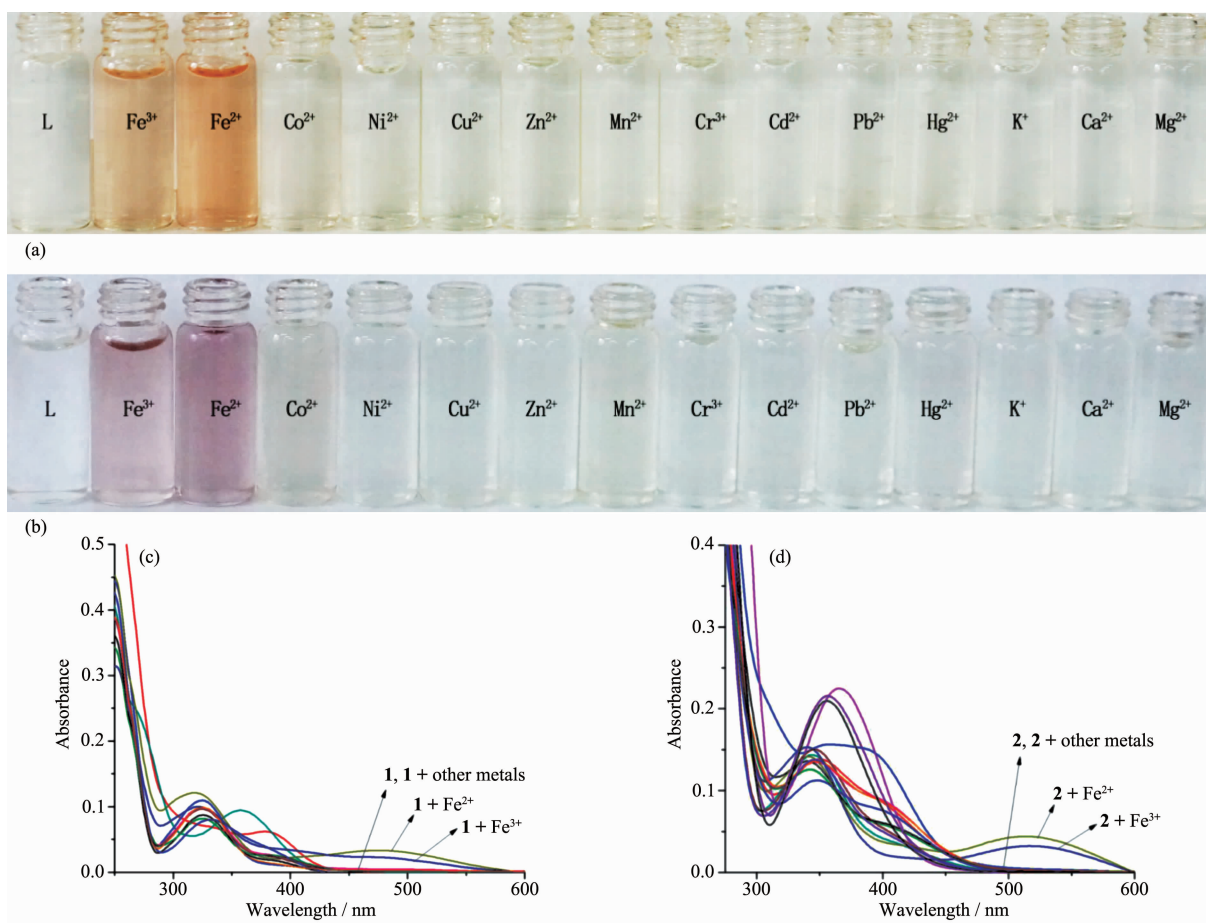
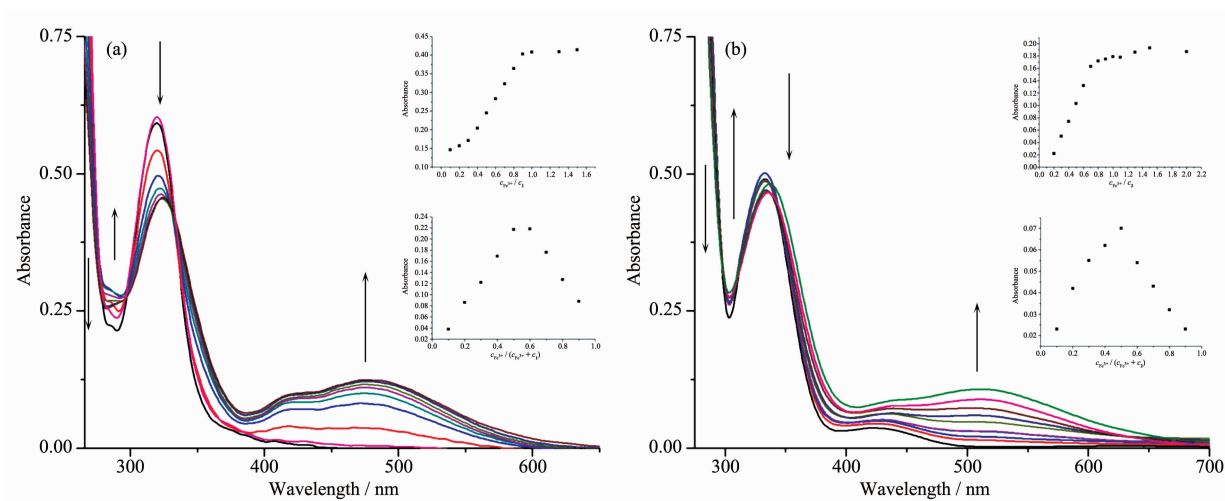


