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Subcomponent self-assembly of a Fe(II) based mononuclear complex for potential NH_3 sensing applications

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Abstract
Metal oxide and conducting polymer solid state sensors have occupied a substantial portion of NH_3 gas sensor applications. Here, we present a new mononuclear Fe(II) complex with formula $[FeL_2](BF_4)_2$ (L = (*E*)-2-((pyridin-2-ylmethylene)amino)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione) (**1**) for potential NH_3 sensing applications. Complex **1** was synthesized via subcomponent self-assembly. Clear color differentiation from pink to black can be observed by the naked eye at ambient conditions after adsorbing NH_3 gas. ^{57}Fe Mössbauer spectroscopy was employed to study the driving spin state change of the material **1**@NH_3, paving the way to the design of a new generation of sensors based on coordination complexes.

Keywords Fe(II) complexes · Sensor · ^{57}Fe Mössbauer spectroscopy · Spin crossover

1 Introduction

In recent years, NH_3 gas detection techniques have been highly demanded due to the extensive use in different industrial production sectors and its highly toxic and corrosive properties to human health and the environment [1–3]. Metal oxide and conducting polymer based solid state sensors have been widely studied. However, because of the intrinsic shortcomings, such as the relatively high temperature (metal oxide), the poor mechanical strength and slow reaction kinetics (conducting polymer), they are not hopeful sensor in terms of simplicity, energy efficient operation, portability, etc. [4–6] Good candidates for overcoming these defects

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are Fe(II)-based coordination complexes. Because the metal center is extremely sensitive to the subtle change in the coordination environments caused by guest intercalation, the optical outputs will be alterated [7, 8]. In addition, some of them operate at room temperature [9, 10]. Recently, our group reported one mononuclear Fe(II) complex with the formula $[Fe(H_2btm)_2(H_2O)_2]Cl_2$ (H_2btm = di(1H-tetrazol-5-yl)methane), which is chemically responsive and able to distinguish different volatile organic compounds and hazardous gases [11]. Particularly, it can rapidly detect and discriminate vapors of NH_3 and amines in the gas phase through displaying different colors. ^{57}Fe Mössbauer spectroscopy spectra and magnetic susceptibility measurements proved that the discoloration mechanism is due to the spin state switching after adsorption of the analytes. One of the possible reasons for the magnetic property change is that the guest molecule forms a hydrogen bond with the nitrogen-rich ligand, which modulates the coordination environment around the iron, thereby causing a spin state switching [11]. Inspired by this idea, we designed a new oxygen-rich ligand which was reacted to Fe(II) to lead to the complex $[FeL_2](BF_4)_2$ (L = (*E*)-2 -((pyridin-2-ylmethylene)amino)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione) (**1**) obtained through subcomponent self-assembly [12]. It shows a significant response to vapors of $NH_{3(g)}$ through a rapid color change from pink to black, which can be detected by the naked eye at ambient conditions. In the present work, we applied ^{57}Fe Mössbauer spectroscopy to investigate the spin state change after adsorbing $NH_{3(g)}$ in this potential Fe-based coordination complex sensor.

2 Experimental

Subcomponent of ligand (S1) was synthesized through a condensation reaction between 1,8-naphthalic anhydride (10 mmol, 1.98 g) and hydrazine hydrate (10 mmol, 0.5 g) in methanol (50 mL). Light yellow color solid was separated out after 8 h. The precipitate was filtered out and recrystallized in methanol to afford a pure product. Yield: 85% (1.8 g). ^{1}H NMR (DMSO-d6, 300 MHz, ppm) δ: 8.47 (m, 4H), 7.86 (t, 2H), 5.78 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d6) δ: 160.58, 134.64, 131.33, 127.33, 126.05, 121.78. As shown in Fig. 1, complex **1** was prepared by subcomponent self-assembly: S1 (42.4 mg, 0.2 mmol), 2-formylpyridine (19.1 μL, 0.2 mmol) and $Fe(BF_4)_2{\cdot}6H_2O$ (33.7 mg, 0.1 mmol) were added to a Schlenk flask with 30 mL acetonitrile. The reaction mixture was stirred under argon at 50 °C overnight and then cooled to room temperature, leading to a purple solution. Large amount of diethyl ether were added into the solution and a pink precipitate, as a microcrystalline powder, was filtered after centrifugation, and then dried under vacuum at 70 °C. Yield: 67% (55.7 mg). **1**@NH_3 was prepared after adsorbing NH_3 gas molecules at room temperature.

