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Short communication

# Selective sensing of 2,4,6-trinitrophenol and detection of the ultralow temperature based on a dual-functional MOF as a luminescent sensor

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ABSTRACT

A novel 3D Cd(II) MOF, $\{[Cd(Ccbp^-)(4.4'\text{-}bpy)\cdot H_2O]\cdot(ClO_4^-)\cdot 2H_2O\}$ (**1**), ($Ccbp^-$ = 3-carboxy-1-(4-carboxybenzyl)pyridin-1-ium, 4.4′-bpy = 4.4′-bipyridine), has been successfully synthesized and characterized. Complex **1** possesses a 3D 4-fold interpenetrating **dia** network with a pyridine cation basic skeleton. This Cd-MOF **1** can be applied as the first potential dual-functional luminescent sensing material for high selective and recyclable sensing of 2,4,6-trinitrophenol and quantitatively detecting the ultralow temperature from 10 to 60 K.

In the past decades, the selective and rapid detection of the nitro compounds, such as nitromethane (NM), nitrobenzene (NB), nitrotoluene (NT) and 2,4,6-trinitrophenol (TNP), has drawn great interest due to its importance in homeland security, civilian safety, and environmental protection. Among such nitro compounds, TNP is the most well-known explosive and commonly used for military applications and terrorism all over the world [1]. Although many methods like gas chromatography [2], ion mobility spectrometry [3], mass spectrometry [4] and X-ray detection [5] have been developed for explosive detection, these detection techniques are limited by their equipment demands, time-consuming and cost drawbacks. Compared with those traditional methods, fluorescence detection has obvious advantages and gains more attentions owing to its high sensibility, simplicity, short response time and convenient detection [6]. Taking into account this kind of materials are still defective, so the synthesis and development of new materials for fluorescent detection of nitro compounds are still a challenge work. The immense interests in the development of luminescent materials based on metal–organic frameworks (MOFs) is of considerable increasing in recent years due to their intriguing structural topologies and potential applications in high selectivity and sensitivity for detecting anions [7], cations [8], explosives [9], small molecules [10] and vapor [11]. Recently, a large amount of luminescent MOF sensors for detecting the nitro compounds have been reported, most of which exhibit high selectivity and most of which were constructed by $d^{10}$ transition metal ions and π-conjugated ligands [12]. However, those luminescent MOFs reported so far exhibit mainly mono-function detection. Only a few rare MOFs in dual functional luminescent detection have been reported [13].

Temperature is one of the most fundamental physical properties in many scientific fields, and temperature-dependent luminescence is a common phenomenon. Besides conventional thermometers, luminescent sensors based on MOFs are considered to be attractive alternatives for sensing and on-line monitoring temperature because of their accuracy, non-invasive nature, fast response, and working capability in strong electric or magnetic fields [14]. Over the past few years, a large number of temperature probes based on MOFs have been realized [15]. However, only a small number of these luminescent MOFs sensors have been reported which are capable of quantitative detection [16].

As an effective combination of the above mentioned aspects, we design a new 3D Cd-MOF, $\{[Cd(Ccbp^-)(4.4'\text{-}bpy)\cdot H_2O]\cdot(ClO_4^-)\cdot 2H_2O\}$, as a luminescent sensor not only exhibits high selective sensing of TNP in the ethanol solution but also can quantify the temperature from 10 K to 60 K. To the best of our knowledge, no single Cd-MOF that exhibiting dual-function of detecting TNP and temperature at the same time has been reported. Thus, this is the first Cd-MOF that can selectively detect TNP and quantify the temperature.

The zwitterion ligand $H_2CcbpCl$ synthesized and characterized by $^1H$ NMR and $^{13}C$ NMR (Figs. S1 and S2) [17]. The single crystal of **1** suitable for X-ray diffraction studies was obtained by the solvothermal reaction of $Cd(ClO_4)_2\cdot 6H_2O$ (0.3 mml), $H_2CcbpCl$ (0.1 mml), NaOH (0.2 mml) and 4.4′-bipyridine (0.1 mml) in 10 ml $H_2O$/ethanol (1:1). The detailed procedure of synthesis of ligand and complex **1** are given in the ESI.

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**Table 1**
Crystal data and structure refinement for **1**.

| Compound reference | Cd-MOF **1** |
|---|---|
| Chemical formula | $C_{24}H_{24}CdClN_3O_{11}$ |
| Formula mass | 678.31 |
| Crystal system | Monoclinic |
| $a$/Å | 11.9869(15) |
| $b$/Å | 17.717(2) |
| $c$/Å | 12.6414(16) |
| $\alpha$/° | 90 |
| $\beta$/° | 103.650(2) |
| $\gamma$/° | 90 |
| Unit cell volume/$Å^3$ | 2608.8(6) |
| Temperature/K | 298(2) |
| Space group | $P2(1)/n$ |
| No. of formula units per unit cell, $Z$ | 4 |
| Radiation type | MoKα |
| Absorption coefficient, $\mu$/$mm^{-1}$ | 1.007 |
| No. of reflections measured | 17,719 |
| No. of independent reflections | 6155 |
| $R_{int}$ | 0.0644 |
| Final $R_1$ values ($I > 2\sigma(I)$) | 0.0496 |
| Final w$R(F^2)$ values ($I > 2\sigma(I)$) | 0.1132 |
| Final $R_1$ values (all data) | 0.0930 |
| Final w$R(F^2)$ values (all data) | 0.1420 |
| Goodness of fit on $F^2$ | 0.971 |
| CCDC number | 1455989 |

