

# A Fluorescent Magnesium-Based Metal-Organic Framework with a Sensitive Sensing Property for Carbon Disulfide

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**Abstract** Presented here are the solvothermal synthesis, structural characterization and fluorescent properties of a magnesium metal-organic framework (Mg-MOF), namely  $[\text{Mg}_4(1,4\text{-NDC})_4(\text{DMA})_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2] \cdot \text{DMA} \cdot \text{CH}_3\text{OH}$  (**1**, 1,4- $\text{H}_2\text{NDC}$  = 1,4-naphthalene dicarboxylic acid, DMA = *N,N'*-Dimethylacetamide). Single-crystal X-ray diffraction studies revealed that compound **1** crystallized in the monoclinic space group  $P2_1/c$  (No. 14) with  $a = 2.06090(12)$  nm,  $b = 2.21014(13)$  nm,  $c = 1.50385(10)$  nm,  $\beta = 111.399(3)^\circ$ ,  $V = 6.3776(7)$  nm<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.403$  g/cm<sup>3</sup>,  $F(000) = 2824$ ,  $R = 0.0596$  and  $wR = 0.1225$  ( $I > 2\sigma(I)$ ). The structure of compound **1** features a three-dimensional (3D) network constructed from the 1,4-NDC ligands as bridging linkers and binuclear magnesium clusters as the secondary building units, with cages occupied by different solvent molecules of DMA and CH<sub>3</sub>OH. Notably, fluorescence studies revealed that compound **1** demonstrated sensitive sensing towards carbon disulfide (CS<sub>2</sub>); remarkably, the fluorescence intensity of compound **1** could be almost completely quenched at the low concentration of 0.4% (volume fraction) of CS<sub>2</sub>. Thermal stability was investigated by thermogravimetric analysis which indicated that compound **1** could be stable up to 140 °C.

**Keywords** magnesium; metal-organic framework; fluorescence sensor; carbon disulfide

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With growing concerns over the major ecosystem and health risk, the detection of harmful volatile organic compounds (VOCs) has attracted tremendous attention over the decades. Acting as a typically toxic molecule of VOCs, carbon disulfide (CS<sub>2</sub>) can trigger severe multiorgan diseases when people are continuously exposed to it even in extremely low concentrations<sup>[1-2]</sup>. Currently, well-trained canines, sophisticated analytical instruments, chemiluminescence-based methods and nanoprobe are used for CS<sub>2</sub> sensing<sup>[3-6]</sup>. However, the above detection methods have different degrees of weakness, such as low sensitivity, high costs and high complexity. Hence, it is a significant but challenging task to explore new sensing materials for rapid and selective detection of the CS<sub>2</sub>.

Fluorescent metal-organic-frameworks (MOFs) have received much attention due to their potential application in sensitive and selective detection of hazardous substances<sup>[7-11]</sup>. As a new type of chemosensor, the fluorescent detection based on MOFs can be conveniently monitored by using changes in fluorescent