All chemicals and solvents were purchased from commercial sources of analytical grade and used without further purification. NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer. Proton chemical shifts (δ) are reported relative to the solvent residual peak (2.50 ppm for dimethyl sulfoxide). ^{57}Fe Mössbauer spectra were measured in transmission geometry with a constant acceleration mode conventional spectrometer equipped with a 50 mCi ^{57}Co(Rh) source and a Reuter Stokes proportional counter. The powdered samples were sealed in aluminum foil and spectra were recorded at 298 K. The spectra were fitted using Recoil 1.05 Mössbauer Analysis software [13] and the isomer shift values are given with respect to α-Fe at room temperature.

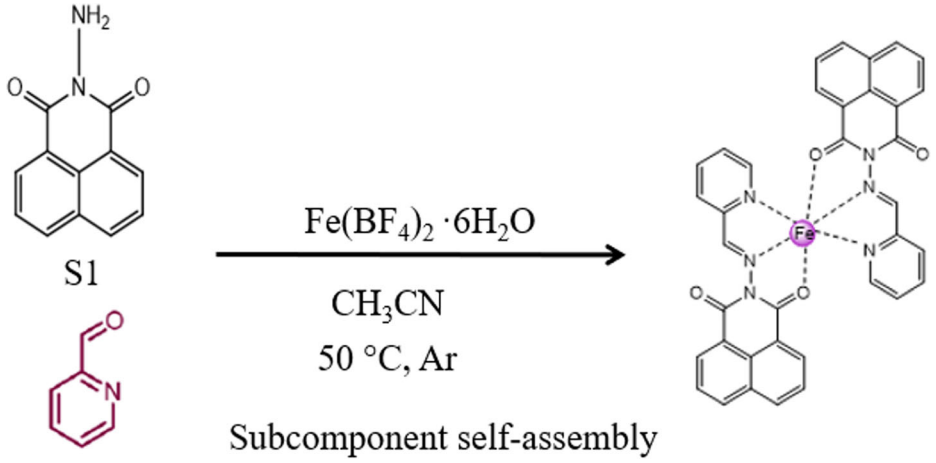

Fig. 1 Schematic representation of the formation for complex **1** through subcomponent self-assembly approach

3 Results and discussion

^{57}Fe Mössbauer spectroscopy was employed to study the stability (iron oxidation) and spin states of **1** and **1**@NH_3 at room temperature. Related parameters are shown in Table 1. As shown in Fig. 2, the spectrum of **1** exhibits a major quadrupole doublet with an isomer shift δ = 1.00 (2) mm s^{-1} and a quadrupole splitting ΔE_Q = 2.58 (4) mm s^{-1} of area fraction A = 74%, which are characteristic of high-spin (HS) Fe(II) ions. Another quadrupole doublet characteristics of low-spin (LS) Fe(II) ions are revealed, with δ = 0.22 (5) mm s^{-1} and ΔE_Q = 0.42 (1) mm s^{-1}. Similar parameters can be found in other Fe(II) complexes with tridentate Schiff base ligands with *N,N,O* donor sets, like qsalH (N-(8-quinolyl)salicylaldimine) [14], 2-hydroxy-N′-((pyridin-2-yl)-methylene) benzohydrazide [15] and pyridyl aroylhydrazone [16], to name but a few.

