Synthesis of Pyridyl-Imine Complex of Iron(III) as a Fluorescent Sensor for Hydrazine Detection Based on Redox Chemistry

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Abstract

A six-coordinated iron(III) pyridyl-imine complex was synthesized by one-pot reaction and was demonstrated as a fluorescent sensor for the detection of hydrazine in solution based on the redox reaction. The fluorescence signal generated was attributed to the reduction of the oxidative iron-center of Fe(III) to Fe(II) by the reductive hydrazine. A good linear relationship for the analysis of hydrazine was obtained with the concentration range of 0.06-0.15 mM ($R^2 = 0.99114$) in DMF solution. The limit of detection (LOD) estimated was 14.8 μM and the limit of quantitation (LOQ) was 49 μM. Moreover, the color change of the iron(III) pyridyl-imine complex solution from dark green to reddish brown was able to observed by naked eye, indicating that the Fe(III)-complex may be also utilized as a colorimetric sensor for hydrazine at millimolar level. The present study demonstrated an interesting fluorescent sensing system based on redox chemistry of an iron(III) complex that generated fluorescence response upon reacting with its redox pair such as the reducing agent hydrazine.

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Introduction

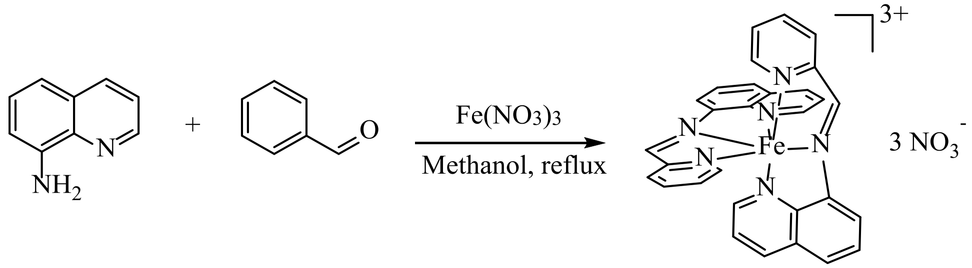
Hydrazine (H_2N-NH_2) is an important and widely used compound in both fine chemical and pharmaceutical industries including pharmaceuticals, pesticides, and chemical-blowing agents.[1, 2] It is flammable, corrosive, toxic, and hazardous to health and the environment.[3] Hydrazine can be found naturally in trace amounts as an intermediate in nitrogen fixation of anammox bacterium such as *Kuenenia stuttgartiensis* in the nitrogen cycle.[4] However, industrial processes and human activities contribute significantly more hydrazine than natural processes.[5] For instance, industrial ammonia electro-oxidation reactions, fuel cells powered by ammonia, electrochemical sensors, etc. These reactions usually involve the coupling process of two intermediate NH_2 groups and produce hydrazine as a result, with accelerating hydrazine generation rates on a suitable catalyst surface.[6]

More common applications of hydrazine include serving as rocket fuels and foaming agents.[1, 5, 7] Both applications exploit the gas-generating properties of hydrazine decomposition. The reduction reaction of hydrazine usually produces nitrogen gas, which makes hydrazine good gas generators. The use of foaming agents in polymerization process is very common in industry. For example, the synthesis of polyurethane foams requires the reaction of di-isocyanates with water to generate carbon dioxide gas to lower the polymer density with expanding gas, known as "flexible foaming". Hydrazine can also function similarly, participating in natural rubber and resin syntheses as blowing agents.[8] In addition, hydrazine is well-known as serving as an excellent reductant in chemical reactions because its reduction potential is up to +1.15 V,[9] which makes it easy to form redox pairs with other species, particularly the oxidants such as iron(III) complexes.

