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Pattaweepaiboon, Supak
Department of Chemistry and Centre of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University

Phiromphu, Natchayapak
Department of Chemistry and Centre of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University

Kaewchangwat, Narongpol
Functional Nanomaterials and Interfaces Laboratory, National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA)

Suttisintong, Khomson
Functional Nanomaterials and Interfaces Laboratory, National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA)

他

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A spirooxazine-based chemical sensor for ferric-ion detection with the application in drinking water

Supak Pattaweepaiboon[1], Natchayapak Phiromphu[1], Narongpol Kaewchangwat[2], Khomson Suttisintong[2],
Weekit Sirisaksoontorn[1,*]

[1]Department of Chemistry and Centre of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University, Chatuchak, Bangkok, 10900 Thailand
[2]Functional Nanomaterials and Interfaces Laboratory, National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Pathum Thani, 12120 Thailand.
Corresponding author email: fsciwks@ku.ac.th

Abstract: *A solution of the spirooxazine (1.0 x 10^{-4} M) was freshly prepared in 1,4-dioxane with the subsequent addition of one equivalent solution of each relevant cation such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Sn^{2+}, Pb^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cr^{3+} and Fe^{3+} (1.0 x 10^{-4} M). The metal-ligand complexes were mainly investigated by UV-Vis spectroscopy. In the case of ferric ions, spirooxazine provides the new absorption response at 654 nm, indicating the complex formation of Fe^{3+} with spirooxazine in the open form. Meanwhile, other metal ions did not strongly bind to spirooxazine, giving rise to no absorption peak at 654 nm observed. The stoichiometry of complex was investigated via Job's method as the 1:1 ratio of spirooxazine with Fe^{3+}. The detection limit of ferric ions is 2.61 μM. Moreover, the spirooxazine-based molecular sensor was further developed for determination of spiked ferric ions in drinking water.*

Keywords: spirooxazine; chemical sensor; ferric ion

1. INTRODUCTION

Nowadays, one of the most important problems facing many countries is the environmental pollution, especially contaminated toxic metals. Several activities, including geogenic, industrial, agricultural human activities, can cause the release of those toxic metals into the environmental water resource [1,2]. For the positive perspective, some relevant metals, for example Co, Cu, Cr, Fe, Mg, Mn, Mo, Ni, as well as Zn play an important role as the micronutrient for many biological systems [3]. Among other metals, iron has considered to be part of many biological mechanisms, namely oxygen metabolism, catalysis and electron transfer [4]. Importantly, the ferrous (Fe^{2+})/ferric (Fe^{3+}) electron transfer in the human body involves the production of the reactive oxygen-based compounds which can cause the damage to targeted cells and tissues [5]. And also, the excess accumulation of ferric, especially, can lead to the neurodegenerative diseases; i.e. Alzheimer and Parkinson [6-8]. As a result, several techniques have been developed for the need of more effective and selective methods for the Fe^{3+} detection [9].

Spirooxazine is a photochromic molecule that can reversibly isomerize from a closed-ring form to an open-ring form upon the light activation. It has been known that the isomerization occurs through the spiro C-O bond breaking, giving rise to the formation of a zwitterionic open form of spirooxazine, also called merocyanine [10-12]. Interestingly, when a colorless closed form of spirooxazine is activated by light, the solution turns to be colored with the presence of an open-form merocyanine. Besides light activation, the effect of metal coordination on the specific binding site also manages to facilitate the ring-opening process of spiroozaxine in a proper solvent system [13-14]. This phenomena is defined as ionochromism. From the previous reports, a wide variety of metal ions such as Zn^{2+}, Co^{2+}, Cd^{2+}, Mg^{2+}, Ag^+, Pb^{2+}, Cu^{2+}, Tb^{3+} and Hg^{2+}, can selectively form chelating complexes with an open-form merocyanine [14-17]. As a consequence, as-synthesized sprioxazine derivatives have been employed as a potential chemical sensor to detect the specific metal ion.

In this research, we aim to synthesize a spirooxazine-based compound for being used as a chemical sensor to detect ferric ions. The selective and optical behaviors of as-synthesized spirooxazine were investigated by the color change of complexation. The selective interaction of spirooxazine molecule with ferric ion was also studied with the structural isomerization from a closed-form spirooxazine to an open-form merocyanine. The resulting colored complex originated from the formation of a merocyanine-Fe^{3+} complex. For the application, the as-synthesized spirooxazine was further used to monitor the amount of spiked ferric ion in drinking water in comparison with the standard spectroscopic technique.

