

Two Coordination Polymers with High Selectivity for Sensing Iron(III) Constructed from Bifunctional Ligand^①

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ABSTRACT A new ligand [1-{2-(2-pyridyl)-benzo[d]imidazole}-2-(5-hydroxyisophthalic acid) ethane] was used to synthesize cadmium and cobalt based fluorescent organic frameworks successfully under solvothermal conditions. Single-crystal X-ray crystallography of both complexes as well as their thermal stability and luminescence properties was investigated. Much emphasis was placed on the newly synthesized Cd-complex which shows great sensitivity for the detection of Fe³⁺ ions and could be used as a potential probe to detect the Fe³⁺ ions.

Keywords: coordination polymer, fluorescence sensing, Fe³⁺ ions detection;

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1 INTRODUCTION

Fast and highly selective detection of heavy metal ions has attracted increasing attention concerning public health and ecological safety^[1]. Especially highly charged metal ions, for example Fe³⁺, when released into the atmosphere or water bodies, would induce many environmental pollutions which are harmful to human health and environment^[2, 3]. Many detection technologies have been employed in the detection of heavy metals, but they are limited by their equipment demands, time-consuming and cost drawbacks^[4]. Florescent based detection comparably has advantages over the traditional detection methods in virtue of the simplicity, short response time, sensibility, and its ability to be applied in both solid and liquid phases^[5]. However, there are some hindrances in relation to stability, toxicity, sensitivity and biodegradability of these materials^[4] and therefore the call for a rather more significant and challenging task to synthesize novel materials for the florescence detection of metal ions.

Coordination polymers (CPs) are a fascinating material class that are both fundamentally important and technologically relevant. They have been extensively studied, recently, for their rich structural chemistry^[6] and potential applications in numerous areas^[7], including but not limited to, gas storage^[8], gas separation^[9, 10], catalysis^[11], chemical sensing^[12, 13, 14], optoelectronics (ferro-electronics, non-linear optics, and LEDs)^[15], energy storage and conversion (batteries and solar

cells)^[16, 17], drug delivery and bio-imaging^[18]. Many luminescent coordination polymers (LCP) as sensors have been developed for detecting nitroaromatic explosives. For example, 2,4-dinitrotoluene (DNT) and 2,3-dimethyl-2,3-dinitrobutane (DMNB) have been reported by Lan et al as the first LCP that is able to detect trace nitroaromatic explosives (NEs) in the vapor phase^[19]. Ma et al. also reported the first case of a dual functional luminescent sensor that can quantitatively detect nitrobenzene (NB)^[20]. Meanwhile, reports on high sensitivity and selectivity for heavy metal ions have been widely reported, therefore posing a significant challenge to develop new LMOF sensors. In this paper, two CPs; Cd-complex (1) and Co-complex (2), were synthesized under solvothermal conditions and characterised. Of particular interest, the Cd-complex's florescence response to metal ions and NEs was also further investigated.

2 EXPERIMENTAL

2.1 Materials and instruments

Reagents and solvents were all purchased commercially and used without any further purification. Powder X-ray diffraction (PXRD) data of the samples were recorded on a Bruker D8 Advance X-ray diffractometer using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$), in which the X-ray tube was operated at 40 kV and 40 mA. The thermographic analysis (TGA) of the samples was also characterized on a Perkin

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Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K at a heating rate of 10 K min⁻¹ under N₂ atmosphere. The luminescent spectra of the Cd-complex were also recorded on a Hitachi F-4600 spectrometer.

2.2 Syntheses of complexes 1 and 2

Cd(NO₃)₂·4H₂O (0.10 mg) and the ligand (0.50 mg) were dissolved in a mixture of DMF (2 mL) and H₂O (1 mL). The final mixture was then placed in a Parr Teflon-lined stainless-steel vessel (15 mL) and stored in an autoclave under autogenous pressure and heated at 100 °C for 48 hours, and then cooled to room temperature. Light-yellowish block crystals of Cd-complex were obtained. IR (cm⁻¹): 744(w), 777(w), 985(w), 1070(w), 1127(w), 1263(w), 1367(m), 1547(m), 3426(m). For complex 2, the method used is the same with the synthesis of complex 1 and reddish-brown block crystals of complex 2 were obtained. IR (cm⁻¹): 720(m),

748(m), 777(m), 1070(m), 1131(m), 1259(m), 1367(m), 1429(m), 1547(m), 3412(m).