Since hydrazine is a widely used chemical for industrial manufacturing, its high toxic impact and massive use may pose potential threats to human health and environmental pollution.[3, 10] For this reason, numerous sensors have been developed for hydrazine detection and the recent progress has been reviewed.[11-15] Based on the fundamentals of chemistry, the reductive nature of hydrazine and the oxidative iron(III) complexes should be a prefect redox pair for the redox reaction.[16] Interestingly, there is no study reported in literature on the development of iron(III)-complex as the turn-on fluorescent sensor for molecular sensing and detection of hydrazine. To demonstrate this concept, we synthesized a simple iron(III)-complex using a pyridyl-imine, ((*E*)-1-(pyridin-2-yl)-*N*-(quinolin-8-yl)methanimine),[17] as the coordinating ligand by one-pot synthesis under mild reaction conditions. Our study showed that the six-coordinated $[Fe(pyridyl\text{-}imine)_2]^{3+}$ complex[18] was able to give an intensive and blue fluorescence signal upon reacting with hydrazine in solution. In addition, its remarkable fluorescence signal change due to the fundamental redox chemistry of the oxidative Fe(III) species reduced by the reducing agent, hydrazine, in DMF has not been reported. The fluorescence signal generated can be readily observed by naked eye under a laboratory UV lamp irradiation at 365 nm. The present study aimed to report an interesting fluorescent sensing system for the detection of reducing agents such as hydrazine based on redox chemistry.

Results and Discussion

The iron(III) pyridyl-imine complex was synthesized by one-pot reaction using 8-aminoquinoline and 2-pyridinecarboxaldehyde in the presence of iron(III) nitrate using methanol as the solvent under reflux conditions according to the reported procedures (**Scheme 1**).[18] The deep dark green crystalline was obtained after recrystallization from ethanol by slow diffusion of diethyl ether at room temperature. The [Fe(pyridyl-imine)$_2$]$^{3+}$ complex was characterized with FTIR (**Figure S1**). The results were found in accord with literature reported.[18] The high-resolution mass spectrometry (HRMS) analysis for the complex was shown in **Figure 1**. The isotope distribution for the complex ([$C_{30}H_{22}N_6Fe$]$^+$) was found almost identical with the theoretical simulated.



Scheme 1. One-pot synthesis of [Fe(pyridyl-imine)$_2$]$^{3+}$ complex.

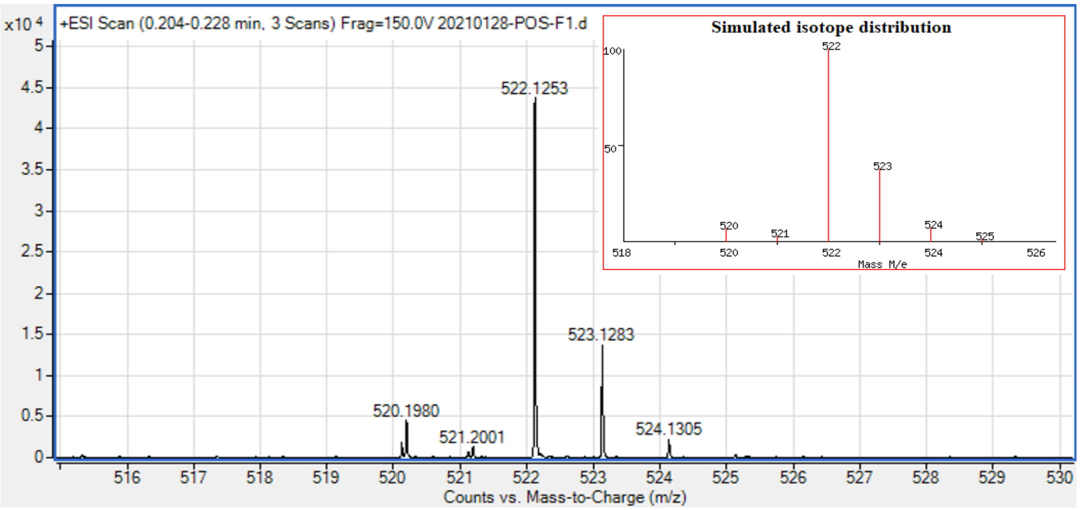


Figure 1. HRMS analysis of iron(III) pyridyl-imine complex ([$C_{30}H_{22}N_6Fe$]$^+$). The inert was a theoretical simulation for the isotope distribution for the complex.

