一种用于选择性检测苯乙烯的Zn-MOFs发光传感器

朱子馨¹ 王萃娟^{*,1} 刘 成¹ 肖玉美¹ 罗 丹¹ 刘冬宁¹ 王尧宇² (¹西南交通大学生命科学与工程学院化学化工系,成都 610031) (²西北大学化学与材料学院,合成与天然功能分子化学教育部重点实验室,西安 710069)

摘要:在溶剂热条件下合成了一种新型金属有机框架(MOF){[Zn₂(tyia)₂(H₂O)₂]·H₂O}_n(1),其中H₂tyia为5-(1H-1,2,4-三唑-1-基) 间苯二甲酸。运用X射线单晶衍射分析其结构,通过元素分析、粉末X射线衍射、热重分析、固体荧光分析等手段对配合物1 进行表征,研究了其与有机小分子相互作用的荧光特性。结果表明其能够对低浓度苯乙烯迅速做出反应,最低识别浓度为 1.06 mmol·L⁻¹。此外,还对其传感机制进行了研究。

A Zn-MOF Luminescent Sensor for Selective Detection of Styrene

ZHU Zi-Xin¹ WANG Cui-Juan^{*,1} LIU Cheng¹ XIAO Yu-Mei¹ LUO Dan¹ LIU Dong-Ning¹ WANG Yao-Yu²

(¹Department of Chemistry and Chemical Engineering, School of Life Science and Engineering, Southwest Jiaotong University, Chengdu 610031, China)
(²Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Department of Chemistry, Northwest University, Xi'an 710069, China)

Abstract: A new three-dimensional Zn^{2+} -based metal-organic framework (MOF), $\{[Zn_2(tyia)_2(H_2O)_2] \cdot H_2O\}_n$ (1), where H_2 tyia is 5-(1*H*-1,2,4-triazol-1-yl) isophthalic acid, was synthesized under solvothermal conditions. The structure of compound 1 was analyzed by X-ray single crystal diffraction, and characterized by elemental analysis, powder X-ray diffraction, thermogravimetric analysis and solid fluorescence analysis. The fluorescence characteristics of the interaction between compound 1 and small organic molecules were studied. The results show that 1 can response quickly to low concentration of styrene, and the minimum identification concentration is 1.06 mmol·L⁻¹. Furthermore, a possible sensing mechanism was investigated. CCDC: 1958896.

Keywords: metal-organic framework; luminescent sensor; styrene

0 Introduction

Metal-organic frameworks (MOFs)^[1-3], are organic and inorganic hybrid materials formed by self-assem-

bly of organic ligands and metal ions or clusters via coordination bonds. Recently, MOFs have been efficiently employed in many fields including chemical separation^[4], gas storage^[5], catalysis^[6-10], polymeriza-

收稿日期:2020-01-08。收修改稿日期:2020-06-13。

国家自然科学基金(No.21401151)、四川省科学技术支持计划(No.2015GZ0233)、成都科技惠民计划(No.2015-HM01-00336-SF)和西南交 通大学研究生院的创新与实践项目(No.2018CYPY07)资助。

^{*}通信联系人。E-mail:wangcuijuan@home.swjtu.edu.cn

tion^[11] and drug delivery^[12]. Another propitious field of application for MOFs is luminescent sensing^[13-14]. Luminescent MOFs have several advantages over the conventional small-molecule-based sensor materials because of their ultrahigh surface areas, adjustable porosities, functionalizable pore walls and π -conjugated backbones^[15-16]. Besides, such luminescent sensors also possess prominent advantages over traditional methods and sophisticated analytical instruments like quickresponse, simplicity, sensitivity, selectivity, portability and inexpensive, and can also be used in both solid state and solution^[17]. Currently, MOFs sensors for the detection of small organic molecules have received increasing attention.

It needs to be mentioned that sensing and detection of small organic molecules also play a significant role in environmental science and industry. With the rapid development of industry, some small organic molecules have proven to be the most severe environmental pollutants^[18]. The harm of plastic pollutants for human and environment is also being paid more and more attention^[19]. Styrene is toxic compound used in large quantities in the production of fiberglass reinforced polyesters. Waste plastics and rubber have caused serious environmental pollution, and have grown up to be an increasingly serious threat to the health of animals and humans^[20]. Humans are very prone to be exposed to styrene occupationally and through air, water and food. How to rapidly detect hazardous styrene has been an important challenge for public security and environmental protection^[21]. Therefore, selective recognition and detection are beneficial to environmental protection and human health.

