一例互穿的阴离子型In@@金属有机骨架 用于选择性检测水中Fe³⁺离子

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摘要:作为一类新型多孔材料,金属有机骨架(MOFs)常被开发作为荧光传感器用来监测水中的污染物,开发稳定且易制备的 MOFs 材料实现选择性检测有毒的 Fe³⁺仍具有较高挑战。本工作中,我们报道一例水稳定的二重穿插 In(III)基 MOF:(NH₂Me₂) [In(fdc)₂]·2H₂O(BUT-205,BUT代表北京工业大学,H₂fdc=呋喃-2,5-二羧酸)。BUT-205的构筑采用生物质衍生配体,其结构通过 单晶 X 射线衍射确立。这个材料可作为高效的水相 Fe³⁺离子传感器,具有高的灵敏度和选择性。检测限达到 1.3 μmol·L⁻¹,低 于美国环保局规定的饮用水中安全标准(15.7 μmol·L⁻¹),并且该传感材料可以回收利用至少4次。

关键词:金属有机骨架; 阴离子框架; 荧光检测;金属阳离子; 水安全
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An Interpenetrated Anionic In(III) Metal-Organic Framework for Selective Sensing of Fe³⁺ in Water

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Abstract: As an emerging type of porous material, metal-organic frameworks (MOFs) have been developed as sensors for monitoring environmental pollutants in water. It is of high significance to develop fluorescent MOFs with simple precursors for selective detection of toxic Fe³⁺ ions. In this work, we present a water-stable two-fold interpene-trated indium-based metal-organic framework (NH₂Me₂)[In(fdc)₂]·2H₂O named BUT-205 (BUT stands for Beijing University of Technology, H₂fdc=furan-2,5-dicarboxylic acid) constructed from a biomass-derived ligand. BUT-205 has been structurally characterized by single-crystal X-ray diffraction. BUT-205 was an efficient sensor for Fe³⁺ ions in water with high sensitivity and selectivity. The limit of detection (LOD) was calculated to be 1.3 μ mol·L⁻¹ being lower than the US - EPA (U. S. Environmental Protection Agency) standard (15.7 μ mol·L⁻¹) in drinking water. Furthermore, BUT-205 could be recycled and used for at least four cycles. CCDC: 2033659.

Keywords: metal-organic frameworks; anionic framework; fluorescent sensing; metal cations; water safety

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0 Introduction

A large amount of wastewater produced in modern industrial activities is discharged into our environment, leading to a high threat to human health. For example, the excessive amount of Fe³⁺ causes some serious diseases in the heart, pancreas, and liver, as well as Parkinson's and Alzheimer's^[1-3]. Various technologies have been evolved for the detection of Fe³⁺ and fluorescence sensing is a promising technology for fast and sensitive detection, especially suitable for the rapid screening of a large number of samples by environmental control agencies^[4-5].

Metal - organic frameworks (MOFs) are emerging porous materials constructed from inorganic clusters and organic linkers. Their diverse structural topologies, permanent porosity, and tunable optical properties have made them attractive materials for applications such as gas storage/separation^[6-9], chemical sensing^[10-11], and drug delivery^[12-13]. Recently, MOFs have been developed as unique materials for the recognition of metal anion/cation^[14-19], persistent organic pollutants^[20-21], antibiotics^[22-23], and explosives^[24], owing to their tunable pore size and surface functionality for selective binding of a targeted analyte to boost their sensing selectivity and sensitivity. The luminescence of MOFs can be tuned by organic linkers and metal ions. The combination of electrically noble d^{10} metal cations with aromatic organic linkers produces MOFs with strong fluorescence for efficient sensing^[25].

In the last decade, water-stable MOFs have been developed rapidly through various strategies with a deeper mechanistic understanding^[26-28]. MOFs constructed with high valence metals such as $Zr(\mathbb{N})$ and $In(\mathbb{II})$, have shown good stability in water, weak acid, and base solutions^[29-31], which further pushed advanced applications of MOFs in aqueous media. Besides the good water stability, In-MOFs with the anionic $In(COO^-)_4$ unit enables post-synthetic cation exchange as an efficient functionalization strategy^[32]. Such ionic nature of In-MOFs is potentially useful to promote their interaction with ionic analytes to boost the sensitivity.