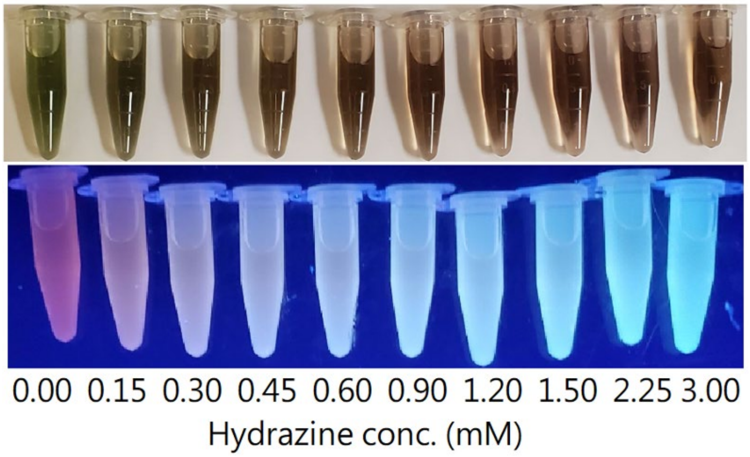


Figure 2. A demonstration of fluorescent change of the iron(III) pyridyl-imine complex (0.15 mM) with different hydrazine concentrations (0-3 mM) in DMF solution under UV lamp irradiation (Upper panel: without irradiation; Lower panel: irradiation at 365 nm).

Since hydrazine and the iron(III) pyridyl-imine complex could be a redox pair and undergo redox reaction, we thus attempted to utilize the iron(III) pyridyl-imine complex as a fluorescent sensor to detect hydrazine. The fluorescence of the complex is expected to be changed when the Fe(III) metal center was reduced to Fe(II) by hydrazine due to their different electronic transitions in metal to ligand and ligand to metal charge transfer bands.[19, 20] For proof of concept, we first examined the fluorescence signal changes by mixing the Fe(III)-complex (0.15 mM) with hydrazine at high concentration (0-3 mM) so that the generated emission could be possibly visualized by naked-eye under a laboratory UV lamp irradiation (λ_{ex} = 365 nm). As shown in **Figure 2**, the blue fluorescence signal was observed markedly as increasing the concentration hydrazine. The result may support the idea that the iron(III) pyridyl-imine complex could be possibly developed as a fluorescent sensor for hydrazine detection based on redox chemistry.[21]

We thus further investigated the sensitivity of the iron(III) pyridyl-imine complex at micro-molar concentration conditions. The Fe(III)-complex at 15 μM was titrated with hydrazine at various concentrations (0-0.3 mM). From **Figure 3**, the fluorescence intensity (λ_{ex} = 350 nm; emission peak at 475 nm) was found increased markedly as increasing the hydrazine concentration in the solution. From the fluorescence titration curve (**Figure 4**), a linear response range for hydrazine was found to be 0.06-0.15 mM and a good linear relationship of the signal intensity and hydrazine concentration was obtained ($R^2 = 0.99114$). The limit of detection (LOD) value was estimated to be 14.8 μM and the limit of quantitation (LOQ) was 49 μM, according to ICH Guideline[22]: LOD = 3×SD/m, LOQ

=10×SD/m; where SD is the standard deviation of intercept and m is the slope of the fitting curve (**Figure S2**).

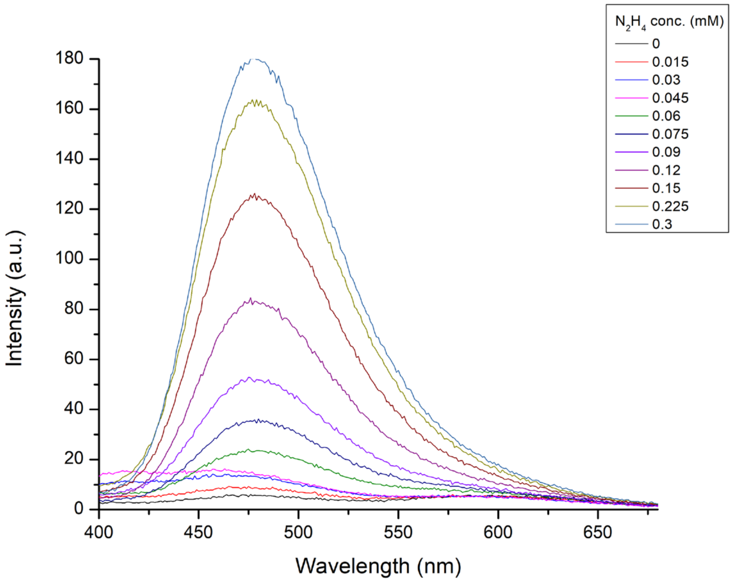


Figure 3. Fluorescence titration for the iron(III) pyridyl-imine complex (15 μM) with hydrazine (0-0.3 mM), λ_{ex} = 350 nm. (The average value of three sets of data was used for plotting the graph).