Fig.2 (a) and (b) Color changes of sensors **1** and **2** ($50 \mu\text{mol}\cdot\text{L}^{-1}$) upon addition of various metal ions (5 equiv) in DMSO/H₂O (1:9, V/V); (c) and (d) UV-Vis absorption spectra of sensors **1** and **2** ($10 \mu\text{mol}\cdot\text{L}^{-1}$) in the presence of 5 equiv of different metal ions in DMSO/H₂O (1:9, V/V)



Inset 1: Job plot of sensor **1** or **2** with Fe³⁺ in DMSO/H₂O (1:9, V/V) solution, the total concentrations of sensors **1** or **2** and Fe³⁺ were $1 \text{ mmol}\cdot\text{L}^{-1}$; Inset 2: Plot of the UV-Vis absorbance at 488 nm, 519 nm as functions of Fe³⁺ concentration for sensors **1** and **2**, respectively

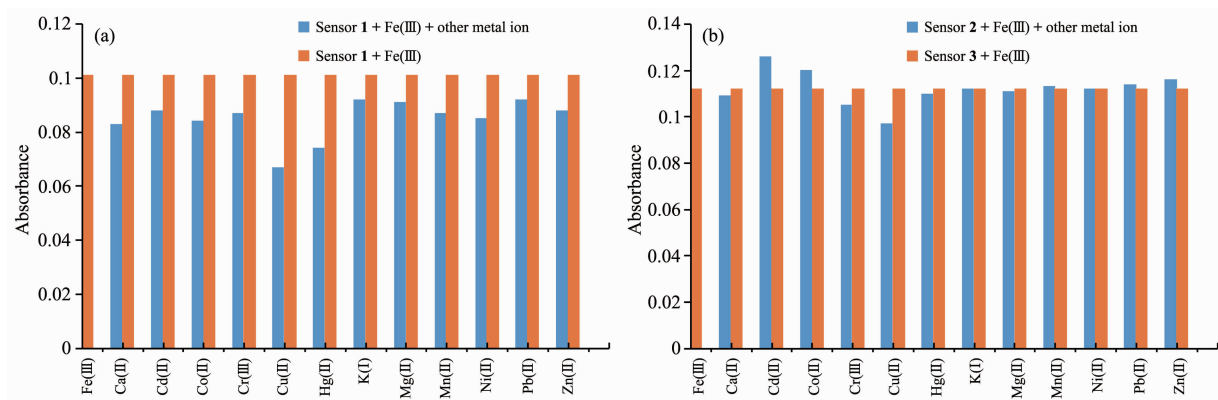
Fig.3 UV-Vis absorption spectra of sensors **1** (a) or **2** ($0.1 \text{ mmol}\cdot\text{L}^{-1}$) with gradual addition of Fe³⁺ (0~1 equiv) in DMSO/H₂O (1:9, V/V) solution

respectively, are higher than those relative to the Fe-based $d-d$ transitions. Thus, these new peaks might be attributed to metal-to-ligand charge-transfer (MLCT)^[38-39], which are responsible for the color changes of the solution.