Herein, we report a water - stable In (III) - based MOF: (NH₂Me₂)[In(fdc)₂]·2H₂O (BUT-205, BUT stands for Beijing University of Technology) constructed with a furan-2,5-dicarboxylic acid (H₂fdc) ligand, a biomassderived compound. The framework has a doubly interpenetrated diamondoid structure with 1D channels. The MOF showed good stability in water and exhibited sensitive and selective sensing for Fe³⁺ in water. The LOD (limit of detection) was determined as 1.3 μ mol· L⁻¹ for Fe³⁺, being much lower than the US-EPA (U.S. Environmental Protection Agency) standard (15.7 μ mol·L⁻¹).

1 Experimental

1.1 Reagents and general characterization

All the reagents (AR grade) were commercially available and used without further purification. FT-IR data were recorded on a SHIMADZU IR Affinity - 1 instrument by using KBr pellets, and the spectra data were acquired in a range of 500-4 000 cm⁻¹. Elemental microanalysis was performed by a Vario Macro cube Elementar. ICP-AES was performed by a PerkinElmer Optima 8000 spectrometer. The powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Smartlab3 X-ray powder diffractometer equipped with a Cu sealed tube (Cu $K\alpha$, $\lambda = 0.154$ 178 nm) with 40 kV and 30 mA at room temperature. The scanning range was from 5° to 30°. Simulation of the PXRD patterns was carried out by the single-crystal data and the diffractioncrystal module of the Mercury program available free of charge at http://www.ccdc.cam.ac.uk/mercury/. Thermogravimetric analysis (TGA) data were obtained on a TGA - 50 (SHIMADZU) thermogravimetric analyzer. The fluorescence spectra were recorded via an F-7000 fluorescence spectrophotometer, whose excitation source came from a xenon lamp. UV-Vis spectra were obtained with a UV-2600 spectrophotometer in a range of 200-800 nm at room temperature.

1.2 Synthesis

In(NO₃)₃·6H₂O (15 mg, 0.05 mmol), H₂fdc (16 mg, 0.1 mmol), and 5 - aminobezotetrazole (ATZ) (8.5 mg, 0.1 mmol) were ultrasonically dissolved in 2 mL of DMF in a 10 mL Pyrex vial and sealed. The mixture was then heated at 95 °C for 72 h in an oven. After cooling to room temperature, the resulting colorless crystals

were collected by filtration, washed with fresh DMF and acetone, and then dried in the air. The composition by inductively coupled plasma mass spectrometry (ICP-MS) and elemental analysis for $C_{12}H_4InO_{10}(NH_2(CH_3)_2)(H_2O)_2$ was In 22.3%, C 32.8%, H 3.3%, O 38.6%, N 3.0% (Theoretical composition: In 22.7%, C 33.3%, H 3.2%, O 38.0%, N 2.8%).

1.3 Single-crystal X-ray diffraction

The X-ray diffraction data of as-synthesized BUT-205 were collected using an Agilent Supernova CCD diffractometer (a mirror monochromator, Cu Ka source, λ =0.154 184 nm). The datasets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structure was solved using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement using the SHELXTL software package. Hydrogen atoms of the ligand were refined with isotropic displacement parameters. The disordered solvents in pores could not be modeled in terms of atomic sites but were treated by using the MASK routine in the Olex2 software package. The crystal parameters and structure refinement of BUT - 205 are summarized in Table S1 (Supporting information).

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1.4 Sample activation and stability test

As-synthesized BUT-205 samples were activated by immersing first in DMF for 24 h. Then, the supernatant DMF was removed and the DMF treated samples were kept in fresh acetone for 48 h at room temperature when fresh acetone was exchanged three times a day. Finally, the sample was collected by filtration and dried for further analytical characterizations. The stability of as-synthesized BUT-205 was tested by soaking the samples in water at room temperature for 24 h. Then, the samples were collected by filtration, washed with water, and soaked in acetone for further analysis.