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properties caused by host-guest interactions as interpretable signals<sup>[12]</sup>. Magnesium as a candidate metal ion for the construction of MOFs has caused the climax of researches over the past few years because of its low-cost, nontoxicity and especially the unique  $3d^0$  electron configuration favoring ligand-centered emission<sup>[13-15]</sup>. Some Mg-MOFs have been explored as fluorescence sensors for typical VOCs and water, such as  $[\text{Mg}_2(\text{BINDI})_2(\text{DMF})_2] \cdot \text{H}_2\text{O}$  ( $\text{H}_4\text{BINDI} = N, N'$ -bis(5-isophthalic acid) naphthalenediimide)<sup>[14]</sup>,  $[\text{NH}_2(\text{CH}_3)_2][\text{Mg}_3(\text{NDC})_{2.5}(\text{HCO}_2)_2(\text{DMF})_{0.75}(\text{H}_2\text{O})_{0.25}] \cdot 1.25\text{DMF} \cdot 0.75\text{H}_2\text{O}$  ( $\text{H}_2\text{NDC} = 1,4$ -naphthalene dicarboxylic acid)<sup>[16]</sup>,  $\text{Mg}_3(\text{OH})_2(\text{BTEC})_2(\text{H}_2\text{O})_4 \cdot 11\text{H}_2\text{O}$  ( $\text{H}_4\text{BTEC} = 1,2,4,5$ -benzenetetracarboxylic acid)<sup>[17]</sup> and  $[\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_2] \cdot \text{DMA}$  ( $\text{H}_4\text{dhtp} = 2,5$ -dihydroxy-terephthalic acid)<sup>[18]</sup>. Herein, we present the solvothermal synthesis, crystal structure and characterizations of a new fluorescent Mg-MOF named as  $[\text{Mg}_4(1,4\text{-NDC})_4(\text{DMA})_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2] \cdot \text{DMA} \cdot \text{CH}_3\text{OH}$  (**1**). Fluorescence measurements demonstrated that the title compound displayed a purple light emission ( $\lambda_{\text{em}} = 385 \text{ nm}$ ) and further fluorescent study indicated that compound **1** exhibited a selective and sensitive sensing property for  $\text{CS}_2$  with a low concentration.

## 1 Experimental

### 1.1 Reagent and Instrument

All reagents and chemicals were purchased from commercial sources and used without further purification.  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $\geq 99\%$ , Tianjin BoDi Chemical Co., Ltd.); 1,4- $\text{H}_2\text{NDC}$  ( $\geq 95\%$ , Beijing HWRK Chem Co., Ltd.); DMA ( $\geq 99\%$ , Shanghai Titan Chemical Co., Ltd.); methanol anhydrous ( $\geq 99.5\%$ , Shanghai Titan Chemical Co., Ltd.). Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Miniflex II diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154178 \text{ nm}$ ). Elemental analyses (EA) of C, N, H were performed on a German Elementary Vario III instrument. Thermogravimetric analysis (TGA) was carried out with a NETZACH STA 449F3 unit at a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$  under a nitrogen atmosphere. Emission and excitation spectra of compound **1** in the solid state and at a suspension system were recorded on a Perkin-Elmer LS55 luminescence spectrometer at room temperature.

### 1.2 Synthesis of compound 1

A mixture of 1 mmol  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.256 g) and 1 mmol 1,4- $\text{H}_2\text{NDC}$  (0.216 g) in 4 mL DMA ( $N,N$ -dimethylacetamide) and 1 mL anhydrous methanol was sealed into a stainless steel reactor with a 20 mL teflon-lined bomb. The mixture was heated at  $130 \text{ }^\circ\text{C}$  for 3 days and then was slowly cooled to room temperature. The colorless block-shaped crystals were obtained after being filtered and air-dried. Yield, 84.3% (0.284 g) based on Mg. Anal. (calc.) for compound **1**: C 55.90% (56.16%), H 4.82% (5.01%), N 3.08% (3.12%).

### 1.3 Determination of crystal structure

A suitable single crystal of compound **1** was carefully selected under an optical microscope and glued to a thin glass fiber. The intensity data were collected on a SuperNova CCD diffractometer with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.071073 \text{ nm}$ ) at  $100(2) \text{ K}$ . The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELX-2016 program package<sup>[19]</sup>. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms bonded to carbon were located by geometrical calculations, while those for O atoms were located from difference-Fourier maps and refined with restrained O-H distances. The empirical formula of compound **1** was further confirmed by the EA and TGA results. The crystallographic data and details of structural refinements for compound **1** are listed in Table 1.

