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Recognition of trace organic pollutant and toxic metal ions *via* a tailored fluorescent metal–organic coordination polymer in water environment†

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A novel fluorescence material $\text{H}_2\text{Sr}_2(\text{bqdc})_3(\text{phen})_2$ (**1**) for trace recognition of organic pollutant and toxic metal ions is designed and prepared by two weak fluorescent ligands and Sr^{2+} . The latter was selected although it played no role in the modulation process of luminescence and despite low-cost, alkaline earth, metal–organic coordination polymers lacking competitive functionality. The strong fluorescence of the fluorescence material was based on the propeller configuration of the metal–organic coordination polymer, which was characterized by X-ray single crystal diffraction showing that the N active sites inside the crystal channels can interact with external guests. Convenient fluorescence detection of 3-AT can be realized using an ultraviolet lamp and test strip and the determination of Cd^{2+} showed good reusability with a detection limit of $1 \times 10^{-9} \text{ mol L}^{-1}$, which is lower than the standard stipulated by the Environmental Protection Agency. Detailed experiments results revealed that the material was a promising candidate for specifically recognizing amitrole and Cd^{2+} because of its selective fluorescence quenching and sensitive detection in water.

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Introduction

As a result of global development of industrial and agricultural production, the intensity of environment pollution is becoming increasingly serious.¹ Toxic organic and inorganic contaminations in water environment are one of the most problematic issues because of their negative effect on the human body. An example of such an organic pollutant is amitrole (3-AT), a widely used herbicide that has strong biological toxicity and carcinogenicity, and can enter the human body when dissolved in water.² A well-known example of heavy-metal poisoning is the itai-itai disease (itai = pain in Japanese), which was originally caused by cadmium pollution in the Jinzhu River Basin in Japan, and is chronic cadmium poisoning caused by long-term consumption of polluted water.³

The water quality of samples needs to be determined using an appropriate standard.⁴ Therefore, it is important to develop effective and efficient detection methods to measure pollution

levels. To date, various techniques have been used for this purpose, including electrochemistry,⁵ mass spectroscopy,⁶ gas chromatography,⁷ ion mobility spectrometry,⁸ biological detection⁹ and other techniques.¹⁰ Because of its high sensitivity, low cost and simple pretreatment, fluorescence sensing technology has attracted considerable attention in water-quality detection.¹¹

Fluorescent metal–organic coordination polymers (MOCPs) have shown huge potential in chemical sensing because their hybrid structures can offer tunable fluorescence, and have been extensively studied for sensing molecules,¹² metal ions,¹³ gases,¹⁴ vapors¹⁵ and explosives,¹⁶ *etc.* With well-defined constructions, dense packed pore structures, excellent stability and potential optical properties, luminescence MOCPs have attracted increasing attention due to the promise they show in sensing. Very recently, MOCPs-based sensing materials have showed very promising results in detection of organic molecules or metal ions in water.¹⁷ Well-defined MOCPs possess unique, tunable optical properties, and their strong fluorescence intensity and internal active sites are advantageous for fluorescence sensing.¹⁸

Researchers are eager to obtain fluorescence MOCPs with the configuration of a propeller.¹⁹ Non-planar fluorescent molecules are often characterized by an aggregation-induced emission (AIE) effect; in particular, a propeller configuration can largely prevent close $\pi \cdots \pi$ interactions, thereby inhibiting nonradiative deactivation, leading to fluorescence

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Table 1 Crystallographic data and structure refinement summary for 1

Data	Complex
Formula	C ₈₄ N ₁₀ O ₁₂ H ₄₈ Sr ₂
Formula weight (g mol ⁻¹)	782.28
T (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Triclinic
Space group	P $\bar{1}$
a (Å)	11.6980(13)
b (Å)	13.2000(15)
c (Å)	13.5640(15)
α (°)	64.143(2)
β (°)	83.737(2)
γ (°)	67.919(2)
V (Å ³)	1742.8(3)
Z	2
D _{calcd} (g cm ⁻³)	1.491
μ (mm ⁻¹)	1.606
F(000)	794
θ range (°)	1.84–25.00
Goodness-of-fit on F ²	1.105
R ₁ ^a [$I > 2\sigma(I)$]	0.0658
wR ₂ ^b (all data)	0.2164