1.5 Fluorescence measurements

For the fluorescence quenching measurements, 5 mg of finely grounded BUT-205 was added to 20 mL of deionized water and sonicated for 30 min to get a uniform suspension. For the testing of cation quenching selectivity, 1 mL of cation solutions (Ca^{2+} , Cd^{2+} ,

Cu²⁺, Ni²⁺, Mn²⁺, Mg²⁺, Co²⁺, Al³⁺, Cr³⁺, and Fe³⁺) were acquainted into cuvettes pre-filled with 1 mL of BUT-205 suspension, and the mixture was agitated for homogeneity. The K_{sv} and LOD of Fe³⁺ were determined by the drop-off in the fluorescence intensity of BUT-205 after consecutive addition of different amounts (0-500 μ L) of Fe³⁺ solution (1 mmol·L⁻¹) into 2 mL of MOF suspensions in water. The interference of other cations was evaluated by the addition of 500 μ L of other cations (1 mmol·L⁻¹ for each cation) into 1 mL of BUT-205 suspension, followed by the addition of 500 μ L of Fe³⁺ solution (1 mmol·L⁻¹).

2 Results and discussion

2.1 Synthesis and structural description

Our experiment aimed at the preparation of mixed ligand MOF by using H_2 fdc and ATZ with indium salt. Through different protocols of various solvents and temperatures, all attempts constantly produced the crystal with a single fdc^{2–} ligand. However, without using ATZ, we got amorphous materials after a series of attempts. Finally, we synthesized BUT-205 with a single ligand in the presence of ATZ as an essential additive in the reaction system.

The single-crystal study shows that BUT-205 crystallizes in the tetragonal crystal system with the space group $P4_122$ as shown in Fig. 1. The asymmetric unit contains tetradentate linker fdc²⁻ and one In³⁺ ion. Each In³⁺ ion is connected to eight oxygen atoms of four carboxylate groups, and each fdc2- is connected with two separate In³⁺ ions, forming a 2-fold interpenetrated 3D framework. The In³⁺ ion act as a 4-connected knob which is linked to each other by fdc²⁻ to construct a diamondoid framework (Fig.S1). The topological study discovered the existence of a 4-connected In³⁺ node and the entire architecture has a *dia*-topological net with a point symbol {6⁶} and can be classified as an extended Schläfli point symbol $(6_2, 6_2, 6_2, 6_2, 6_2, 6_2)$. The $[In(O_2C)_4]$ can be viewed as a four-connected node with In-O distances ranging from 0.222 to 0.237 nm. Interpenetration for MOFs with *dia* topology is usually observed, and some of them have shown guest response for gas separation^[33-34] and sensing^[35] applications. Although



H atoms are omitted for clarity

Fig.1 Crystal of BUT-205: (a) 4-connected [In(O₂C)₄] node and ligand (Color code: In, green; C, black; O, red);
(b) perspective view of a single net with tetragonal channels; (c) view of the 2-fold interpenetrated 3D framework; (d) topological representation of 2-fold interpenetrated *dia*-net

being doubly interpenetrated, the structure was still highly porous, with a 1D channel of *ca*. 0.6 nm and a void space of 57.0% calculated by PLATON. Such pore size is suitable for small ions diffusion. Interestingly, such structure is also different from some other In - MOFs based on the same linker. The V - shaped linker is prone to form 2D structures rather than the *dia* topology. As shown in Fig. S2, ¹H NMR spectra show that one dimethylamine cation was found per $[In(O_2C)_4]^-$ cluster to keep charge balance. And the molecular formula of BUT-205, namely $[In(fdc)_2$ $(NH_2Me_2)^+(H_2O)_2]$ (InC₁₄H₁₆O₁₂N), was also determined along with ICP-MS, and elemental analysis.

2.2 PXRD and TGA

The phase purity of BUT-205 was confirmed by the PXRD pattern of as - synthesized sample which matched well with the simulated pattern from the singlecrystal structure. After treatment with water for 24 h at room temperature, the PXRD pattern of the sample remained the same as shown in Fig. 2, indicating its high stability in water. BUT-205 was thermally stable up to 300 °C as determined by a thermal analyzer in a temperature range of 25 to 800 °C with a heating range of 10 °C •min⁻¹ under a nitrogen atmosphere. TGA curve of BUT-205 is shown in Fig.S3a and the FT-IR spectrum is shown in Fig.S3b.