2.3 Crystal structure determination

X-ray crystallographic data of 1 and 2 were collected at room temperature using epoxy-coated crystals mounted on glass fiber. All measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-97 (Sheldrick, 2008) using a full-matrix least-squares procedure based on F^2 values^[21]. The positions of hydrogen atoms were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The selected bond lengths and bond angles are listed in Table 1, and the crystal data are listed in Table 2.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for Complexes 1 and 2

Bond	Dist.	Bond	Dist.	Bond	Dist.
Complex 1					
Cd(1)–O(4)b	2.195(7)	Cd(1)–O(1W)	2.262(9)	Cd(1)–N(2)a	2.550(12)
Cd(1)–N(1)a	2.253(9)	Cd(1)–O(2)	2.271(8)		
Complex 2					
Co(1)–O(1W)	2.093(3)	Co(1)–O(2)a	2.107(2)	Co(1)–N(2)b	2.112(3)
Co(1)–O(4)	2.112(3)	Co(1)–O(5)	2.188(2)	Co(1)–N(1)b	2.121(3)
Angle	(°)	Angle	(°)	Angle	(°)
Complex 1					
O(4)b–Cd(1)–O(2)	97.0(3)	N(1)a–Cd(1)–O(2)	88.9(3)	O(1W)–Cd(1)–O(2)	131.2(4)
O(4b)–Cd(1)–N(3)a	89.7(3)	N(1)a–Cd(1)–N(3)a	69.6(4)	O(1W)–Cd(1)–N(3)a	116.8(4)
O(4b)–Cd(1)–N(1)a	159.1(4)	O(4)b–Cd(1)–O(1W)	93.3(3)	N(1)a–Cd(1)–O(1W)	97.8(3)
O(2)–Cd(1)–N(3)a	110.8(4)				
Complex 2					
O(1W)–Co(1)–O(2)a	89.75(1)	O(1W)–Co(1)–N(2)b	91.72(1)	O(2)a–Co(1)–N(2)b	171.68(1)
O(1W)–Co(1)–O(4)	161.27(1)	O(2)a–Co(1)–O(4)	95.19(1)	N(2)b–Co(1)–O(4)	86.00(1)
O(1W)–Co(1)–N(1)b	97.09(2)	O(2)a–Co(1)–N(1)b	94.30(1)	N(2)b–Co(1)–N(1)	77.39(1)
O(4)–Co(1)–N(1)b	100.54(1)	O(1W)–Co(1)–O(5)	100.19(1)	O(2)a–Co(1)–O(5)	94.45(9)
N(2b)–Co(1)–O(5)	93.35(11)	O(4)–Co(1)–O(5)	61.46(1)	N(1)b–Co(1)–O(5)	160.63(1)

Symmetry codes: a = x, -y, -0.5 + z; b = -0.5 + x, 0.5 - y, -0.5 - z for complex 1;

a = -0.5 + x, 0.5 - y, -0.5 - z; b = x, -y, -0.5 + z for complex 2

Table 2. Crystallographic Data and Structure Refinement Details for Complexes 1 and 2

	Complex 1	Complex 2
Formula	C ₄₄ H ₃₆ Cd ₂ N ₆ O ₁₃	C ₂₂ H ₂₁ CoN ₃ O ₈
Formula weight	1081.61	514.35
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
a (Å)	12.109(3)	13.690(2)
b (Å)	22.116(5)	21.091(3)
c (Å)	16.409(3)	15.636(2)
α (°)	90.00	90.00

To be continued

β (°)	103.248(6)	109.070(2)
γ (°)	90.00	90.00
Z	4	8
V (Å ³)	4277.4(16)	4266.9(10)
D_c (g·cm ⁻³)	1.680	1.601
μ (MoK α) (mm ⁻¹)	1.069	0.861
$F(000)$	2168	2120
Theta min-max (°)	3.15, 25.01	1.93, 25.01
Tot., uniq. data	27160, 3762	10794, 3771
R_{int}	0.1285	0.0503
Observed data ($I > 2\sigma(I)$)	1917	2370
R, wR ($I > 2\sigma(I)$)	0.0742, 0.2241	0.0498, 0.1307
S	1.039	1.067

2. 4 Solvent sensing experiment of complex 1

Well-grounded Cd-MOF powder (2 mg) was immersed in different organic solvents (2 mL) and treated by ultrasonication for 20 min. Then, the fluorescence response in the range of 380~580 nm was monitored upon excitation at 305 nm.