2.2 Evaluation of selectivity

Since selectivity is an important parameter in evaluating the behavior of an optical sensor, the interference effect of common coexistent metal ions

was investigated on the detecting sensitivity of chemosensors towards Fe(III). The results reported in Fig.4a and 4b indicate that all the competing metal ions such as Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Hg^{2+} , K^+ , Mg^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} did not interfere noticeably with naked-eye detection of Fe^{3+} . These results indicate that the tested sensors can act specifically for the detection of Fe^{3+} .



Yellow bars represent the absorbance of the sensors in presence of 1 equiv. Fe(III) and blue bars represent the absorbance of **1** or **2**+Fe(III) after the subsequent addition of other metal ions; (λ_{max} =488 and 519 nm for sensors **1** and **2**, respectively)

Fig.4 Competitive selectivity of sensors **1** (a) or **2** (b) ($0.1 \text{ mmol} \cdot \text{L}^{-1}$) towards various metal ions ($0.1 \text{ mmol} \cdot \text{L}^{-1}$)

2.3 Stoichiometry and binding mode studies

The stoichiometry of metal complexes formed between the sensors and Fe^{3+} ions was determined by Job's titration method and the molar ratio method^[40]. As shown in Fig.3a and Fig.3b, the maximum values of the absorbance curves were obtained at a 0.5 molar ratio, indicating 1:1 stoichiometry of the resulting Fe(III) complexes. The molar ratio method also showed the same results for these complexes. The stoichiometries of these complexes were further confirmed by LC-MS spectrometry analysis. The positive-ion mass spectrum of the sensors upon addition of 1 equiv of Fe^{3+} showed the formation of the sensor **1**- $3\text{H}^+ + \text{Fe}^{3+}$ complex (m/z : 722.3; Calcd., 722.2) and the sensor **2**- $3\text{H}^+ + \text{Fe}^{3+}$ complex (m/z : 602.2; Calcd., 602.15) (Fig.5a and 5b, respectively). The crystal structure of sensor **1**- $3\text{H}^+ + \text{Fe}^{3+}$ complex had also been obtained in our earlier work^[36], which had clearly revealed the 1:1 stoichiometry of the Fe(III) complex (Fig.5c). In this crystal structure, the Fe(III) ion coordinated with imine nitrogen atoms

(N(1), N(2), N(3)) and phenolic oxygen atoms (O(1), O(2), O(3)) from three pendant branches of sensor **1**, located at the center of octahedral coordination sphere; meanwhile, one of the salicylaldimine pendant branches remained uncoordinated, and the phenolic OH and the imine nitrogen were intramolecularly hydrogen-bonded. Based on the UV-Vis titration, Job plot, and LC-MS analysis, as well as the crystal structure analysis, we confirmed the structures of the **1**- Fe^{3+} and **2**- Fe^{3+} complexes with 1:1 stoichiometry. In addition, the binding constants (K_a) of sensors **1** and **2** with Fe^{3+} were calculated to be equal to 1.8×10^4 and 8.5×10^4 , respectively, on the basis of Benesi-Hildebrand analysis. These values fall well within the range of $10^3 \sim 10^5$, as previously reported for other Fe(III) sensors^[2,41]. The detection limits of sensors **1** and **2** for Fe^{3+} ions were determined as 0.19 and $0.21 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$, respectively, based on the IUPAC definition ($C_{\text{DL}} = 3S_b/m$), well below the WHO guideline ($5 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$) for Fe^{3+} in drinking water. It is worth mentioning that the working

