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Short communication

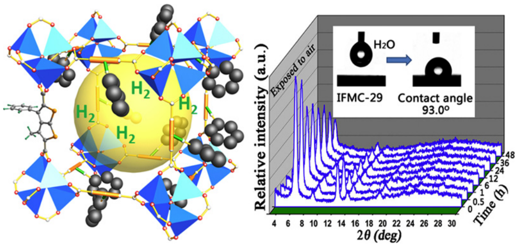
Improved moisture resistance of a new Zn_4O-based metal-organic framework by introducing hydrophobic phenyl groups

Cong Cheng[a], Guang-Sheng Yang[a,*], Li-Hong Yan[a], Xin Wang[a], Chun-Jie Jiang[a,*], Nan Li[a], Zhong-Min Su[b]

[a] *School of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, PR China*
[b] *Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, PR China*

GRAPHICAL ABSTRACT

A Zn_4O-based isoreticular MOF constructed from a thiophene carboxylate ligand substituted by hydrophobic phenyl groups represents improved moisture resistance.



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ABSTRACT

A new Zn_4O–based isoreticular MOF, $Zn_4O(CH_3PhTDC)_3$ (**IFMC-29**, IFMC corresponds to Institute of Functional Material Chemistry) has been synthesized by using an asymmetrical rigid carboxylate ligand 3-methyl-4-phenylthieno[2,3-*b*]thiophene-2,5-dicarboxylic acid (H_2CH_3PhTDC). Powder X-ray diffraction (PXRD) experiments and contact angle measurements indicate that **IFMC-29** possesses improved moisture resistance, which is attributed to the introduction of hydrophobic phenyl groups around the water-sensitive $Zn_4O(COO)_6$ clusters. At 77 K and 1 bar, **IFMC-29** displays a relatively high hydrogen storage capacity (1.75 w%) among the Zn_4O-based isoreticular MOFs. This work can provide a useful strategy for designing water-stable Zn_4O-based MOFs in practical application.

Metal-organic frameworks (MOFs) have achieved considerable attentions due to their promising applications in various crucial areas such as energy storage, molecular separation, sensors, heterogeneous catalysis and drug delivery, etc. [1–5]. Generally, MOFs can be predesigned and conveniently predictable constructed, assisted by network synthesis, polyhedron assembly and step-wise synthesis [6,7]. In recent years, some novel synthesis approaches for the scalable preparation of MOFs, including electrochemical [8], mechanochemical [9], solvent free [10] and high-rate (rapid solvent mixing) methods [11], have accelerated the proceeding of industrialization and commercialization for MOF-based materials. Rapid development in preparation and application of MOF-based materials indicates that the industrialization and commercialization of MOFs will come true. However, many MOFs have a fatal disadvantage about the stability in the presence of moisture, which greatly limit their practical applications [12]. Thus, stabilizing these MOF materials under ambient humidity would make them more suitable for specialized applications.

Zn_4O-based MOFs, such as MOF-5 (IRMOF-1), have high specific surface area and have been widely studied as adsorbent for molecule adsorption and separation. These porous materials can be easily prepared from zinc nitrate and carboxylate ligands. However, these $Zn_4O(COO)_6$ secondary building units are very sensitive to water molecules,

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* Corresponding authors.
E-mail addresses: yanggs693@nenu.edu.cn (G.-S. Yang), jiangcj@lnnu.edu.cn (C.-J. Jiang).

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resulting that most Zn_4O-based MOFs are unstable in moisture atmosphere [13,14]. Therefore, it is very significant to build moisture-resistant Zn_4O-based MOFs for practical applications. An effective approach to improve the moisture-resistance of MOFs is isolating the sensitive metal carboxylate clusters from water molecules. By covering some hydrophobic groups around the metal carboxylate clusters, introduced by covalent-linked on organic ligands, some moisture-resistant MOFs have been obtained [15–19]. In our previous work, a Zn_4O based isoreticular MOF containing hydrophobic methyl groups, $Zn_4O((CH_3)_2TDC)_3$ (IFMC-28, $H_2(CH_3)_2TDC$ = 3,4-dimethylthieno[2,3-*b*] thiophene-2,5-dicarboxylic acid) reveals good air-stability in comparison with MOF-5 [20]. This result inspired us to synthesize more moisture-resistant MOFs by decorating hydrophobic groups. We reasoned that big hydrophobic groups can increase the cover degree of sensitive Zn_4O clusters, which can effectively enhance the moisture-resistance of MOFs. Bearing this in mind, one linear dicarboxylate ligand decorated with the hydrophobic phenyl group, 3-methyl-4-phenylthieno[2,3-b] thiophene-2,5-dicarboxylic acid (H_2CH_3PhTDC), was used for preparing new Zn_4O-based isoreticular MOF. The pre-designed compound, **IFMC-29**, was successfully isolated and structurally characterized. It exhibits significant improvement in moisture stability. Furthermore, it also features comparable H_2 storage capacity to MOF-5 in the low-pressure range at 77 K.