Fig.2 PXRD patterns of BUT-205

2.3 Fluorescence and sensing properties

The fluorescence property of BUT-205 has been determined at room temperature and the emission spec-

trum showed an emission peak at 404 nm, whereas excited at a wavelength of 300 nm. The emission band observed for BUT-205 is likely from ligand to ligand charge transfer $(n-\pi^* \text{ and } \pi-\pi^*)$ based on the similar fluorescence spectra between free ligand and BUT-205, as shown in Fig. S4^[33]. The strong fluorescence and anionic nature motivated us to explore its application of sensing Fe³⁺ in aqueous media.

As shown in Fig.3a, the luminescence intensity of BUT-205 decreased continuously as the amount of added Fe^{3+} solution (1 mmol·L⁻¹) increased. To study the fluorescence quenching efficiency, the Stern - Volmer (S-V) equation $(I_0/I=1+K_{SV}c_{E^{3+}})$ was established, where $K_{\rm SV}$ is the quenching constant, $c_{\rm Fe^{3+}}$ is the concentration of Fe^{3+} , I_0 and I are the fluorescence intensities of the suspension before and after the addition of Fe3+ solution. The S-V plot for Fe³⁺ displayed a good linear correlation (R^2 =0.995) as shown in Fig.3b. The calculated $K_{\rm sv}$ for Fe³⁺ was 1.34×10⁴ L·mol⁻¹ which was quite high compared with reported benchmark materials (Table S2). The LOD for Fe³⁺ was calculated as 1.3 μ mol·L⁻¹ using equation LOD= $3\sigma/K_{sy}$, and σ (standard deviation) was calculated with three repeated fluorescence measurements of blank solution (Fig. S6). The K_{sv} and LOD values of BUT-205 for Fe³⁺ ion were quite good among the reported MOF-based sensors in an aqueous medium as shown in Table S2. Especially, the LOD value for Fe³⁺ was lower than the permissible value determined by US-EPA standards (15.7 μ mol·L⁻¹) in drinking water^[36].

Selectivity is another important factor for practical sensing applications because many other metal ions present in the analytes might also interfere with the target ions. To evaluate the sensing selectivity, the solution of cations (K⁺, Na⁺, Fe²⁺, Ca²⁺, Cd²⁺, Cu²⁺, Ni²⁺, Mn²⁺, Mg²⁺, Co²⁺, Al³⁺, and Cr³⁺) were added into the suspension of BUT-205. As a result, a small drop-off in fluorescence intensity was observed indicating low quenching efficiency. Fluorescence intensity decreased significantly when Fe³⁺ solutions were added to the suspension respectively as shown in Fig.4a. The luminescence quenching efficiency of Fe³⁺ was 99% while those for other cations are in a range of 3%-24%, which demonstrated the good selectivity of BUT-205 towards Fe³⁺ (Fig. 4c). Further, interference of other cations was evaluated, as shown in Fig.S5. Upon addition of other cations, the luminescence exhibited very limited quenching, which corresponds to their low quenching efficiency. Subsequently, the addition of Fe³⁺ solution quenched 99% of the luminescence, indicating no significant interference of the sensing sensitivity from other cations. Besides, in a real water sample, there may be coexisting anions that may interfere with the sensing of Fe³⁺, therefore we also explored the quenching effect towards BUT-205 suspension of some common anions. As shown in Fig.4b, the solution of common anions (NO2, F, Br, Ac, Cl, SO4, PO4, WO4, and NO_3^{-}) could quench the fluorescence intensity of suspension of BUT-205 in a range of 1%-12%, which proves that the presence of anions has little effect on



Fig.3 (a) Fluorescent spectra of BUT-205 suspension after the addition of different amounts of Fe³⁺ solution (1 mmol·L⁻¹);
(b) Corresponding fitting curve of the S-V plot, where the error bar is based on three parallel experiments

the fluorescence of BUT-205 (Fig.4d).