In this contribution, we present a porous Zn(II)MOF, { $[Zn_2(tyia)_2(H_2O)_2] \cdot H_2O$ }, (1), which is generated based on a newly synthesized unsymmetrical ligand, 5-(1*H*-1,2,4-triazol-1-yl) isophthalic acid, H₂tyia, containing a triazole moiety with multiple N-donor atoms and the carboxylate group by solvothermal reaction. As expected, luminescence study revealed that compound 1 could be used as high selectivity luminescence sensor for sensing styrene. To the best of our knowledge, this is the first exploration for the application of MOFs in the detection/sensing of styrene. Single crystal structure of the MOF was investigated, showing interesting three-dimensional (3D) structure. In addition, we also discuss the photoluminescence mechanism of compound **1**, and the quenching response mechanism of sensing styrene in detail via UV-Vis absorption spectra.

1 Experimental

1.1 Materials and methods

All reagents and solvents commercially available were employed and used without further purification. Thermal gravimetric analysis (TGA) was performed on a NETZSCHSTA 499 C microanalyzer with a heating rate of 10 $^{\circ}$ C ·min⁻¹ from room temperature to 800 $^{\circ}$ C under N₂ atmosphere (Flow rate: 10 mL·min⁻¹). Powder X-ray diffraction (PXRD) data were collected over a 2 θ range of 5° ~50° using a SmartLab diffractometer with Cu K α radiation (λ =0.154 18 nm) at room temperature. Its working voltage is 40 kV and current is 40 mA. Elemental analyses of C, H and N were achieved with a Perkin - Elmer 240 elemental analyzer. Luminescencet spectra were determined on a Varian CARY Eclipse spectrophotometer. The UV-Vis spectrum were determined by UV-1800.

1.2 Synthesis of $\{[Zn_2(tyia)_2(H_2O)_2] \cdot H_2O\}_n$ (1)

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.05 mmol) and H_2 tyia (0.05 mmol) were dissolved in a solvent mixture of EtOH (2 mL) and H_2O (8 mL). Then, the mixture was transferred into a Teflon reactor (15 mL) and heated at 135 °C for 72 h. The solution was filtered, and colorless transparent thin piece of crystals (1) were obtained. They were washed with deionized water and dried in air. Yield based on Zn: 38%. Elemental analysis Calcd. for $C_{20}H_{16}N_6O_{11}Zn_2(\%)$: C 37.15, H 2.48, N 13.00; Found (%): C 37.04, H 2.05, N 12.83.

1.3 X-ray crystallographic study

Crystal data for compound **1** was performed on an Agilent Gemini E diffractometer equipping with a graphite-monochromated Cu $K\alpha$ (λ =0.154 184 nm) radiation at 293(2) K. The intensity data was collected by the x-scan technique. The structure was solved by direct methods and refined with SHELXS-2018 and

-

SHELXL-2018. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C atoms were located at geometrically calculated positions to their carrier atoms and refined with isotropic thermal parameters included in the final stage of the refinement. A summary of the crystallographic data and structure refinements for compound **1** is given in Table 1. Selected bond lengths and bond angles are summarized in Table S1 (Supporting information). CCDC: 1958896.

Empirical formula	C H N O Zn	F(000)	1 304
Empirical formula	$C_{20} \Gamma_{16} \Gamma_{6} C_{11} \Sigma \Gamma_{2}$	<i>I</i> (000)	1 504
Formula weight	647.13	Crystal size / mm	0.08×0.07×0.07
Crystal system	Orthorhombic	θ range for data collection / (°)	4.19~67.21
Space group	Pbcn	Reflection collected, unique	14 128, 1 933 (R _{int} =0.118 4)
<i>a</i> / nm	1.558 53(11)	Max. and min. transmission	0.797 1 and 0.772 9
<i>b</i> / nm	0.673 05(5)	Data, restraint, parameter	1 933, 432, 177
<i>c</i> / nm	2.108 79(12)	Goodness of fit on F^2	1.079
Volume / nm ³	2.212 1(3)	Final R indices $[I > 2\sigma(I)]^*$	R_1 =0.084 0, wR_2 =0.215 8
Ζ	4	<i>R</i> indices (all data)	R_1 =0.117 0, wR_2 =0.263 9
$D_{\rm c}$ / (Mg · m ⁻³)	1.943	Largest diff. peak and hole / $(e \boldsymbol{\cdot} nm^{-3})$	883 and -1 507
Absorption coefficient / mm^{-1}	3.394		