After adsorbing NH_3 gas molecules, the Mössbauer spectrum is dramatically modified (Fig. 3). **1**@NH_3 exhibits a minor quadrupole doublet with δ = 1.21 (1) mm s^{-1} and ΔE_Q = 2.31 (2) mm s^{-1}, which only accounts for 7% of the total spectra. Such doublet is characteristics of HS Fe(II) ions [17]. Another quadrupole doublet characteristic of LS Fe(II) ions with a major fraction of 93% is also detected [10]. Such change of spin states could be caused by weak interactions between the oxygen-rich ligands and the guest NH_3 molecules, resulting in a

Table 1 Overview of selected ^{57}Fe Mössbauer parameters for **1** and **1**@NH_3

Sample	Spin State (Fe(II))	A/A$_{tot}$	Mössbauer parameters		
			δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ/2
1	HS (red)	74	1.00 (2)	2.58(4)	0.18(3)
	LS (blue)	26	0.22 (5)	0.42(1)	0.16(1)
1@NH_3	HS (red)	7	1.21(1)	2.31(2)	0.11(1)
	LS (blue)	93	0.33(2)	0.70(4)	0.28(3)

δ: isomer shift (with respect to α-Fe at 298 K); ΔE_Q: quadrupole splitting; Γ/2: half width at half maximum

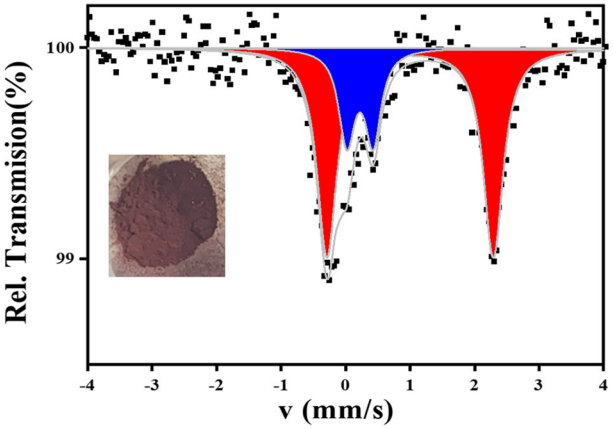

Fig. 2 ^{57}Fe Mössbauer spectrum of **1** recorded at 298 K. The red and blue quadrupole doublets correspond to HS and LS Fe(II) ions, respectively. The inset shows the pink colour of the powder

subtle change of the coordination environment of iron centres [11], and thereby leading to a spin state change observed at room temperature.

4 Conclusions

In conclusion, we report a new mononuclear Fe(II) complex **1**, synthesized by subcomponent self-assembly approach, which exhibits potential sensor application for $NH_{3(g)}$ at room temperature. Complex **1** shows remarkable and quick color change from pink to black after exposure NH_3, which can be observed by the naked eyes. Compared with complex **1**, the high-spin Fe(II) fraction, recorded by ^{57}Fe Mössbauer spectroscopy, shows a huge decrease from 74% to 7%, as a result of a spin state change induced by the gas analyte. Further studies on the response of **1** to other stimuli are currently underway in our laboratory.

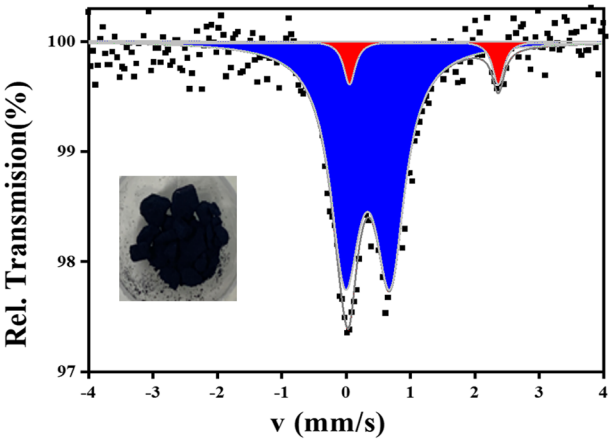

Fig. 3 ^{57}Fe Mössbauer spectrum of **1**@NH3 recorded at 298 K. The red and blue quadrupole doublets correspond to HS and LS Fe(II) ions, respectively. The inset shows a black colour of the transformed powder

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