Table 1 Crystallographic data and structural refinement details for compound 1

Empirical formula	C <sub>63</sub> H <sub>67</sub> Mg <sub>4</sub> N <sub>3</sub> O <sub>24</sub>	<i>D</i> <sub>calc.</sub> /(g·cm <sup>-3</sup> )	1.403
Formula mass	1 347.431 00(2)	λ/nm	0.071 073
<i>T</i> /K	100(2)	μ/mm <sup>-1</sup>	0.142
Crystal system	Monoclinic	<i>F</i> (000)	2 824
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	Reflections measured	28 773
<i>a</i> /nm	2.060 90(12)	Independent reflections	12 199
<i>b</i> /nm	2.210 14(13)	No. of parameters	878
<i>c</i> /nm	1.503 85(10)	GOF on <i>F</i> <sup>2</sup>	1.033
α/(°)	90	<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.059 6
β/(°)	111.399(3)	<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.122 5
γ/(°)	90	<i>R</i> <sub>1</sub> [all data]	0.089 9
<i>V</i> /nm <sup>3</sup>	6.377 6(7)	<i>wR</i> <sub>2</sub> [all data]	0.146 1
<i>Z</i>	4	CCDC	1552691

*a.*  $R_1 = \Sigma ||F_o| - |F_c| || / \Sigma |F_o|$ ,  $wR_2 = \{ \Sigma w[ (F_o)^2 - (F_c)^2 ]^2 / \Sigma w[ (F_o)^2 ]^2 \}^{1/2}$ .

1.4 Fluorescence detection measurements

The fluorescence properties of compound **1** and the 1,4- H<sub>2</sub>NDC ligand were investigated in the solid state at room temperature and the fluorescent spectra were recorded. Then 2 mg of compound **1** ( the as-made crystalline sample of compound **1** was loaded into an agate mortar and was manually ground with the pestle to afford a fine powder ) was dispersed in 2 mL of CS<sub>2</sub>, CH<sub>3</sub>OH, acetone, DMA and acetonitrile, respectively. After ultrasonic treatment for a few seconds, the suspension was placed in a quartz cell of 1 cm width for fluorescence detection. Detailed detections were carried out by gradually adding the CS<sub>2</sub> as quenchers in an incremental fashion with a pipette. The corresponding fluorescent spectra were recorded at 298 K. For all the measurements, the dispersed suspensions of compound **1** were excited at λ<sub>ex</sub> = 345 nm ( λ<sub>em</sub> = 385 nm ) and the corresponding emission wavelengths were monitored from 360 nm to 650 nm.

2 Results and discussion

2.1 Crystal structure descriptions

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c*. The crystallographic asymmetric unit contains one formula unit. All the Mg<sup>2+</sup> ions are six-coordinated except that there are some differences in the coordinated modes. The Mg(1) and Mg(3) atoms have similar coordination modes that are coordinated by five carboxylic O atoms from four 1,4-NDC<sup>2-</sup> ligands ( one carboxylic group adopts a chelating coordination mode ) and one O atom from a water molecule ( Fig. 1A ) ; while the Mg(2) and Mg(4) are both coordinated by four carboxylic O atoms from four 1,4-NDC<sup>2-</sup> ligands in a monodentate way and one O atom from a methanol molecule and one O atom from a DMA molecule ( Fig. 1A ). The Mg—O bond lengths range from 0.1991(3) nm to 0.2206(3) nm, which are comparable to those in the reported magnesium-carboxylate compounds<sup>[20-23]</sup>. As shown in Fig.1B, the 1,4-NDC ligands ( **L1**, **L2**, **L3**, **L4** ) adopt different coordination modes which can be depicted as ( *k*<sup>1</sup>-*k*<sup>1</sup>-μ<sub>2</sub> )-( *k*<sup>1</sup>-*k*<sup>1</sup>-μ<sub>2</sub> )-μ<sub>4</sub> ( **L1** and **L3** ) and ( *k*<sup>1</sup>-*k*<sup>1</sup>-μ<sub>2</sub> )-( *k*<sup>1</sup>-*k*<sup>2</sup>-μ<sub>2</sub> )-μ<sub>4</sub> ( **L2** and **L4** ), respectively.