 Table 1
 Crystal data and structure refinement for compound 1

 ${}^{*}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|; wR_{2} = \{ \sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [(F_{o}^{2})^{2}] \}^{1/2}$

1.4 Styrene sensing experiment

The powder sample (3 mg) of Zn-MOF (1) was immersed in 4 mL different solvent containing acetonitrile, isopropanol, MeOH, DMSO, ethyl acetate, EtOH, DMF, DMA and styrene for 12 h at room temperature. The luminescence data of the solution were collected after ultrasonication for 20 min. The compound 1 was dispersed into distilled water to form an aqueous suspension, and then various amounts of styrene were added into the above aqueous suspensions, respectively. The relation between luminescent intensity and varying concentrations were analyzed.

2 **Results and discussion**

2.1 Crystal structure of $\{[Zn_2(tyia)_2(H_2O)_2] \cdot H_2O\}_n$ (1)

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the orthorhombic system *Pbcn* space group featuring a 3D new topological framework. The asymmetric unit includes one Zn(II) cation, one tyia²⁻ ligand, one coordinated H₂O molecule and half a lattice H₂O molecule. As depicted in Fig. 1a, the Zn(II) ion is penta-coordinated by one N atom from one tyia²⁻ ligand, three carboxylate O atoms from other two tyia²⁻ ligands and one oxygen atom from H₂O molecule (O5) to form triangular double cone. The distances of Zn-O bonds vary from 0.195 8 to 0.259 0 nm, while the length of the Zn-N bond is 0.200 9 nm, which are in the normal range. The Zn-O/N bond lengths are all consistent with corresponding bond lengths found in the literature^[22]. As shown in Fig. 1b, 1D zigzag chain ([Zn-H₂tyia]_n) is formed by the tyia²⁻ ligands and Zn(II) without considering carboxyl coordination. Furthermore, the neighboring 1D chains are connected by tyia²⁻ ligands to form an infinite 3D framework (Fig.1c).

2.2 PXRD and thermal properties

The phase purity of compound **1** was confirmed using PXRD and the simulated single crystal data (Fig.2a), since the as-synthesized samples and simulated patterns were in good agreement with each other. In order to investigate the stability of the compound, TGA was carried out (Fig.2b). For **1**, it remained stable in a range of 30~80 °C and the first weight loss of 3.93% in a range of 80~109 °C corresponds to the loss of one lattice water molecule (Calcd. 2.79%). Another weight loss of 5.27% in a range of 109~300 °C corresponds to two coordinated water molecules (Calcd. 5.57%). Due to the decomposition of ligands, the overall framework structure began to collapse over 300 °C.



Symmetry codes: #1: 0.5+x, 0.5-y, 1-z; #2: 0.5+x, y-0.5, 0.5-z; #3: 0.5-x, y-0.5, z





Fig.2 (a) PXRD patterns of simulated and as-synthesized compound 1; (b) TGA curve of compound 1

2.3 Luminescence properties

Photoluminescence properties of zinc MOFs are well-known for their promising applications in chemical sensors. The luminescence properties of the free ligands H₂tyia and compound **1** were investigated separately in the solid phase at ambient temperature. As shown in Fig.S1, the free ligand H_2 tyia showed a wide emission band ranging from 425 to 550 nm upon excitation at 400 nm. Under excitation at 300 nm, the spectrum of compound **1** showed emission centered at 445

nm. Compared with the free H₂tyia ligand, the luminescence of compound **1** had blue-shift of 10 nm with stronger intensity. The emission of compound **1** can probably be attributed to the intra-ligand (π - π *) charge transition^[23]. The excitation spectra of the free ligand and compound **1** are shown in Fig.S2.