IFMC-29 was synthesized via the solvothermal reaction of H_2CH_3PhTDC and $Zn(NO_3)_2{\cdot}6H_2O$ in *N*,*N*-Dimethylformamide (DMF) or *N*,*N*-Diethylformamide (DEF) (Fig. 1). Single-crystal diffraction data shows that **IFMC-29** crystallizes in the cubic crystal system with *Fm*-3*m* space group. This is an isostructural phase in contrast with classic MOF-5 framework, in which the BDC^{2-} organic spacers are replaced by the CH_3PhTDC^{2-} spacers. In our previous work, solvothermal reaction of $H_2(CH_3)_2TDC$ and $Zn(NO_3)_2{\cdot}6H_2O$ in DMF only afforded a two-fold penetrating Zn_4O-based framework (IFMC-27). Only the solvent DMF was replaced by DEF, the non-penetrating Zn_4O framework of IFMC-28 could be obtained. Compared with IFMC-27 and IFMC-28, the steric hindrance of phenyl group on H_2CH_3PhTPC can effectively reduce the opportunity of framework interpenetration, and the non-penetrating model framework of **IFMC-29** has been obtained not only in DEF but also in DMF.

The TGA data of **IFMC-29** (Fig. S5) indicated one step mass decrease of ca. 28.8% up to a temperature of 160 °C corresponding to the loss of seven DMF molecules approximately (calc. 29.4%). No decrease in weight occurred in the temperature range of 160–280 °C. Subsequently, the sample suffers incessant weight loss until the temperature reaches 450 °C, demonstrating the collapse of crystal skeleton. Thermogravimetric experimental results indicate that **IFMC-29** has a high decomposition temperature of ca. 280 °C.

In order to verity the effects of hydrophobic phenyl groups on moisture-resistance of MOFs, the solvent-free samples of IFMC-28 and **IFMC-29** were exposed to air and then were characterized by PXRD measurements to gain insight into the integrity of the materials under ambient conditions. As shown in Fig. 2a, within 6 h, no new peaks appeared for IFMC-28, and the intensity of original peaks gradually decreases over that time. After exposing it to air for over 12 h, new peaks at 7.1° and 24.5° appeared. This result displays that the hydrophobic methyl groups could not afford a stable structure with strong moisture-resistance. In contrast, the addition of hydrophobic phenyl substituents obviously stabilizes the bulk crystallinity of the isoreticular MOF structure in air (Fig. 2b). Over the period of 3 days, no new peaks appeared for **IFMC-29** and the decreasing rate of peak intensity is much slower than that of IFMC-28. The PXRD data indicate that hydrophobic phenyl groups can appreciably retain the crystallinity of this framework under atmospheric conditions. In order to further check its moisture resistance, the PXRD experiments of IFMC-29 exposed in variable humidity between 0%RH (dry conditions) and 80%RH for 24 h were performed. The results show that the degree of crystallinity of IFMC-29 declined with the increase of humidity from 0% to 60%RH, and the framework decomposed at ~80% relative humidity (Fig. S7).

The water stabilities of MOFs, including MOF-5, IFMC-28 and **IFMC-29**, were also examined. When these samples were immersed into water, MOF-5 immediately decomposed, IFMC-28 decomposed at a lower rate than observed for MOF-5, while **IFMC-29** did not reveal evident expansion and decomposition (Fig. S6). The PXRD data also confirmed that the main reflections of **IFMC-29** still exist after immersing in water for 30 min (Fig. S8), which means that **IFMC-29** can retain and maintain its structure even in water for a certain time. After 60 min immersion in water, the disappearance of the main reflections, disclosing that **IFMC-29** lost its crystallinity. Obviously, the introduction of the hydrophobic phenyl groups efficiently postpones the decomposition of MOFs in water to a great extent.

In regard of the composition of MOFs and the stereoscopic effect of phenyl groups, every Zn_4O cluster is surrounded by three phenyl groups of organic ligands based on the average of probability. Hydrophobic phenyl groups, methyl groups and S atoms of thienyl rings form three potential hydrophobic environments around water-sensitive ZnO_3 units (Fig. S9a–c) resist the intrusion of H_2O molecules and improve the moisture-resistance and even water-stability of MOFs. The introduction of hydrophobic phenyl groups can delay the decomposition of MOF materials in water. In order to investigate the hydrophobic character of the crystal surface, we measured the contact angle of the crystal surface of **IFMC-29** and found that the contact angle of this crystal surface to water was ca. 93.0°, just into the hydrophobic region (Fig. S9d). Meantime, the contact angles of MOF-5 and IFMC-28 were not measurable due to their immediate decomposition in water (some works have reported that the contact angle of MOF-5 is ca. 0°) [21]. The measurements of contact angle also proved improved hydrophobicity by introduction of phenyl groups, which further greatly promoted the stability of the material to the air. Microstructure and surface hydrophobicity give good explanation for the improved moisture-resistance of **IFMC-29**.

Enhanced stability encouraged us to study its gas adsorption

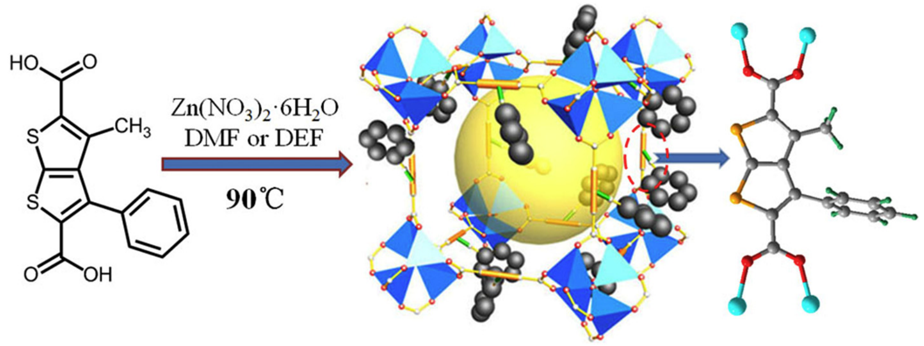

Fig. 1. Schematic diagram of synthesis and crystal structure of **IFMC-29**.