Further, UV - Vis spectra of tested ions were measured. As shown in Fig.5a, the absorption spectrum of Fe^{3+} ion showed a broad peak in a range of 250-350 nm which overlapped with the excitation spectrum of BUT - 205. Therefore, the inner filter effect (IFE) is a

feasible quenching mechanism for Fe³⁺ ions. While other cations or anions showed limited or no absorbance in this range (Fig.5a and 5b), indicating unfavorable quenching through the IFE mechanism. Especially, Fe ions of different oxidation states also exhibited distinct UV-Vis absorption with little overlap with the



Fig.4 (a) Luminescence spectra of BUT-205 upon addition of Fe^{3+} or other cations (500 μ mol·L⁻¹); (b) Luminescence spectra of BUT-205 upon addition common anions (500 μ mol·L⁻¹); (c) Luminescence quenching efficiency of different cations (500 μ mol·L⁻¹) towards BUT-205; (d) Luminescence quenching efficiency of different anions (500 μ mol·L⁻¹) towards BUT-205



Fig.5 UV-Vis absorption spectra of tested (a) cations and (b) anions in comparison with the excitation and emission spectra of BUT-205

excitation spectrum of BUT-205, which makes the IFE quenching pathway inefficient. The emission spectrum of BUT-205 almost showed no overlap with any cations or anions (Fig. 5), suggesting the Förster resonance energy transfer (FRET) mechanism is not likely to happen.

The reusability of a sensory material is desired for a reduced cost in practical applications. The used BUT-205 samples were recovered by centrifugation, washed with ethanol, and dried for the next test. The quenching efficiency of the regenerated sample was almost identical for four cycles as shown in Fig.6.





3 Conclusions

In summary, a water-stable 2-fold interpenetrated 3D luminescent metal-organic framework (MOF) BUT-205 was synthesized. An open channel of about 0.6 nm can be found in this structure as revealed by single-crystal X-ray diffraction. The material exhibited sensitive and selective sensing towards Fe^{3+} ions in water. The LOD towards Fe^{3+} ion was calculated to be 1.3 µmol·L⁻¹. The MOF could be recycled and reused for about four cycles without an evident loss of function. The high sensing performance, recyclability, and facile synthesis from simple precursors make the material high promising for practical sensing applications.

Conflict of interest: The authors declare no competing financial interest.

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

References:

- [1]Mitchell E, Frisbie S, Sarkar B. Exposure to Multiple Metals from Groundwater — A Global Crisis: Geology, Climate Change, Health Effects, Testing, and Mitigation. *Metallomics*, 2011,3:874-908
- [2]Xiang Z H, Fang C Q, Leng S H, Cao D P. An Amino Group Functionalized Metal-Organic Framework as a Luminescent Probe for Highly Selective Sensing of Fe³⁺ Ions. J. Mater. Chem. A, 2014,2:7662-7665
- [3]Chen C H, Wang X S, Li L, Huang Y B, Cao R. Highly Selective Sensing of Fe³⁺ by an Anionic Metal-Organic Framework Containing Uncoordinated Nitrogen and Carboxylate Oxygen Sites. *Dalton Trans.*, 2018,47:3452-3458
- [4]Rasheed T, Nabeel F. Luminescent Metal Organic Frameworks as Potential Sensory Materials for Various Environmental Toxic Agents. *Coord. Chem. Rev.*, 2019,401:213065
- [5]Kreno L E, Leong K, Farha O K, Allendorf M, Van Duyne R P, Hupp J T. Metal-Organic Framework Materials as Chemical Sensors. *Chem. Rev.*, 2012,112:1105-1125
- [6]He Y B, Zhou W, Qian G D, Chen B L. Methane Storage in Metal-Organic Frameworks. Chem. Soc. Rev., 2014,43:5657-5678
- [7]Li J R, Kuppler R J, Zhou H C. Selective Gas Adsorption and Separation in Metal-Organic Frameworks. *Chem. Soc. Rev.*, 2009, 38: 1477-1504
- [8]Xu T T, Jiang Z Z, Liu P X, Chen H N, Lan X S, Chen D L, Li L B, He Y B. Immobilization of Oxygen Atoms in the Pores of Microporous Metal-Organic Frameworks for C₂H₂ Separation and Purification. ACS Appl. Nano Mater., 2020,3:2911-2919
- [9]Li J H, Xie Y, Zhou M Y, Lin R B, Chen X M. Microporous Zinc Formate for Efficient Separation of Acetylene over Carbon Dioxide. *Chem. Res. Chin. Univ.*, 2022,38:87-91
- [10]李江, 韩森, 陈团结, 苟召曦, 张琦, 聂晓双, 曹海如. 两个金属有机框架化合物对硝基芳香化合物在气/液相的荧光传感. 无机化学学报, 2020,35(10):1843-1852
 LI J, HAN S, CHEN T J, GOU Z X, ZHANG Q, NIE X S, CAO H R. Two Homologous Metal Organic Frameworks Based on Zn²⁺ and Cd²⁺: Luminescent Sensors for Nitro Aromatic Compounds in Solution and Vapor Medium. *Chinese J. Inorg. Chem.*, 2020,35(10):1843-1852
- [11]刘志强,曹师虎,张哲,武峻峰,赵越,孙为银.2,6-二(1-咪唑基)萘 和二羧酸构筑的金属-有机框架化合物:合成、晶体结构和荧光 识别性能.无机化学学报,2019,35(11):2145-2151