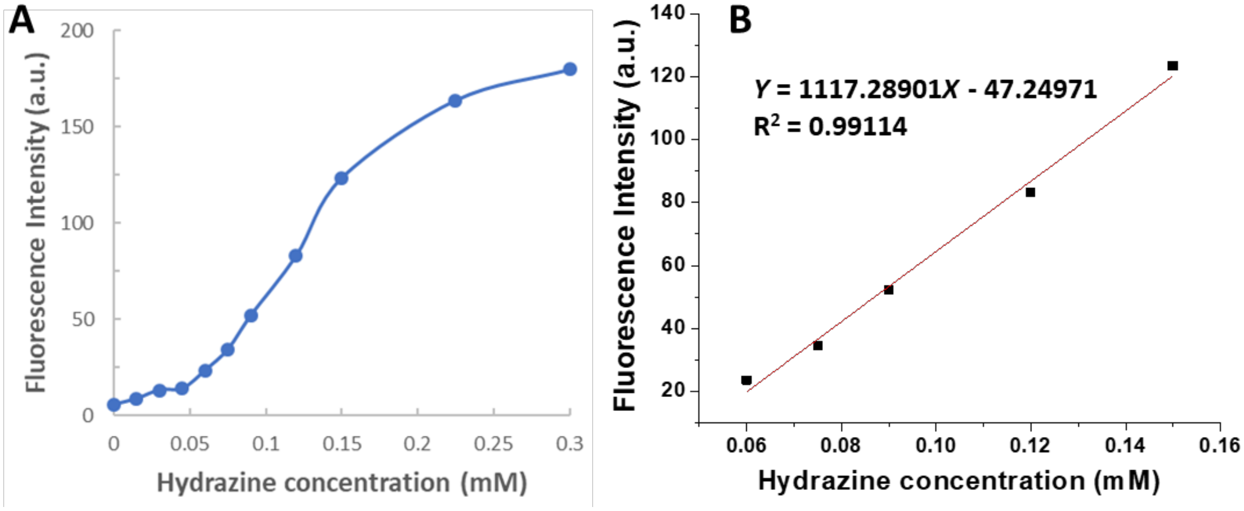


Figure 4. (A) The fluorescence titration curve and (B) the linear response range for the detection of hydrazine in DMF solution. (The average value of three sets of data was used for plotting the graph).

We further examined the UV-vis absorption changes for the redox reaction of the iron(III) pyridyl-imine complex with hydrazine despite the sensitivity of absorption method is much less than that of fluorescence detection; however, it may show observable color changes upon reacting with hydrazine and could be developed as colorimetric sensor.[12] The concentration of the Fe(III)-complex used was 0.15 mM and was titrated with hydrazine. From **Figure 5**, the iron(III) pyridyl-imine complex itself shows a distinctive long wavelength absorption band (peak at 660 nm), which is not commonly found in literature.[23] Moreover, the absorption in the region from 500-600 nm was found increased while the peak at 660 nm was decreased with the increasing concentration of hydrazine from 0.15-3.0 mM. The color of the solution was found changed from dark green to reddish brown (**Figure 2**), indicating that Fe(III) metal center was reduced to Fe(II).[16]

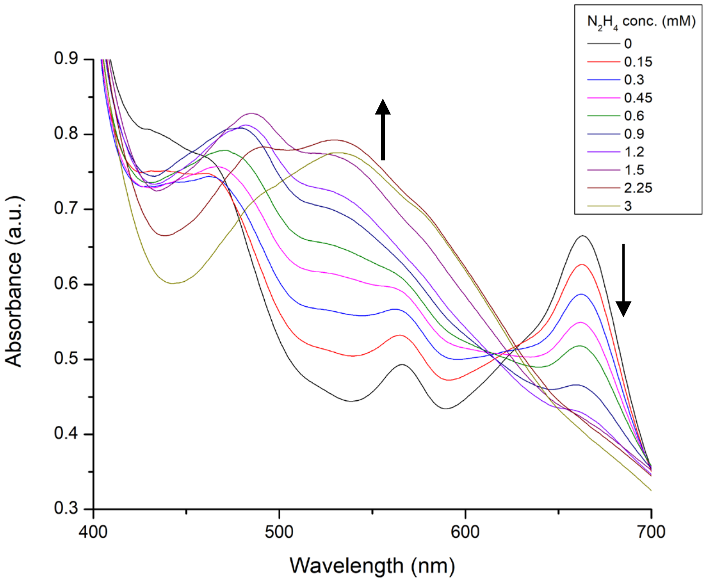


Figure 5. UV-Vis titration curves of iron(III) pyridyl-imine complex (0.15 mM) with hydrazine (0.15-3 mM) in DMF solution.