As shown in Fig.1C and Fig.1D, there exist corner-shared coordination polyhedra of dinuclear [Mg1Mg2] and [Mg3Mg4] units in the structure which can be viewed as the secondary building units(SBU) for compound **1**. Then, the adjacent [Mg1Mg2] and [Mg3Mg4] units are, respectively, interconnected by the COO<sup>-</sup> groups of ligands **L1** and **L3** to form one-dimensional ( 1D ) infinite chains of [—Mg1—Mg2—Mg1—Mg2—] and [—Mg3—Mg4—Mg3—Mg4—] along the *c*-axis. Further, each [—Mg1—Mg2—Mg1—Mg2—] chain connects to four adjacent [—Mg3—Mg4—Mg3—Mg4—] chains by the ligands **L3** and **L4** to form a 3D skeleton. The coordinated and free DMA, methanol, water molecules

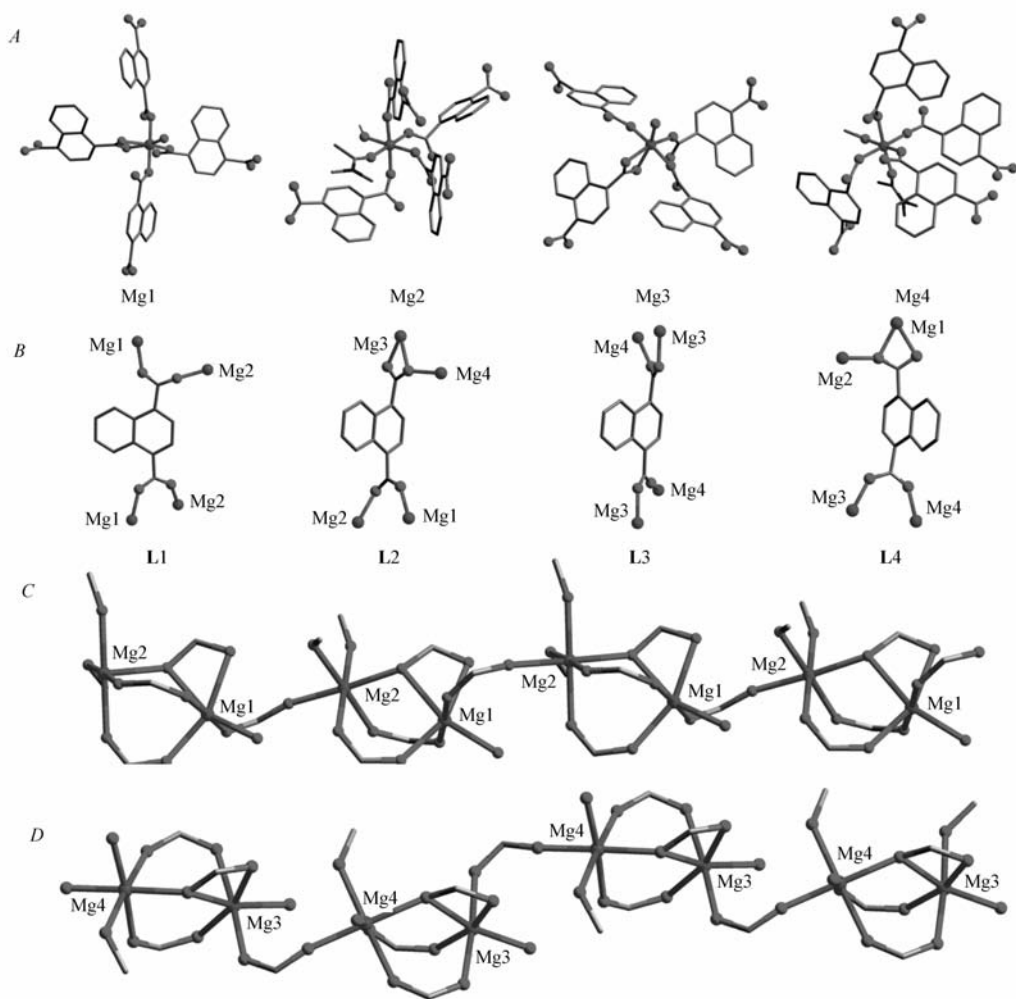


Fig. 1 The coordination environments of Mg atoms(A), coordination modes of the four crystallographically independent 1,4-NDC<sup>2-</sup> ligands(B), and the 1D chains in compound **1** extended along the *c* axis(C,D)