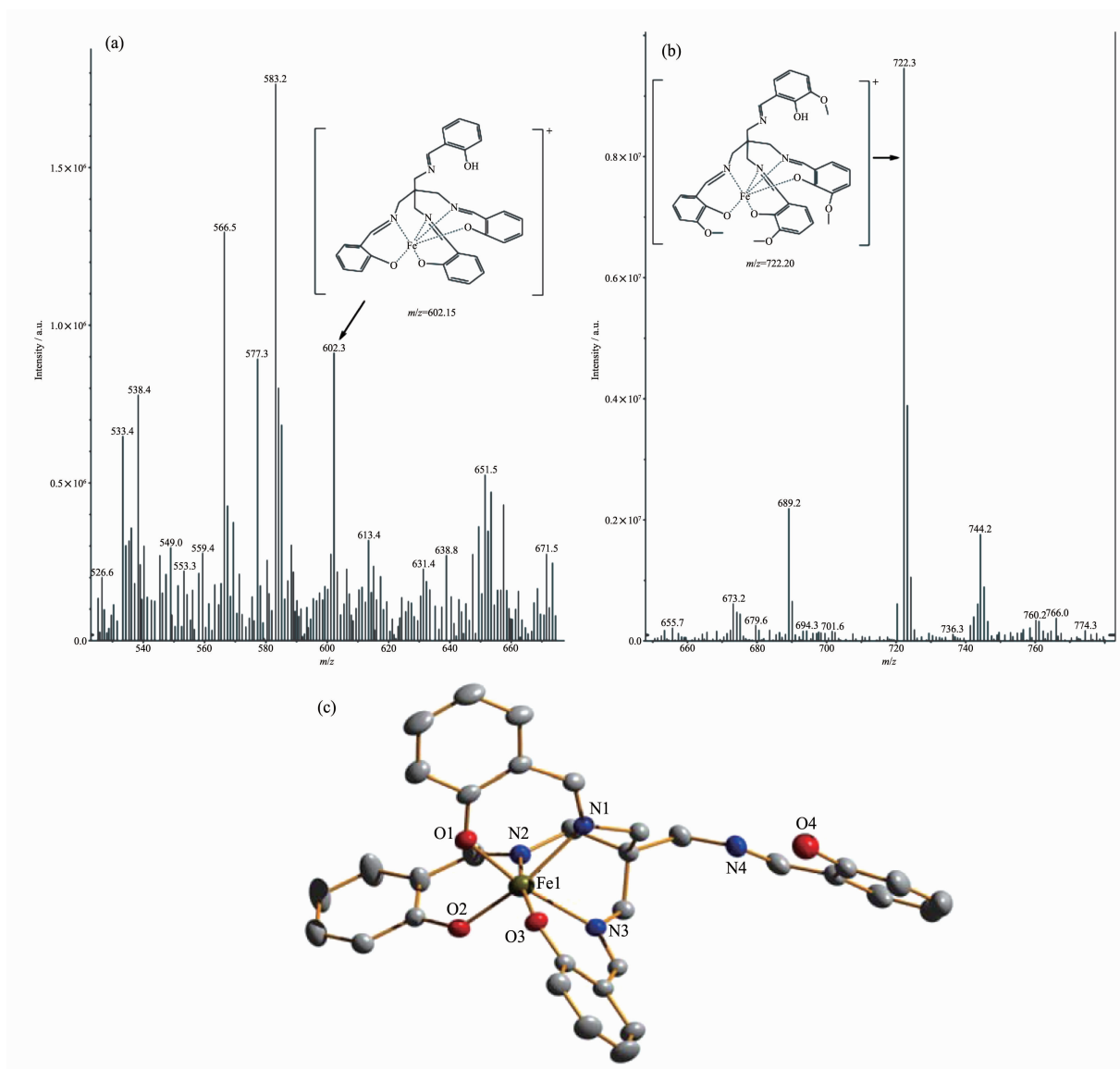


Fig.5 (a) Positive-ion electrospray ionization mass spectrum of sensor **1** ($50 \mu\text{mol}\cdot\text{L}^{-1}$) upon addition of 1 equiv. of $\text{Fe}(\text{NO}_3)_3$ in acetonitrile solution; (b) Positive-ion electrospray ionization mass spectrum of sensor **2** ($50 \mu\text{mol}\cdot\text{L}^{-1}$) upon addition of 1 equiv. of $\text{Fe}(\text{NO}_3)_3$ in acetonitrile solution; (c) Crystal structure of the sensor **1**- 3H^+ + Fe^{3+} complex