In order to study the potential luminescence sensing application of **1** for detection of small molecules, the luminescent properties of **1** dispersed in various types of solvents were investigated. The results indicate that the luminescence intensity of compound **1** are largely dependent on the solvent molecules, especially dispersed in styrene, which presents distinct fluorescence quenching (Fig.3a). Moreover, the relative intensity of a major emission peak (650 nm) can be mirrored by the histogram intuitively (Fig.3b). In addition, the PXRD patterns of **1** immersed in different organic solvents matched well with the simulated patterns obtained from the single crystal data, demonstrating the excellent stability of **1** under these conditions (Fig.S3).

Meanwhile, the suspensions of 1 in H₂O showed the strongest emission band. Therefore, the fluorescent detection experiment was performed in H₂O solution. In order to further investigate the sensitivity and limit detection of compound 1 for styrene, 8.698 mmol·L⁻¹ styrene was gradually added into a suspension of $1^{[24]}$. When the excitation was 325 nm, the luminescence intensity of 1 at 650 nm was gradually quenched with the increase in concentration of the styrene. When the volume of styrene reached 30 µL, the luminescence intensity quenched 15% for 1. When the amount of styrene increased to 240 µL, the fluorescence was almost quenched (Fig.4a). Quantitatively, this quenching effect can be well-fitted by the Stern-Volmer plots $(I_0/I=1+K_{sy}c_0)$ of the relative fluorescence intensity



Fig.3 (a) Emission spectra of **1** at 325 nm after immersion in different solutions; (b) Corresponding luminescence intensity of **1** with different solutions at 650 nm



Fig.4 (a) Fluorescence intensities of aqueous solution of 1 in the presence of various amounts of styrene;(b) Stern-Volmer plots for 1 upon addition of styrene

versus the styrene concentration as shown in Fig. 4b, where I_0 and I are the fluorescence intensities of **1** suspension without and with addition of styrene, respectively, c_q is the molar concentration of styrene and K_{sv} is the quenching effect coefcient of organic solvents^[25]. The K_{sv} value was calculated to be 4.472× $10^4 \text{ L} \cdot \text{mol}^{-1}$, proving the high quenching efficiency of styrene on the emission of **1**. Based on the K_{sv} values and the standard error (σ) for three repeated fluorescence measurements of blank solutions, the detection limits $(3\sigma/K_{sv})$ are calculated to be 1.06 µmol·L⁻¹ for **1**, which are a clear indication of the high sensing sensitivity of **1** towards styrene.

In order to check the selectivity of compound 1 towards styrene in the presence of other potentially competing organic solvents, competitive fluorescence titration experiments were performed. In these competitive titration measurements, fluorescence emission spectra were recorded upon the incremental addition of styrene to the stable aqueous suspensions of compound 1 containing the potentially intrusive organic solvents. The changes in the luminescence intensity of compound 1 upon the addition of styrene in the absence and presence of other competing organic solvents are presented in Fig. 5. The competitive experiment also confirms that the sensor is not influenced by the coexisting components, indicating that the sensor is a highly selective and sensitive towards organic solvent styrene.



Fig.5 Comparison of luminescence intensity of 1 (650 nm) with 0.01 mol·L⁻¹ of interfering substances in the absence and presence of styrene

The cycling experiments of the luminescence sensing of compound **1** was conducted to determine its recyclability. Compound **1** can be recovered by centrifugation and washed with ethanol. There was only minor reducing of quenching effect after five cycles. However, there was a slight change in the luminescence intensity of the compound in each cycle because of the residual target material, which is within the acceptable range (Fig. 6). As verified by the PXRD experiments (Fig. S4), all the MOF materials retained most of their initial crystallinity (thus structural robustness) after five successive cycles of fluorescence titration experiments.



Fig.6 Recyclability of sensor 1 immersed in water with 10 mmol·L⁻¹ styrene

To examine the mechanism of luminescence quenching of **1** toward styrene, further experiments were conducted. The PXRD pattern of **1** after detecting styrene was consistent with the original sample, indicating that the quenching phenomenon was not caused by the collapse of the framework (Fig.S4). As shown in Fig. S5, the UV-Vis absorption spectra of different organic small molecules in the aqueous phase show that there was an observable absorption intensity of styrene in a wavelength range of 290~330 nm, while other organic small molecules did not absorb in this wavelength range. There exists competition between the absorption of styrene and the excitation of Zn-MOF (**1**), resulting in the decrease and even quenching in luminescence^[26-27].