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b wR_2 = \left[\frac{\sum [w(F_o^2) - (F_c^2)^2]}{\sum [w(F_o^2)]} \right]^{1/2}.$$

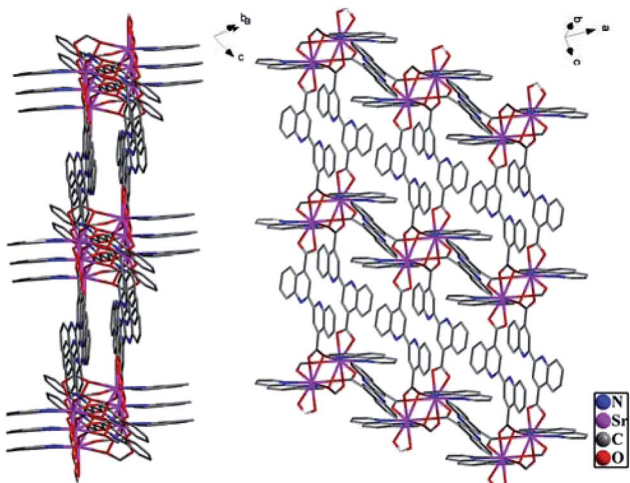


Fig. 1 Illustration of the MOCPh₂Sr₂(bqdc)₃(phen)₂. All of the H atoms are omitted for clarity.

Obviously, this complex possessed a porous structure with suitable dimensions to improve accessibility of the external metal ions to the active sites and increase the response rate to specific recognition.

With rigid fan-shaped structure, six bqdc and two phen coordinated with a Sr²⁺ cluster centre to form a segment of H₂Sr₂(bqdc)₃(phen)₂, which shows a very interesting configuration similar to a propeller as shown in Fig. 2a. Complex 1 does not dissolve in water, and the thermogravimetric analysis (TGA) revealed that 1 is a good heat-resistant material until 200 °C, which is stable enough to allow external ions or



Fig. 2 (a) The crystal structure of the title complex. (b) The emission intensities of phen, bqdc and H₂Sr₂(bqdc)₃(phen)₂.

molecules to enter inside its channels (Fig. S1†). The powder X-ray diffraction (XRD) pattern of as-synthesized 1 was identical to the simulated data, indicating that the structural integrity of 1 is maintained (Fig. S2†).

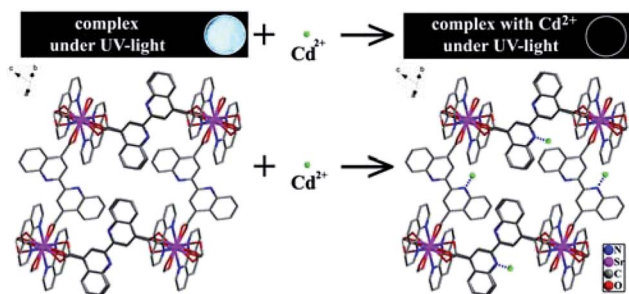
Fluorescence properties

The emission spectra of ligands bqdc and phen showed weak fluorescence peaks with a maxima at 403 nm ($E_x = 266$ nm) and 363 nm ($E_x = 297$ nm), respectively (Fig. S3 and 4†). Both of these broad peaks were ascribed to $\pi \cdots \pi^*$ electronic transitions inside the ligands. The emission spectrum of complex 1 contained peaks at 426 and 492 nm ($E_x = 365$ nm) (Fig. S5†). The red shift and enhanced intensity of emission observed for 1 are attributed to the increased rigidity of the ligands upon coordination with the alkaline earth metal ion Sr²⁺, which suppresses intramolecular proton transfer.²⁵ Surprisingly, compared with the emission intensities of bqdc and phen, the emission intensity of 1 greatly increased by around 21 or 101 times, respectively (Fig. 2b). It is believed that the propeller configuration of 1 limited the close $\pi \cdots \pi$ interactions at the most extent, which extremely decreases the amount of energy lost through nonradiative decay and thus enhances the intensity of fluorescence emission from 1 compared with that from the ligands.