3 RESULTS AND DISCUSSION

3. 1 Crystal structure of $\{[\text{Cd}(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}]_n\}$ (1)

Complex 1 belongs to the monoclinic crystal system with space group $C2/c$. The asymmetric unit includes one Cd²⁺ ion,

one ligand, one coordinated and one free water molecules. As shown in Fig. 1a, the coordination center Cd(II) has a penta-coordinate center. All the carboxylic groups are monodentate coordinate. Among the coordinated O atoms, two of them come from two ligands and the last one from one coordinated water molecule. Two N atoms from one ligand adopt a bidentate chelate mode, showing a twisted trigonal bipyramidal configuration. The Cd–O distances range from 1.195(7) to 2.271(8) Å, and the Cd–N distances are 2.253(9) and 2.550(12) Å, all close to those of the reported Cd complexes^[22]. The main bond lengths and bond angles are shown in Table 1.

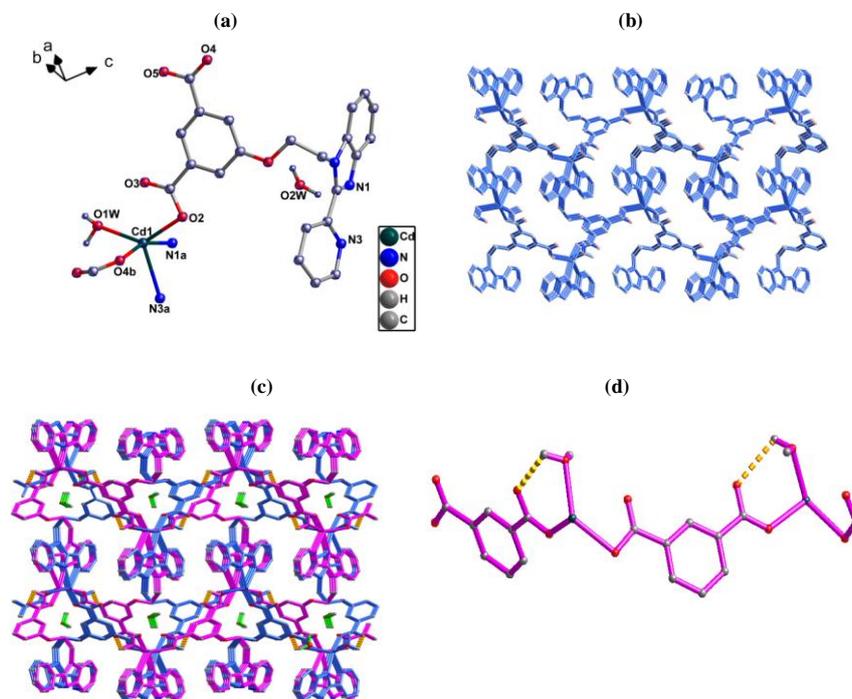


Fig. 1. (a) Coordination environment of Cd(II). $a = x, -y, -0.5 + z$; $b = -0.5 + x, 0.5 - y, -0.5 - z$. (b) Three-dimensional framework constructed by ligand and Cd²⁺. (c) 2-Fold penetrated frameworks. (d) Various H-bonds between uncoordinated O atoms and water molecules

All the O and N atoms are connected by Cd(II) to form a three-dimensional framework (Fig. 1b). Two three-dimensional frameworks penetrated together to reduce the void and stabilize the framework (Fig. 1c). Further study reveals that the coordinated water molecules connect the uncoordinated carboxylic O atoms by weak O–H··O interactions (Fig. 1d).