settle in the cages of the 3D framework(Fig. 2A). The solvent accessible volume is 43.6% if all the solvent molecules are removed according to the calculation performed by PLATON analysis. Topologically, when regarding the 1,4-NDC<sup>2-</sup> ligands and each dinuclear secondary building unit as 3-connected and 5-connected nodes respectively, the structure of compound **1** could be simplified as a typical fsc-3, 5-C2/*c* topology, Fig. 2B.

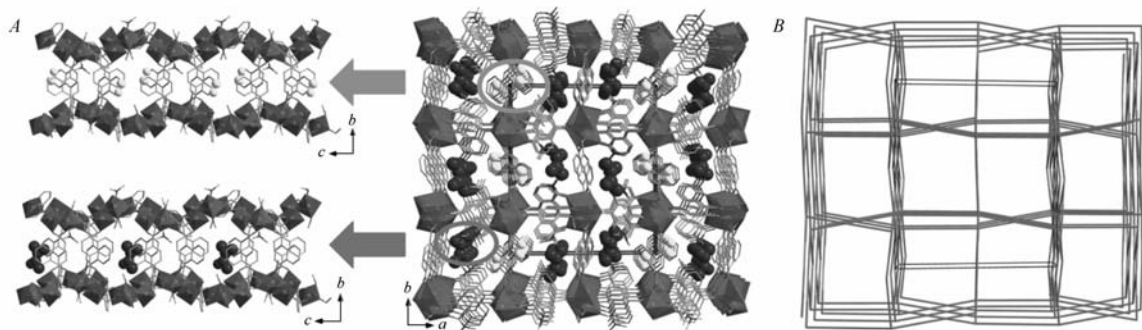


Fig. 2 View of the 3D framework of compound **1** along the *c* axis showing the cages in which the DMA and methanol molecules are filled(A) and the topology of compound **1**(B)

## 2.2 Thermal stability

The phase purity of compound **1** was confirmed by PXRD (see Fig. S1 in Supporting Information) carried out with the polycrystalline sample of compound **1**. Thermogravimetric analysis of compound **1** was performed under a N<sub>2</sub> atmosphere from 25 to 800 °C with a heating rate of 10 °C /min on pure powdered sample. The thermogravimetric curve for compound **1** is shown in Fig. 3. The 9.01% mass loss from room temperature (RT) to ~180 °C should be attributed to the loss of the free guests (calcd. 8.84%); the 19.72% mass loss of compound **1** from 180 to 500 °C corresponds to the departure of the coordinated water, CH<sub>3</sub>OH and DMA molecules in the structure (calcd. 20.36%). The mass of the samples remained nearly constant from 600 to 800 °C and the characterization of PXRD suggested that the residual powder was MgO (see Fig. S2, in Supporting Information).