LIU Z Q, CAO S H, ZHANG Z, WU J F, ZHAO Y, SUN W Y. Metal-Organic Frameworks with 2,6-Di(1*H*-imidazol-1-yl)naphthalene and Dicarboxylate Ligands: Synthesis, Crystal Structure and Photoluminescence Sensing Property. *Chinese J. Inorg. Chem.*, **2019**, **35**(11): 2145-2151

- [12]Horcajada P, Serre C, Vallet-Regi M, Sebban M, Taulelle F, Ferey G. Metal-Organic Frameworks as Efficient Materials for Drug Delivery. Angew. Chem. Int. Ed., 2006,45:5974-5978
- [13]Chen Y J, Li P, Modica J A, Drout R J, Farha O K. Acid-Resistant Mesoporous Metal-Organic Framework toward Oral Insulin Delivery: Protein Encapsulation, Protection, and Release. J. Am. Chem. Soc., 2018,140:5678-5681
- [14]Maity R, Chakraborty D, Nandi S, Yadav A K, Mullangi D, Vinod C P, Vaidhyanathan R. Aqueous-Phase Differentiation and Speciation of Fe³⁺ and Fe²⁺ Using Water-Stable Photoluminescent Lanthanide-Based Metal-Organic Framework. ACS Appl. Nano Mater., 2019, 2: 5169-5178
- [15]张春丽.两个基于 Cd(II)金属有机骨架化合物在金属离子和有机 分子发光传感中的应用. 无机化学学报, 2019,35(1):165-173 ZHANG C L. Two Cd(II)-Based Metal-Organic Frameworks for Luminescence Sensing of Metal Ions and Organic Molecules. *Chinese J. Inorg. Chem.*, 2019,35(1):165-173
- [16]Talha K, Alamgir, Ahmed N, Xie L H, Zhang X, Li J R. Construction of a Zeolite A-Type Multivariate Metal-Organic Framework for Selective Sensing of Fe³⁺ and Cr₂O₇²⁻. *CrystEngComm*, **2021**,**23**:4923-4929
- [17]Jin M, Wei L H, Yang Y T, Run M T, Yin C X. A New Turn-On Fluorescent Probe for the Detection of Palladium(0) and Its Application in Living Cells and Zebrafish. *New J. Chem.*, 2019,43:548-551
- [18]Li E Z, Kang J, Ye P Y, Zhang W J, Cheng F Q, Yin C X. A Prospective Material for the Highly Selective Extraction of Lithium Ions Based on a Photochromic Crowned Spirobenzopyran. J. Mater. Chem. B, 2019,7:903-907
- [19]Wu Y C, Yin C X, Zhang W J, Chao J B, Huo F J. A Red-Emitting Fluorescent Probe Imaging Release of Calcium Ions from Lysosome Induced by Chloroquine Based on a Photochromic Crowned Spirobenzopyran. *Dyes Pigment.*, 2021,193:109467
- [20]Wang B, Wang P L, Xie L H, Lin R B, Lv J, Li J R, Chen B. A Stable Zirconium Based Metal-Organic Framework for Specific Recognition of Representative Polychlorinated Dibenzo-p-Dioxin Molecules. *Nat. Commun.*, 2019,10:3861
- [21]Singh D, Nagaraja C M. A Luminescent 3D Interpenetrating Metal-Organic Framework for Highly Selective Sensing of Nitrobenzene. *Dalton Trans.*, 2014,43:17912-17915
- [22]Yuan R R, He H M. State of the Art Methods and Challenges of Luminescent Metal - Organic Frameworks for Antibiotic Detection. *Inorg. Chem. Front.*, 2020,7:4293-4319
- [23]Wang B, Lv X L, Feng D, Xie L H, Zhang J, Li M, Xie Y, Li J R, Zhou H C. Highly Stable Zr(N)-Based Metal-Organic Frameworks for the Detection and Removal of Antibiotics and Organic Explosives in Water. J. Am. Chem. Soc., 2016,138:6204-6216