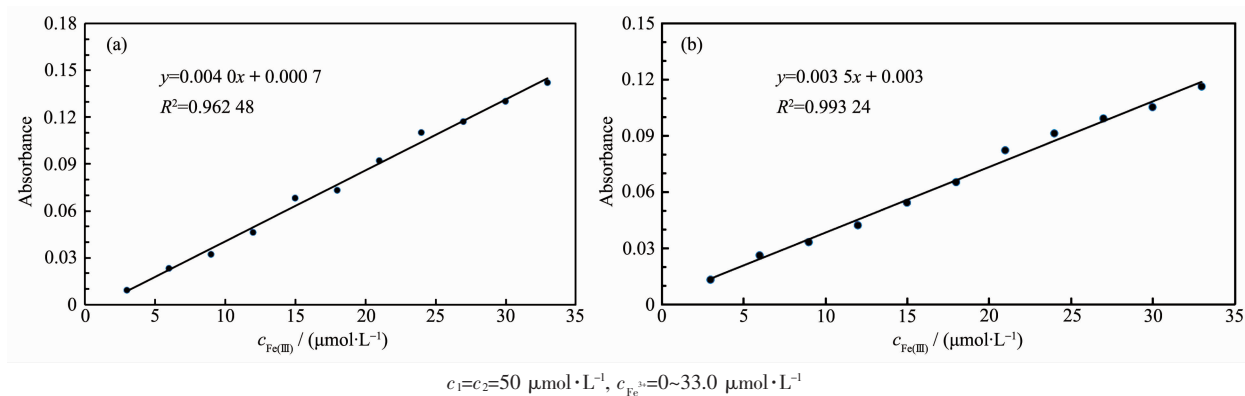


Fig.6 Absorbance at 488 and 519 nm for sensor **1** (a) and sensor **2** (b) as a function of Fe^{3+} concentration

curves for measurement of Fe^{3+} showed good linear relationships within the concentration range of $3 \sim 33 \mu\text{mol} \cdot \text{L}^{-1}$ for both sensors (Fig.6a and 6b). These results suggest that the tested sensors **1** and **2** can be adequately employed as probes for the detection of micromolar concentrations of Fe^{3+} in real water samples.

2.4 Effect of pH value

The sensitivity of the colorimetric sensor complexes (**1**- Fe^{3+} or **2**- Fe^{3+}) at different pH values was

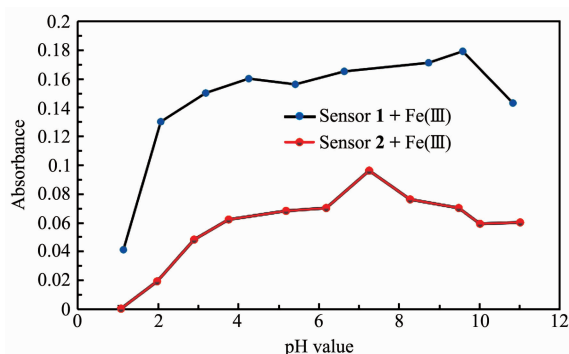


Fig.7 pH value sensitivity of Fe^{3+} detection of sensors **1** and **2**

studied in a $\text{DMSO}/\text{H}_2\text{O}$ (1/9, V/V) solution. Experiments were conducted by adjusting pH using NaOH and HCl. As depicted in Fig.7, both sensors were found to be quite effective in the neutral pH range. In an acidic medium, the absorbance of **1**- Fe^{3+} or **2**- Fe^{3+} complexes decreased due to the decomposition of the Fe(III) complexes; while in a basic medium, the absorbance decreased because of the formation of the Fe(OH)_3 colloid. These results suggest that these colorimetric sensors are suitable for application under the biologically relevant pH range of 6.0~7.6.

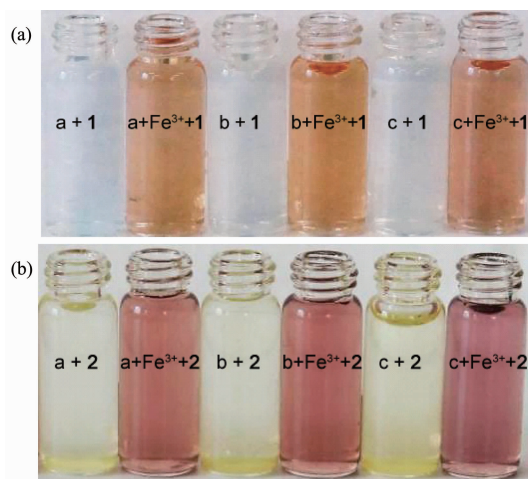
2.5 Application studies

To determine the applicability of the proposed sensors in a real-case scenario, we examined their colorimetric behavior in the detection of Fe^{3+} in different environmental water samples, under the same conditions. As shown in Fig.8a and 8b, the changes in color of the environmental water samples are clearly observable when even trace levels of Fe(III) were present. Furthermore, recovery experiments of eighteen samples were conducted at three different levels of the Fe(III)