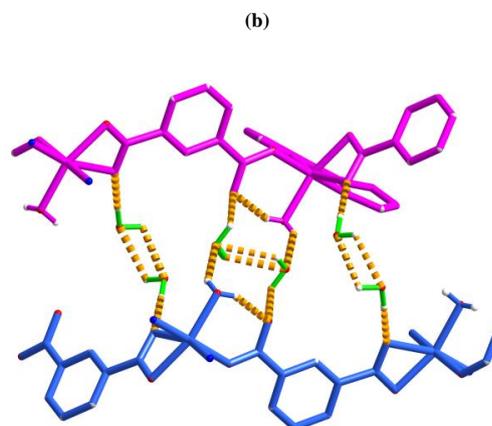
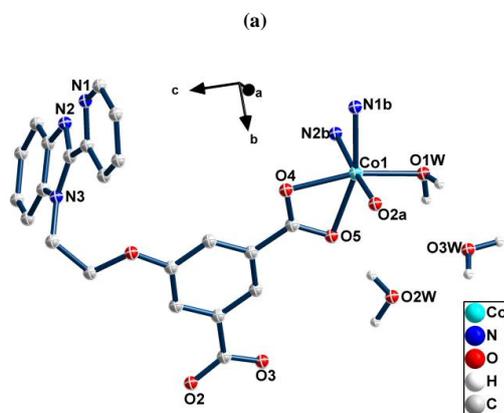


Fig. 2. Coordination environment of Co(II), $a = -0.5 + x, 0.5 - y, -0.5 - z$; $b = x, -y, -0.5 + z$.
(b) Various H-bonding between uncoordinated O atoms and water molecules

Table 3. Hydrogen Bond Lengths (Å) and Bond Angles (°) for Complex 2

D–H··A	d(D–H)	d(H··A)	d(D··A)	∠DHA
O(1W)–H(1WA)··O(3W)	0.91	2.05	2.855	147
O(1W)–H(1WA)··O(3)a	0.82	1.78	2.547	155
O(2W)–H(2WD)··O(5)	0.96	1.79	2.749	178

Symmetry code: (a) $x - 1/2, -y + 1/2, z - 1/2$

3.3 PXRD results and analysis

The XRD analysis was performed to confirm whether the crystal structures were true representative of the bulk material.

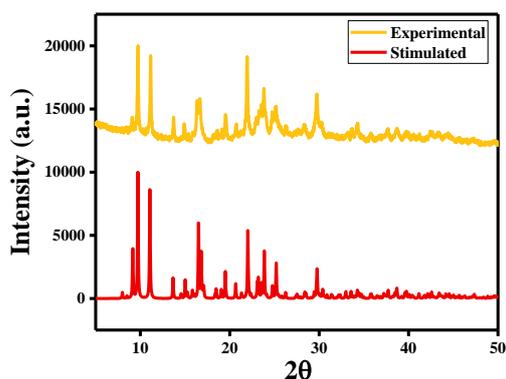


Fig. 3a. Powder X-ray diffraction pattern of the Cd-complex

The experiment and PXRD patterns depicted that the bulk synthesized materials and the measured single crystals are the same for both complexes. (Fig. 3a and 3b).

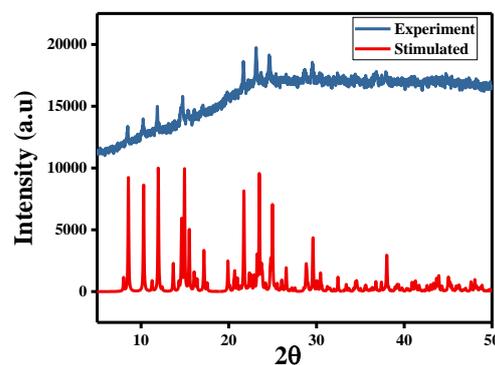


Fig. 3b. Powder X-ray diffraction pattern of the Co-complex

3.4 Thermal analysis

To investigate the thermal stabilities of Cd- and Co-complexes, both MOFs were subjected to thermogravimetric

analysis. For the Cd-complex, it can be observed from the graph (Fig. 4) that, there is a steady continuous weight loss from 45 to 250 °C, attributed to the release of lattice and

coordinated water. As the Cd-complex further absorbs heat at 370 °C, it further loses weight steeply due to the decomposition of the analytes of the ligand. It can also be seen from the graph (Fig. 4) of the Co-complex that, there is a steady continuous weight loss when the complex absorbs heat, from

45 to 230 °C attributed to loss of water. The Co-complex further absorbs heat at 350 °C and further loses weight steeply due to the decomposition of the analytes of the ligand. Both thermal behaviours depict good thermal stability.