2. EXPERIMENT

2.1 Chemicals and instrumentation

All chemicals and reagents are used as received without any purification. All inorganic salts were obtained as chloride salts. Drinking water was obtained from a water dispenser located in the Kasetsart University campus, Bangkok, Thailand. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 for ^1H (500 MHz) and ^{13}C (125 MHz) in $CDCl_3$ or $(CD_3)_2SO$ solution. Mass spectrometry (MS) was performed on a Micromass Quattro micro TM API. UV-Vis spectra were recorded on a UV-visible spectrophotometer (Shimadzu, UV-1800). The amount of ferric ions was also determined by an atomic absorption spectrometer (Perkin-Elmer analyst 800).

2.2 Methods

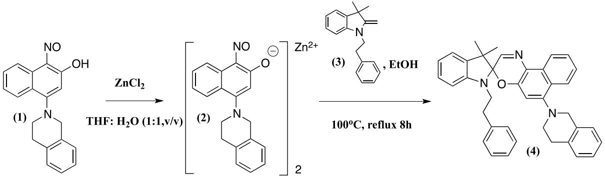
The selectivity and sensitivity of a spirooxazine sensor for binding with metal ions were investigated by UV-Vis spectroscopy. Firstly, a spirooxazine solution (1.0 x 10^{-4} M) was prepared in 1,4-dioxane at room temperature. The mixtures of spirooxazine with each metal ion (1.0 x 10^{-4} M) as follows: Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Sn^{2+}, Pb^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cr^{3+}, and Fe^{3+} were freshly prepared. Job's plot was demonstrated by using the equimolar solutions of spirooxazine and metal ions with the variation of volumetric ratios between Fe^{3+} ions and spirooxazine solution. Regarding the sensitivity study of Fe^{3+} ions, the various concentrations of metal ions were systematically added to the spirooxazine solution. To investigate the effect of competing ions, the mixture was prepared by adding 5.0 equivalent of Fe^{3+} into spirooxazine solution with the presence of 5.0 equivalent of other competing metal ions.

The as-synthesized spirooxazine was applied for the quantitative analysis of ferric ions in sample obtained from the water dispenser. Initially, drinking water was spiked by the standard solution of Fe^{3+} with 3 and 5 μM, respectively. Then, the amount of spiked ferric ions in the water sample was monitored by the spirooxazine sensor in comparison with the flame atomic absorption spectroscopy.

3. RESULTS AND DISCUSSION

3.1 Spirooxazine synthesis

A spirooxazine-based derivative was successfully prepared by the synthetic route in Scheme 1. The as-obtained spirooxazine was structurally confirmed by ^1H NMR, ^{13}C NMR and mass spectrometry. In brief, 12.0 mmol of $ZnCl_2$ was added to mixed solution of tetrahydrofuran and water (1:1 v/v) containing 28.0 mmol of 4-(3,4-dihydroisoquinoline-2(1*H*)-yl)-1-nitrosonaphthalen-2-ol **(1)**. The reaction went completion after 30 min at room temperature, the raw product of 4-(3,4-dihydroisoquinoline-2(1*H*)-yl)-1-nitrosonaphthalen-2-ol zinc salt **(2)** was filtrated, washed with a copious amount of water, and then dried for 2 h in vacuo. The resulting product is brown solid, which was collected and used for next step without purification. 9.0 mmol of compound **(2)** was dissolved in ethanol and stirred under argon at refluxing temperature. Then, the solution of 7.6 mmol 3,3-dimethyl-2-methylene-1-phenethyl indoline **(3)** in ethanol was subsequently added and the mixture was stirred for 8 h. After that, the remaining solvent was removed under the reduced pressure. Finally, the crude product was further purified by column chromatography with 10% ethyl acetate in hexane to obtain black solid of the resulting spirooxazine **(4)** with 37% yield.



Scheme 1. Synthesis of a spirooxazine-based molecular sensor.

3.2 Optical behavior of as-synthesized spirooxazine

With the addition of metal ions into the spirooxazine solution in 1,4-dioxane, the result found that the color of spirooxazine solution was changed from colorless to blue with the presence of ferric ion (Fig. 1). No color change was observed by the naked eye in the case of other relevant metal ions in the spirooxazine solution, indicating no complex formation.

In Fig. 2, the absorption spectra of the solution containing spirooxazine and metal ions show similar absorption peak at 300-400 nm due to a closed form spirooxazine. Since ferric ion was added, the appearance of the absorption response of complexes exhibits a new band at 654 nm. This new absorption peak indicates the formation of merocyanine-Fe^{3+} complex. In the case of other metals, they could not induce the ring-opening process of spirooxazine. Hence, no new absorption peak was observed.