Table 1 Determination of Fe^{3+} in water samples*

Sample	Sensor	Fe(III) added / ($\text{mmol} \cdot \text{L}^{-1}$)	Fe(III) found / ($\mu\text{mol} \cdot \text{L}^{-1}$)	Recovery / %	R.S.D (n=3) / %
River water	1 or 2	0.00	0.00	—	—
	1	8.00	7.75	96.88	1.81
	1	15.00	14.25	95.00	2.47
	1	25.00	23.96	95.85	2.86
	2	8.00	7.85	98.25	2.01
	2	15.00	14.31	95.40	2.31
	2	25.00	24.47	97.90	1.57
	2	25.00	24.47	97.90	1.57
Tap water	1 or 2	0.00	0.00	—	—
	1	8.00	7.80	97.50	1.42
	1	15.00	14.33	95.53	2.14
	1	25.00	23.55	94.21	0.51
	2	8.00	7.57	94.63	1.15
	2	15.00	13.63	90.86	2.03
	2	25.00	21.90	87.61	1.84
	2	25.00	21.90	87.61	1.84
Spring water	1 or 2	0.00	0.00	—	—
	1	8.00	7.78	97.25	1.35
	1	15.00	14.47	96.64	1.65
	1	25.00	23.63	94.54	0.14
	2	8.00	7.94	99.25	2.01
	2	15.00	15.12	100.08	1.57
	2	25.00	25.14	100.50	1.21
	2	25.00	25.14	100.50	1.21

* Sensor **1** or **2**, $50 \mu\text{mol} \cdot \text{L}^{-1}$ in $\text{DMSO}/\text{H}_2\text{O}$ (1/9, V/V) solution.



Water samples (from left to right) a: river water, b: tap water, c: spring water, the concentration of $\text{Fe}(\text{NO}_3)_3$ in each artificial $\text{Fe}(\text{III})$ containing water sample was $0.1 \text{ mmol} \cdot \text{L}^{-1}$, and the concentration of the sensor **1** or **2** was $0.1 \text{ mmol} \cdot \text{L}^{-1}$

Fig.8 Determination of Fe^{3+} in environmental water samples using sensor **1** (a) or **2** (b) as colorimetric sensors

concentration for river water, tap water and spring water, respectively, using the standard curve method^[42-44]. As shown in Table 1, the results showed satisfactory recovery and R.S.D. values for these water samples, this indicates that the sensors **1** or **2** could potentially be used for the determination of the Fe^{3+} ion in environmental water samples. Furthermore, it is well known that Fe^{2+} ion can easily be oxidated to Fe^{3+} ion when exposed to air. It is possible for the determination of the Fe^{2+} ion after its oxidation to the Fe^{3+} ion using the same procedure as described for the Fe^{3+} ion.

3 Conclusions

In summary, two colorimetric sensors were developed for the detection of Fe^{2+} and Fe^{3+} in aqueous media. They exhibited excellent selectivity towards these two ions over other metal cations commonly found in water. The 1:1 stoichiometries of the $\text{Fe}(\text{III})$ complexes have been confirmed by X-ray crystallography, LC-MS spectrometry analysis, and UV-Vis spectrum titration. The detection limits of sensor **1** ($0.19 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$) and **2** ($0.21 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$) for Fe^{3+} are far below the WHO guidelines ($5 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$). Both sensors **1** and **2** were found to be quite effective in the neutral

pH value range and showed good linear relationships within the $3 \sim 33 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$ concentration range for the measurement of Fe^{3+} . The practical applicability studies showed satisfactory recovery and R.S.D. values for the detection of Fe^{3+} ions in environmental water samples.

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