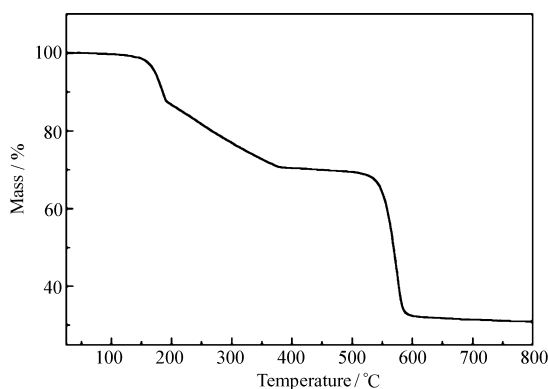


Fig. 3 TG curve for compound **1**

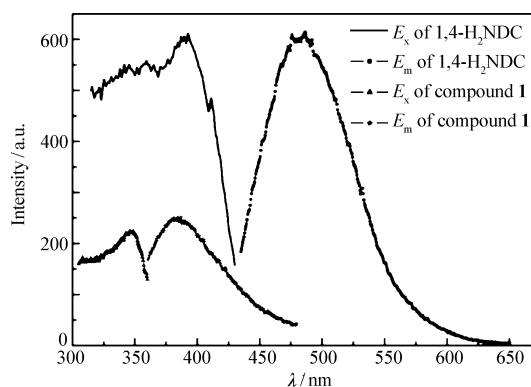


Fig. 4 Solid state fluorescence spectra of compound **1** and 1,4-H<sub>2</sub>NDC

## 2.3 Fluorescence detection properties

As shown in Fig. 4, the fluorescent spectra of compound **1** in the solid state exhibited a purple emission band with an intense peak maximum at 385 nm upon excitation at 345 nm at room temperature. Compared with the emission band of the free 1,4-H<sub>2</sub>NDC ligand ( $\lambda_{em} = 485$  nm monitored at  $\lambda_{ex} = 390$  nm), compound **1** showed blue-shift emission. The title compound should exhibit a ligand-centered emission due to the unique electron configuration of Mg<sup>2+</sup>. Further fluorescence measurement for compound **1** has been carried out to identify whether compound **1** has a luminescent response to volatile organic molecules. As shown in Fig. 5A, compound **1** was dispersed in five kinds of typically used solvents and it was interesting to see that the fluorescence intensities of compound **1** were heavily dependent on the identity of the organic solvent molecules.

Notably, we found that compound **1** exhibited a significant quenching of fluorescence when dispersed in CS<sub>2</sub>. Since compound **1** demonstrated the strongest fluorescence emission in acetone, the acetone was chosen as the dispersed solvent to find the potential fluorescence detection of compound **1** for CS<sub>2</sub>. The sensing sensitivity towards CS<sub>2</sub> was examined in detail through gradually increasing CS<sub>2</sub> contents into the emulsions of compound **1** dispersed in acetone to monitor the emissive response. As depicted in Fig. 5B, the fluorescent intensity of compound **1** was almost completely quenched when only 80  $\mu$ L CS<sub>2</sub> (0.4% (volume fraction)) was added, indicating that compound **1** was a benign candidate for selective sensing of CS<sub>2</sub>. Stern-Volmer equation (SV plot):  $I_0/I = 1 + K_{sv} \times [M]$  was applied to judge the quenching effect ( $I_0$  and  $I$  are the suspension luminescence intensity of compound **1** without and with addition of quencher, and  $[M]$  is the molarity of quencher and  $K_{sv}$  is the quenching constant)<sup>[24]</sup>. As shown in Fig. 5B, the SV plot displays a good linear behavior and the  $K_{sv}$  constant calculated from the experimental data is  $1.45 \times 10^3$  L/mol. Compared to the former reports detecting CS<sub>2</sub> based on the Mg-MOF luminescence intensity, the quenching concentration of CS<sub>2</sub> for the title compound is slightly higher<sup>[17]</sup>. This could be attributed to the larger channels in the former

reported Mg-MOFs, which facilitate the interactions between CS<sub>2</sub> and MOFs<sup>[16-17]</sup>. Further investigation is still required for exploring the mechanism of fluorescence quenching in compound **1**.