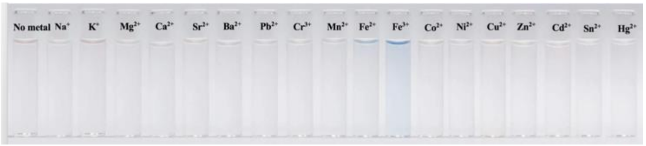


Fig. 1. Color change on the presence of one equivalent of metal ions in spirooxazine solution in 1,4-dioxane.

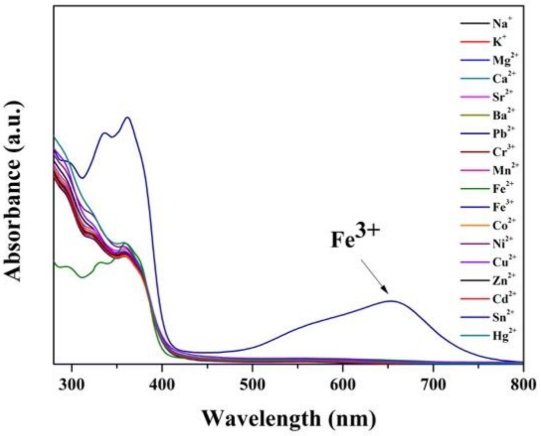


Fig. 2. Absorption spectra of spirooxazine (1 × 10^{-4} M) with the presence of metal ions (1 x 10^{-4} M) in 1,4-dioxane.

The Job's plot of spirooxazine and Fe^{3+} suggests that the absorbance at 654 nm reached the maximum at 0.5 mole fraction (Fig. 3). It confirms that the stoichiometric ratio of spirooxazine and ferric ion was found to be 1:1 for the complexation.

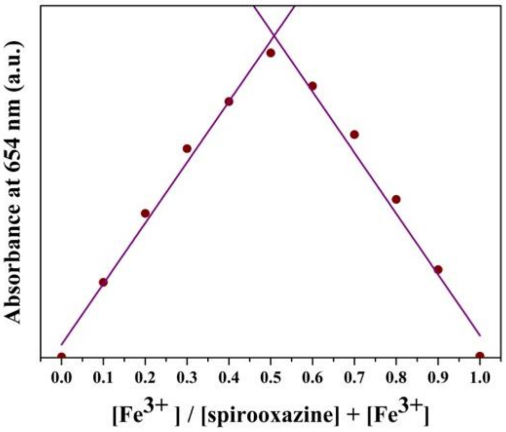


Fig. 3. Job's plot of spirooxazine and ferric ion in 1,4-dioxane.

In terms of complex formation, spirooxazine forms a complex by breaking the spiro C-O bond in the presence of ferric ions. The open-form merocyanine chelates with ferric ions by using both nitrogen and oxygen atoms for complexation as proposed in Fig. 4.

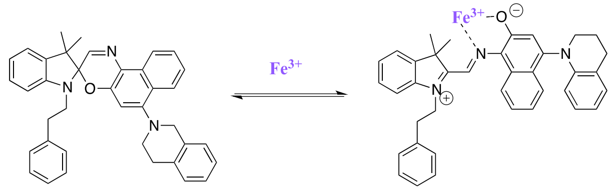


Fig. 4. The formation of merocyanine-Fe^{3+} complex.

To investigate the binding ability between spirooxazine and ferric ions, the titration method of spirooxazine with various ferric concentrations was carried out. The result suggests that the absorbance intensity has a linear response toward ferric ions with the concentrations ranging from 1 to 30 μM (Fig. 5). Based on the linear correlation, the detection limit of ferric ion in 1,4-dioxane was determined to be 2.61 μM, which is lower than 5.36 μM, the standard maximum permissible level of ferric ion in drinking water approved by Environmental Protection Agency (EPA) [18].

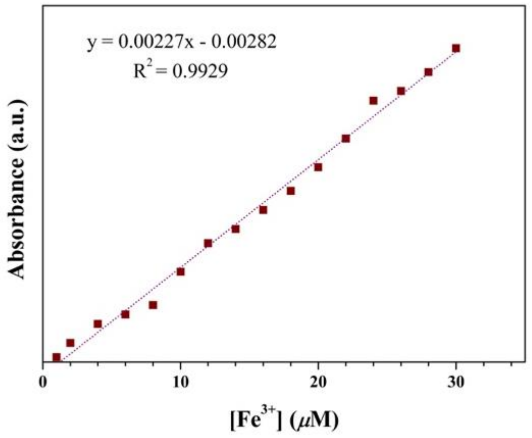


Fig. 5. Absorption titration at 654 nm of a spirooxazine solution (2.0 x 10^{-5} M) with increasing the amount of ferric ions in 1,4-dioxane.