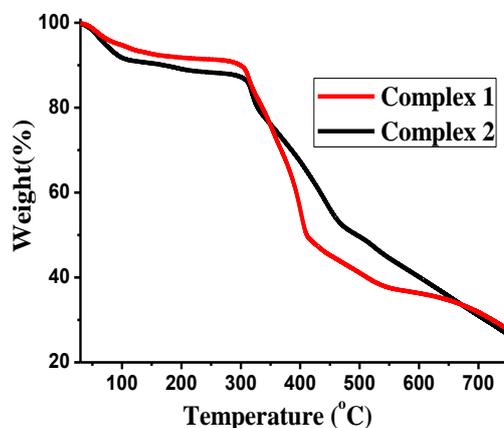


Fig. 4. TG patterns of complexes 1 and 2

3.5 Florescent properties of the Cd-complex

With much emphasis on the Cd-complex, its florescence sensing abilities were also studied. The Cd-complex was dispersed in varieties of solvents such as; acetone, ethanol (EtOH), acetonitrile (CH₃CN), chloroform (CH₂Cl₂), dichloromethane (DCM), just to mention a few. The Cd-complex

displays conspicuously high luminescent intensity in CH₂Cl₂, CH₃CN and DMA whiles exhibiting weaker intensity in DMF and MeOH. However, with comprehensive considerations of luminescent intensity and stabilities of complexes, H₂O was selected as the standard disperse solvent for further examination of florescent sensing performances for metal ions (Fig. 5).

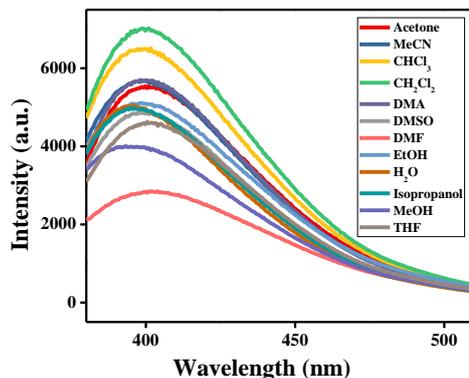


Fig. 5. Fluorescence intensity of Cd-complex dispersed in different solvents

With the fore-idea that the Cd-complex has luminescent properties, its luminescent abilities towards metal ions were further investigated. Some metal ions are recognized as highly toxic and acknowledged as undesirable since they are non-biodegradable, can accumulate in the environment and produce toxic effects on the environment hence the detection

of metal ions in the environment is deemed very essential to human and environmental safety. Thus, in this investigation, a series of metal ions were selected including Cr³⁺, Pb²⁺, Tb³⁺, Eu²⁺, Ag⁺, etc. Then, 2 mg of powdered Cd-complex was dissolved in 2 ml of water, and then sonicated to obtain an aqueous suspension. The photoluminescence spectra were

then analysed by adding 2 ml of the metal ion solutions into the aqueous solution of the Cd-complex. As shown in Fig. 6, under the same conditions, the fluorescence intensity of the Cd-complex was significantly quenched by the Fe^{3+} ions as

compared to the other metals, depicting that, the Cd-complex could be a good sensor material for the detection of Fe^{3+} ions in the environment.

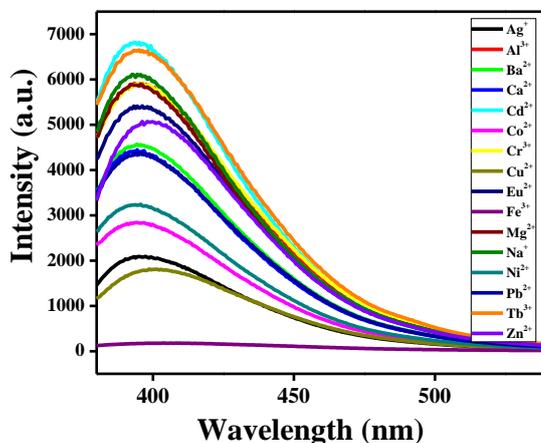


Fig. 6. Fluorescence spectra of Cd-complex (2 mg) in a solution of metal ions (2 mL, 0.1 mM) in H_2O