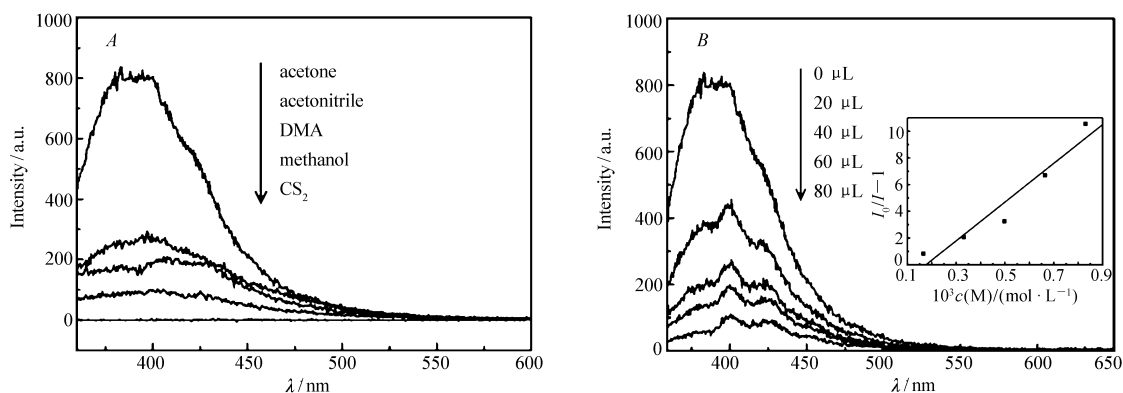


Fig. 5 Emission spectra of compound **1** dispersed in different solvents (A) and emission spectra of compound **1** dispersed in the acetone with various contents of CS<sub>2</sub> (inset is the SV plot for the quenching of compound **1** by CS<sub>2</sub>) (B)

### 3 Conclusions

In summary, a novel 3D Mg-MOF, namely [Mg<sub>4</sub>(1,4-NDC)<sub>4</sub>(DMA)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·DMA·CH<sub>3</sub>OH has been synthesized under solvothermal conditions and characterized. Fluorescence study indicates that the title compound shows a highly sensitive fluorescent response for CS<sub>2</sub> with a low concentration. Future work will continue to study the construction of fluorescent Mg-MOFs, explore their sensing properties towards the harmful volatile organic compounds and aim at a deep understanding of the relationship of structure and property.

Supporting Information [PXRD patterns] is available free of charge on the website of Chinese Journal of Applied Chemistry (<http://yyhx.ciac.jl.cn/>).

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## 一例对二硫化碳具有荧光传感性能的 Mg-金属有机框架化合物

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**摘要** 通过溶剂热合成了一例 Mg-MOF 化合物  $[\text{Mg}_4(1,4\text{-NDC})_4(\text{DMA})_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2]\cdot\text{DMA}\cdot\text{CH}_3\text{OH}$  (**1**, 1,4- $\text{H}_2\text{NDC}$  = 1,4-萘二酸, DMA = *N,N'*-二甲基乙酰胺), 并对其结构表征及荧光性能进行了研究。单晶 X 射线研究结果表明, 化合物结晶于  $P2_1/c$  空间群, 其晶体学数据为  $a = 2.06090(12)$  nm,  $b = 2.21014(13)$  nm,  $c = 1.50385(10)$  nm,  $\beta = 111.399(3)^\circ$ ,  $V = 6.3776(7)$  nm<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.403$  g/cm<sup>3</sup>,  $F(000) = 2824$ ,  $R = 0.0596$ ,  $wR = 0.1225$  ( $I > 2\sigma(I)$ )。化合物 **1** 中, 二核的镁作为次级构筑单元通过桥连配体 1,4-NDC 连接形成沿 *c* 轴方向拓展的一维链。一维链间进一步通过配体连接形成 3D 框架的化合物。荧光性能研究表明, 化合物 **1** 对  $\text{CS}_2$  具有灵敏的荧光传感性能, 在 0.4% 的体积分数条件下可引起  $\text{CS}_2$  荧光的完全淬灭。此外, 化合物 **1** 的热稳定性也通过热重分析进行了研究, 发现其可稳定到 140 °C 左右。

**关键词** 镁; 金属有机框架化合物; 荧光传感; 二硫化碳

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