To further examine the oxidation state of the Fe(II)-complex formed in the redox reaction, *X*-ray photoelectron spectroscopy (XPS) was applied for analysis. From **Figure 6A**, the Fe2p scan of the sample showed a remarkable peak at 709 eV, indicating that the iron metal of the complex was an Fe(II) species.[24] We also examined the possible reaction of the ligand of the iron(III) pyridyl-imine complex with hydrazine (500 times in excess). From **Figure 6B**, the UV-vis absorption of the ligand showed no observable changes. The results may indicate that hydrazine does not react with the ligand of the Fe-complex but it reduces the iron-center of the complex from Fe(III) to Fe(II) and thus it results in blue fluorescence signal. Furthermore, despite the sensitivity of absorption method is not as good as fluorescence method, the iron(III) pyridyl-imine complex could be potentially utilized as a colorimetric sensor for hydrazine sensing at millimolar level.[12]

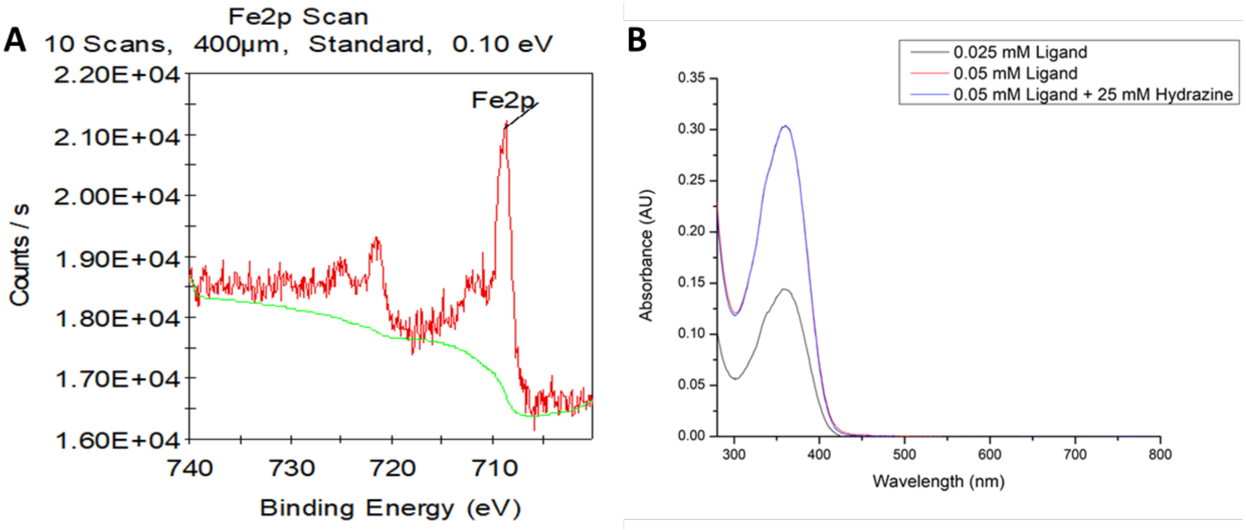


Figure 6. (A) XPS analysis of the iron-complex reduced by hydrazine (Fe2p peak at 709 eV). (B) UV-vis absorption spectra of a DMF solution of hydrazine with the ligand of the iron(III)-complex (no observable change was found for the ligand (0.05 mM) mixed with excess amount of hydrazine (25 mM) at 45 °C).

Conclusion

In conclusion, an iron(III) pyridyl-imine complex was synthesized by one-pot reaction. The oxidative Fe(III)-complex was demonstrated as a fluorescent sensor for the detection of hydrazine in solution. The fluorescence signal observed was attributed to the reduction of the iron metal center of the complex from Fe(III) to Fe(II) by hydrazine. A good linear relationship for analysis of hydrazine was obtained with the concentration range of 0.06-0.15 mM. The limit of detection (LOD) value estimated was 14.8 µM and the limit of quantitation (LOQ) was 49 µM. The present study demonstrated a new and interesting fluorescent sensing system based on Fe(III)-complex that could generate fluorescence response upon reacting with its redox pair such as hydrazine. The finding may provide new insights for the design of novel fluorescence enhancement sensing system based on redox chemistry.