3 Conclusions

In summary, a novel Zn-MOFs {[Zn₂(tyia)₂(H₂O)₂]·

 $H_2O_{l_n}(1)$, based on H_2 tyia was successfully synthesized and characterized. Compound 1 exhibits exceptional thermal and water stability, as well as excellent fluorescence emission. Interestingly, compound 1 shows a highly selective and sensitive fluorescence quenching effect on styrene in an aqueous environment. In brief, compound 1 has been proven to be promising practical fluorescence sensor for detecting styrene with high selectivity and sensitivity. This work provides a promising perspective for designing MOF-based sensors with multi-functional applications.

Supporting information is available at http://www.wjhxxb.cn

References:

- [1] Yaghi O M, O'Keeffe M, Ockwig N W. Nature, 2003, 423 (6941):705-714
- [2] Férey G. Chem. Soc. Rev., 2008,37(1):191-214
- [3] Kitagawa S, Kitaura R, Noro S I. Angew. Chem., 2004,43(18): 2334-2375
- [4] Borjigin T, Sun F X, Zhang J L, et al. Chem. Commun., 2012, 48(61):7613-7615
- [5] Farha O K, Eryazici I, Malliakas C D, et al. Nat. Chem., 2010,2(11):944-948
- [6] Wu C D, Hu A G, Zhang L, et al. J. Am. Chem. Soc., 2005, 127(25):8940-8941
- [7] Wang X K, Liu J, Zhang L, et al. ACS Catal., 2019,9(3):1726-1732
- [8] Wu Y P, Tian J W, Liu S, et al. Angew. Chem. Int. Ed., 2019, 58(35):12185-12189
- [9] Zhou W, Huang D D, Wu Y P, et al. Angew. Chem. Int. Ed., 2019,58(13):4227-4231

- [10]Xu G W, Wu Y P, Dong W W, et al. Small, 2017, 13(22): 1606134
- [11]Ishiwata T, Furukawa Y, Sugikawa K, et al. J. Am. Chem. Soc., 2013,135(14):5427-5432
- [12]Wu M X, Yang Y W. Adv. Mater., 2017, 29(23): 1606134 -1606154
- [13]Zhang X D, Hua J A, Guo J H, et al. J. Mater. Chem. C, 2018,6(46):12623-12630
- [14]Zhang X D, Zhao Y, Chen K, et al. Chem. Asian J., 2019,14 (20):3620-3626
- [15]Kreno L E, Leong K, Farha O K, et al. Chem. Rev., 2011,112
 (2):1105-1125
- [16]Huang W H, Ren J, Yang Y H, et al. Inorg. Chem., 2019,58 (2):1481-1491
- [17]Kumar S, Arora A, Kumar A, et al. Inorg. Chem. Commun., 2018,96:16-19
- [18]Hao Z M, Song X Z, Zhu M, et al. J. Mater. Chem. A, 2013,1 (36):11043-11050
- [19]Verma R, Vinoda K S, Papireddy M, et al. Procedia Environ. Sci., 2016,35:701-708
- [20]Lian X, Miao T F, Xu X Y, et al. Biosens. Bioelectron., 2017, 97(15):299-304
- [21]Du L Y, Wang H, Liu G, et al. Dalton Trans., 2015, 44(3): 1110-1119
- [22]Xu C G, Bi C F, Zhu Z, et al. CrystEngComm, 2019,21(14): 2333-2344
- [23]Zhang Y Q, Blatov V A, Zheng T R, et al. Dalton Trans., 2018,47(17):6189-6198
- [24]Zhang X, Zhuang X R, Ge C Y, et al. CrystEngComm, 2019, 12(21):1948-1955
- [25]Dalapati R, Kökçam-Demir Ü, Janiak C, et al. Dalton Trans., 2018,47(4):1159-1170
- [26]Ma J J, Liu W S. Dalton Trans., 2019,48(32):12287-12295
- [27]Zhao F, Guo X Y, Dong Z P, et al. Dalton Trans., 2018,47 (27):8972-8982