The absorption spectra in Fig. 6 show the effect of increasing concentrations of ferric ions in the spirooxazine solution in 1,4-dioxane. With the ferric concentrations from 0 to 10 equivalents, the absorbance at 654 nm was increased with a slightly bathochromic shift. This can be ascribed to the formation of J-type aggregates of merocyanine with head-to-head arrangement at the high concentration of ferric ions [11].

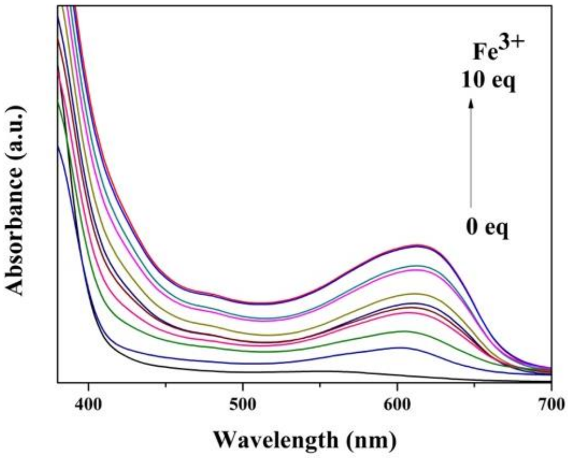


Fig. 6. Absorption spectra of solution containing spirooxazine (1 x 10^{-4} M) with concentrations of ferric ions from 0 to 10 equivalents.

To investigate the competitive selectivity of spirooxazine toward ferric ion compared with other relevant metal ions, we added 5.0 equivalent of ferric ion into spirooxazine (5 x 10^{-5} M) with the subsequent addition of 5.0 equivalent of competing metal ions. This result suggests that the absorbance enhancement caused by the solution of spirooxazine and ferric ion was not significantly affected by those competing metal ions (Fig. 7). The as-synthesized spirooxazine has a highly selective behavior toward ferric ions.

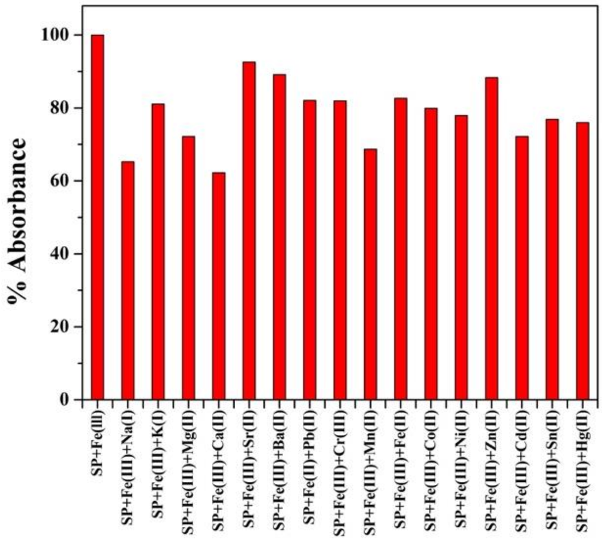


Fig. 7. Competitive selectivity of spirooxazine toward ferric ions with the subsequent addition of competing metal ions in 1,4-dioxane. (SP = spirooxazine)

In this research, we aim to use the sensing spirooxazine molecule to monitor ferric ion in drinking water by the naked-eye detection. Hence, we need to optimize the solvent system and found the suitable condition by mixing water to 1,4-dioxane (6:4 v/v). This condition was further utilized for monitoring the amount of ferric ion in the water sample.

3.3 Application

To test the sensing performance of spirooxazine toward the determination of ferric ions in drinking water, the results from Table 1 demonstrate that the %recoveries for spiked concentration levels of ferric ions in drinking water detected by a spirooxazine sensor were obtained in the range of 93.75−103.75 % which is relatively comparable to the amount of spiked ferric ions monitored by the standard AAS method. This indicates the excellent performance of the as-synthesized spirooxazine as a chemical sensor.

Table 1. Recoveries of ferric ions in drinking water.

Fe^{3+} spiked (μM)	Fe^{3+} determined (μM)			
	Sensor	%Recovery	AAS	%Recovery
0	0	-	0	-
3	2.81	93.75	3.04	101.40
5	5.19	103.75	5.15	102.99

4. CONCLUSION

In summary, the spirooxazine was successfully synthesized with the structural confirmation. The high selectivity of spirooxazine for binding with ferric ions was clearly observed. The detection limit of ferric ions is 2.61 μM. We further demonstrate the development of spirooxazine for the sensitive detection of ferric ions in drinking water. The %recoveries of ferric ions in drinking water was obtained in a range of 93.75−103.75 % with a comparable extent of the standard spectroscopic method.

5. ACKNOWLEDGEMENTS

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