Experimental Section

Materials. Iron(III) nitrate nonahydrate (ACS reagent, ≥ 98%), 8-aminoquinoline (98%), 2-pyridinecarboxaldehyde (99%) and hydrazine (≥ 98%) were purchased from Sigma-Aldrich. The synthesis of the complex was conducted by following the reported procedures with slight modifications on the reaction conditions.[17, 18] Briefly, 0.34 g (0.8 mmol) iron(III) nitrate nonahydrate, 0.242 g (1.6 mmol) 8-aminoquinoline, and 155 μL (1.6 mmol) 2-pyridinecarboxaldehyde were added to a flask with 25 mL methanol. The reaction mixture was heated to refluxed for 6 h. After reaction, the volume of methanol was reduced to 5 mL by rotatory evaporator and then diethyl ether was added to precipitate the complex. The crude product was obtained by filtration and then was washed with ethyl acetate. The dark green solids obtained were further purified by recrystallization in ethanol diffusing diethyl ether at room temperature. The iron(III) pyridyl-imine complex was obtained as the dark green crystalline with about 50% yield. The complex was characterized with FTIR and high-resolution MS. FTIR absorption peaks (KBr, pellets): 1348 cm^{-1} (pyridyl C=N stretching, very strong)[25], 1600-1650 cm^{-1} (aromatic C=C stretching, weak), 3404 cm^{-1} (O-H stretching from H_2O, broad and strong); HRMS for $[C_{30}H_{22}N_6Fe]^+$ m/z: calc. 522.1256, found 522.1253.

In the preparation for sensing assays and fluorescence measurements, all stock solutions were prepared with AR grade *N,N*-dimethylformamide (DMF) and all the solutions were freshly prepared for assays. The stock solutions of iron(III) pyridyl-imine complex were prepared at 15 μM and 150 μM, respectively. The stock solution of hydrazine was 5 mM. Before performing measurements, the well-mixed sample solutions were warmed at 45 °C in an isothermal bath for 30 mins. The solution after cooled to room temperature (25 °C) was then transferred to a quartz cuvette for conducting measurement with the instruments.

Instruments. High resolution mass spectra (HRMS) were recorded with an Agilent 6540 Q-TOF LC/MS instrument using electrospray ionization (ESI). Absorption spectra were measured by Cary 8454 UV-Vis diode array system and the emission spectra were measured by Cary Eclipse fluorescence spectrophotometer. The FTIR spectra were recorded for the solid sample with KBr using an Agilent Cary 670 FT-IR Spectrometer. The *X*-ray photoelectron spectroscopy (XPS) characterization was performed on the *X*-ray photoelectron spectrometer (Thermo Scientific, ESCALAB 250Xi).

Supporting Information Summary

FT-IR spectrum of iron(III) pyridyl-imine complex and the estimation of limit of detection (LOD) and limit of quantitation (LOQ) are presented in the supporting information.

Conflicts of interest

There are no conflicts to declare.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author.

Acknowledgment

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Keywords

Fluorescent iron complex; Hydrazine; Iron(III) pyridyl-imine complex; Reducing agent; Sensors based on redox chemistry;

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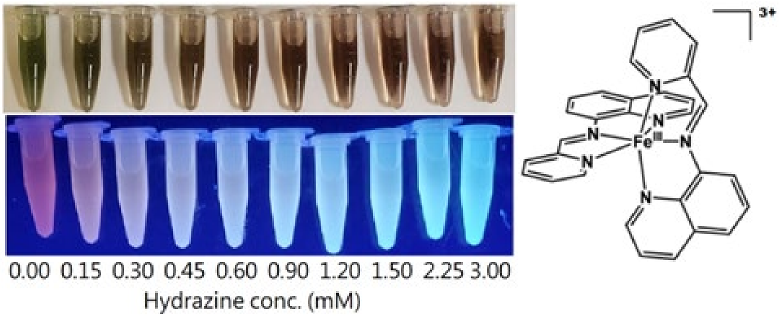

A fluorescent turn-on sensing system based on redox chemistry of a pyridyl-imine complex of iron(III) that generated fluorescence response upon reacting with its redox pair, such as hydrazine, a reducing agent, was demonstrated.