To further understand the luminescent quenching degree of the Cd-complex to Fe^{3+} ions, a detection limit experiment was conducted and the quenching curves were studied by Stern-Volmer equations; (S-V plot): $I_0/I = 1 + K_{SV} \times [M]$, where I_0 represents the intensity of the Cd-complex before the addition of the Fe^{3+} , I also represents the fluorescence intensity of the Cd-complex after the addition of Fe^{3+} ion solutions and the $[M]$ represents the concentration of Fe^{3+} ion respectively. The results obtained (Fig. 7) reveal that, when Fe^{3+} acted as a quencher, the fluorescence intensity of the Cd-complex significantly decreased. The S-V plot (Fig. 8) deduced depicts

good linear relationship between the luminous intensity and low concentrations of Fe^{3+} and the correlation coefficient obtained was up to 0.9723. However, the S-V curve deviated from the linear relationships at higher concentrations. According to the deductions made from the S-V plot and the equations, the Limit of Detection (LOD) reaches 0.036875M and the K_{SV} value obtained was 2.4×10^3 . This result further elaborates that the Cd-complex synthesized could be used as potential probe for the detection of Fe^{3+} ions in the environment thereby enhancing environmental safety.

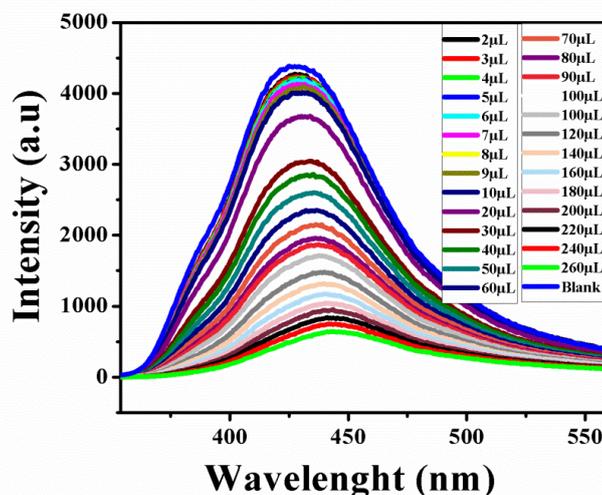


Fig. 7. Fluorescence spectra of Cd-complex with different amounts of Fe^{3+}

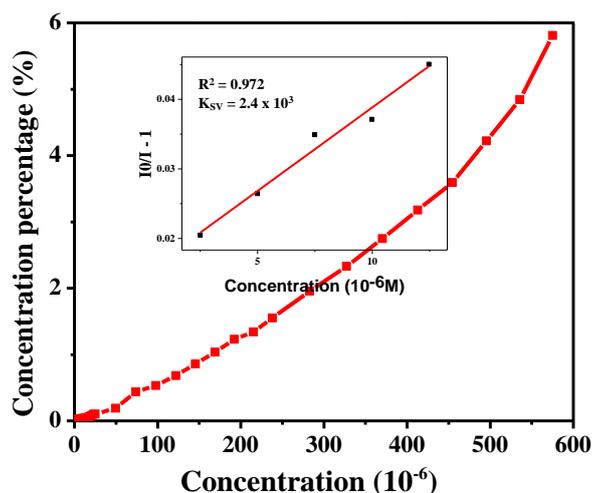


Fig. 8. Quenching percentages upon gradual addition of Fe^{3+}

4 CONCLUSION

In summary, two LMOFs (Cd- and Co-complex) were synthesized successfully under solvothermal conditions and characterized. Both exhibit good thermal stability. With much emphasis on the Cd-complex, its photoluminescence properties were further investigated and it was found that it has good sensitivity for the detection of Fe^{3+} ions. This selective

effect is due to the quenching mechanism caused by the competitive absorption of the excitation energy and host-guest interactions between the MOF and Fe^{3+} ions, thus making the Cd-complex an excellent MOF probe for the detection of Fe^{3+} ions. Further exploration of the abilities of the Cd-complex can expand our knowledge in its applications in other areas such as the chemical and environmental fields.

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