[24]Hu Z C, Deibert B J, Li J. Luminescent Metal-Organic Frameworks for Chemical Sensing and Explosive Detection. *Chem. Soc. Rev.*, 2014,43:5815-5840

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- [25]Cui Y, Yue Y, Qian G D, Chen B L. Luminescent Functional Metal-Organic Frameworks. Chem. Rev., 2012,112:1126-1162
- [26]Wang C H, Liu X L, Demir N K, Chen J P, Li K. Applications of Water Stable Metal-Organic Frameworks. *Chem. Soc. Rev.*, 2016,45: 5107-5134
- [27]Zhang X, Wang B, Alsalme A, Xiang S C, Zhang Z J, Chen B L. Design and Applications of Water - Stable Metal - Organic Frameworks: Status and Challenges. *Coord. Chem. Rev.*, 2020,423:213507
- [28]Devic T, Serre C. High Valence 3p and Transition Metal Based MOFs. Chem. Soc. Rev., 2014,43:6097-6115
- [29]Cavka J H, Jakobsen S, Olsbye U, Guillou N, Lamberti C, Bordiga S, Lillerud K P. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. J. Am. Chem. Soc., 2008,130:13850-13851
- [30]Lv X L, Yuan S, Xie L H, Darke H F, Chen Y, He T, Dong C, Wang B, Zhang Y Z, Li J R, Zhou H C. Ligand Rigidification for Enhancing the Stability of Metal-Organic Frameworks. J. Am. Chem. Soc., 2019,141:10283-10293
- [31]Bu F, Lin Q P, Zhai Q G, Bu X H, Feng P Y. Charge-Tunable Indium-Organic Frameworks Built from Cationic, Anionic, and Neutral Building Blocks. *Dalton Trans.*, 2015,44:16671-16674
- [32]Kumar Maka V, Tamuly P, Jindal S, Narasimha Moorthy J. Control of In-MOF Topologies and Tuning of Porosity through Ligand Structure, Functionality and Interpenetration: Selective Cationic Dye Exchange. Appl. Mater. Today, 2020,19:100613
- [33]Yang H, Guo F, Lama P, Gao W Y, Wu H, Barbour L J, Zhou W, Zhang J, Aguila B, Ma S. Visualizing Structural Transformation and Guest Binding in a Flexible Metal-Organic Framework under High Pressure and Room Temperature. ACS Central Sci., 2018, 4: 1194-1200
- [34]Yang Q Y, Lama P, Sen S, Lusi M, Chen K J, Gao W Y, Shivanna M, Pham T, Hosono N, Kusaka S, Perry J J, Ma S Q, Space B, Barbour L J, Kitagawa S, Zaworotko M J. Reversible Switching between Highly Porous and Nonporous Phases of an Interpenetrated Diamondoid Coordination Network that Exhibits Gate-Opening at Methane Storage Pressures. Angew. Chem. Int. Ed., 2018,57:5684-5689
- [35]Park I H, Mulijanto C E, Lee H H, Kang Y, Lee E, Chanthapally A, Lee S S, Vittal J J. Influence of Interpenetration in Diamondoid Metal-Organic Frameworks on the Photoreactivity and Sensing Properties. *Cryst. Growth Des.*, 2016,16:2504-2508
- [36]Swaidan A, Borthakur P, Boruah P K, Das M R, Barras A, Hamieh S, Toufaily J, Hamieh T, Szunerits S, Boukherroub R. A Facile Preparation of CuS-BSA Nanocomposite as Enzyme Mimics: Application for Selective and Sensitive Sensing of Cr (VI) Ions. Sens. Actuator B -Chem., 2019,294:253-262