Fluorescence responses to organic molecules

Considering the strong emission and good stability of 1, we examined its fluorescence responses to organic molecules, which can potentially affect human health and environmental quality. A series of fluorescence spectroscopy measurements were performed in aqueous solution using different organic molecules including amitrole (3-AT), 1,4-dinitro-benzene (1,4-NB), 2,4,6-trinitrotoluene (TNT), triethylamine (Et₃N), hexane (Hex), toluene (PhMe) and ethyl acetate (EtOAc). The experimental process has been described in Section 2.3. The experimental results showed that indistinct emission decrease occurred for all of the organic molecules except 3-AT. Indistinctive emission decrease (40.57% for 1,4-NB, 31.64% for TNT, 12.81% for EtOAc, 12.01% for Hex, 6.78% for PhMe and 9.10% for Et₃N) was observed for other organic molecules. Remarkably, a distinct emission change was observed for 3-AT, with 98.58% quenching of emission intensity (Fig. 3, S6 and Table S1†). According to a large number of repeated experiments with





Scheme 1 The fluorescence quenching mechanism simulation of the complex with Cd^{2+} metal ion.

As previously mentioned, the N active sites of ligand bqdc are dispersed in the channels of **1**. To explore the mechanism of luminescence quenching, we evaluated the interaction between active sites and guest ions. Regarding the quenching mechanism of **1**, it can be deduced that the active sites of bqdc interacted with external metal ions to achieve a sensing effect, which was also predicted in a simulation (Scheme 1). The strong interaction between the N active sites and Cd^{2+} can perturb the electronic structure of the ligand considerably, and then enhance the efficiency of energy transfer from the ligand to Cd^{2+} . This promoted intramolecular energy transfer in **1**, leading to the fluorescence quenching. These findings are similar to those mentioned in previous work reported including that by our group.²⁸

The reusability of a sensing material is of great importance to commercial feasibility.²⁹ Complex **1** showed excellent reversibility upon simply washing with ethanol or deionized water several times. It was observed that **1** was still stable after being reactivated four times, as confirmed by infrared spectroscopy and XRD patterns (Fig. S12 and S13[†]).

Conclusions

Fluorescent material **1** was synthesized from a non-luminous alkaline earth metal ion, Sr^{2+} , and two weak fluorescence ligands bqdc and phen. Its propeller structure can help to limit the close $\pi \cdots \pi$ interactions that decreased nonradiative decay, greatly enhancing the emission intensity of **1** compared with that of the uncoordinated ligands. Experiments illustrated that **1** can specifically recognize 3-AT and Cd^{2+} through fluorescence quenching. The quenching mechanism involved competitive coordination substitution and intramolecular energy transfer. The strong fluorescence intensity, selective fluorescence alteration, appropriate stability and sensitive detection of **1** make it a promising candidate as sensors for specifically recognizing organic pollutant 3-AT and quantitative detection of toxic Cd^{2+} in water. Moreover, 3-AT can be conveniently detected by an ultraviolet lamp and test strip, and Cd^{2+} can be sensed with good reversibility and reproducibility with a detection limit of $1 \times 10^{-9} \text{ mol L}^{-1}$. The present study represents a large step forward in the effort to develop novel MOCPs for use as fluorescence sensors. Further investigations on modulating the optical properties of MOCPs, especial ligand-based ones, are underway.

Conflicts of interest

There are no conflicts to declare.

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