Single-crystal X-ray diffraction study reveals that complex **1** crystallizes in the monoclinic system with $P2(1)/n$ space group. As shown in Fig. 1a, Cd1 is coordinated by two nitrogen atoms from two different 4.4′-bipyridine, three oxygen atom from two carboxylate oxygen atoms of two different $Ccbp^-$ ligands and the other one oxygen atom of coordination water. The coordination environment of the central $Cd^{2+}$ ion, represented by a coordination polyhedron, is a pseudo-octahedral coordination geometry with the Cd—N/O bond distances for Cd1 fall in the range between 2.276(4) and 2.405(3) Å (Tables 1 and 2, ESI), which are close to those reported in Cd-coordination polymers [18]. Next, each deprotonated $Ccbp^-$ ligand ($\mu_2$-$\eta^2$:$\eta^1$) and each the 4.4′-bipyridine ligand connect to the adjacent two $Cd^{2+}$ ions, resulting in a 3D **dia** network with large cavities (Fig. 1b and c). Furthermore, the large diamondoid cage permits the adjacent equivalent **dia** nets to entangle each other, forming a 4-fold interpenetrating **dia** network (Fig. 1d), in which the $ClO_4^-$ anions are located. It is noteworthy that there are pyridine cations pointing to the zwitterionic pyridinium ligand $Ccbp^-$ of **1**, which can be used to explore the sensing properties. The TG curve for **1** shows a gradual weight loss of 9.1% between 80 and 186 °C, which can be ascribed to the removal of one coordinated water molecule and two free water molecules (Fig. S4). Furthermore, the PXRD patterns for complex **1** is shown in Fig. S3. The diffraction peaks of the experimental patterns are in good consistency with the simulated data, indicating that the synthesized bulk materials are consistent with the determined single-crystal structure.

Considering the previous studies have shown that $Cd^{2+}$ coordination polymers exhibit luminescent properties [19], the luminescence spectra of the free $Ccbp^-$ ligand and the as-synthesized sample of **1** in solid state were investigated at room temperature under excitation at 325 and 296 nm, respectively. (Fig. 2) The emission spectrum of the free ligand exhibits two broad emission bands at 384 and 427 nm, which can be attributed to the ligand-centered electronic transition [20] (Fig. 2). Similar to the free $Ccbp^-$ ligand, the complex **1** displayed emission peak at 367 nm. Compared with the free ligand, the **1** showed a weaker emission band blue-shifted to different extents, which

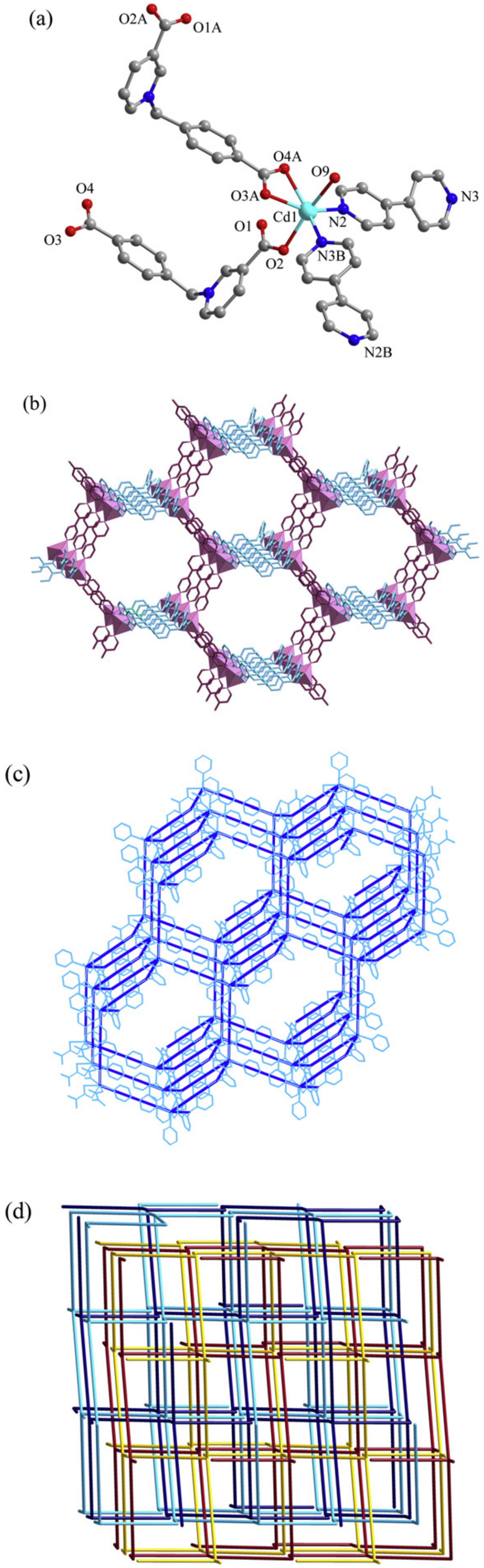

**Fig. 1.** Structure of **1**. The guest species are omitted for clarity. (a) Coordination environment of the metal atom and ligand. Symmetry codes: (A) x + 1/2, −y + 3/2, z + 1/2; (B) x − 1/2, −y + 1/2, z + 1/2. (b) The 3D network of **1**. (c) The 3D network with topology of **1**, (d) Topological representation of the 3D **dia** topology of **1** with 4-fold interpenetration.