Synthesis, structural characterization, and carbon dioxide and hydrogen adsorption of a new three-dimensional metal organic framework Zn(BTC)$_4$

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Abstract
A novel three-dimensional porous metal organic framework Zn(BTC)$_4$ (BTC = benzene-1,3,5-tricarboxylic acid) is synthesized by the solvothermal method. This structure is characterized by single-crystal X-ray diffraction, scanning electron microscopy, and thermogravimetric analysis. This metal organic framework crystallizes in a monoclinic ($P2_1/n$, $V = 1795.7(2)$ Å$^3$, $Z = 4$, $D_c = 1.449$ mg/cm$^3$, $\alpha = 90.00^\circ$, $\beta = 97.2200(10)^\circ$, $\gamma = 90.00^\circ$, $a = 9.5077(5)$ Å, $b = 16.3950(16)$ Å, $c = 11.6119(9)$ Å). The thermogravimetric analysis shows the material can be stabilized up to 350 °C, then the skeleton collapses between 350~510 °C. A luminescence test shows that the material gives out strong emission at 384 and 462 nm. The hydrogen storage capacity of this metal organic framework is 2.01 wt% at 77 K and a pressure of 10 bar. The carbon dioxide storage capacity of this metal organic framework is 4.17 mmol/g at 298 K and a pressure of 10 bar.

Keywords
carbon dioxide, gas adsorption, hydrogen, metal organic frameworks, synthesis

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Introduction
Metal organic frameworks (MOFs) are a type of important hybrid inorganic–organic material, and due to their unique topological structure, their applications have attracted more and more attention. Most MOFs have high porosity and good stability, controllable pore structures, and large specific surface areas. Therefore, MOFs have extensive application prospects compared with other porous materials, for example, in chiral catalysis, adsorption separation, adsorption storage, magnetic materials, and optical materials. As an important part of the framework, organic ligands play a decisive role in the pore properties of these compounds, so we can design and adjust the ligands to selectively adsorb gas.

Today, in the face of energy shortages, seeking new energy sources is a solution to aid the energy crisis. Among new energy sources, the calorific value of gas energy, such as from hydrogen, is relatively high. Hydrogen is also clean, green, and is available from many rich sources. It is also expected to help alleviate the oil crisis. However, the storage and transportation of hydrogen is a significant obstacle to industrial utilization. On the contrary, the greenhouse effect is more and more destructive to the environment. Methods to effectively store and reuse greenhouse gases such as carbon dioxide and methane without emissions into the atmosphere is a key factor in solving this problem.

Among all the various gas storage technologies, adsorption technology has the characteristics of being fast and flexible, so the preparation of efficient adsorption materials has remained an important topic.

Results and discussion
The MOF Zn(BTC)$_4$ was prepared from benzene-1,3,5-tricarboxylic acid and Zn(NO$_3$)$_2$$\cdot$6H$_2$O in H$_2$O at 80 °C in an autoclave.
Crystal structures

The single-crystal diffraction data show that this compound belongs to the monoclinic system and has space group $P2_1(1)/n$. The asymmetric structural unit is shown in Figure 1. The two Zn$^{2+}$ ions are hexacoordinate and are coordinated with four oxygen atoms to form a tetrahedral geometry. Two of these four oxygen atoms come from the same BTC ligand, and the other two oxygen atoms come from two different BTC ligands. Three BTC ligands spread out to become a two-dimensional (2D) layer and the other two BTC molecules serve as pillar-ligands to coordinate with the outer Zn atoms, thus leading to a 3D framework (Figure 2).

Scanning electron microscopy characterization of compound 1

The morphology of compound 1 was examined by scanning electron microscopy (SEM). It can be seen from Figure 3 that the morphology of this sample has two types of structures: a hollow cage ball and a block structure. The size of the ball is about 3–5 μm.

Thermoanalysis

In order to examine the thermal stability of compound 1, thermogravimetric (TG) analysis was carried out in the range of 0–600 °C under nitrogen. Figure 4 shows the TG analysis of this sample. It can be seen from that the weight loss of this sample can be divided into two stages: in the range of 150–330 °C, the loss of thermogravimetry was 16.88%, and the loss of weight was mainly due to the solvent of the sample. In the range of 360–520 °C, the heat loss is 32.45%. As the temperature increased further, the skeleton of the sample collapsed. When the temperature rises to 510 °C, the curve tends to be stable. According to the results of elemental analysis, the final decomposition product is ZnO.

Solid-state luminescence

The luminescence properties of compound 1 were in the solid state at room temperature (Figure 5). When excited with 280-nm light, compound 1 shows very strong emissions at 384 and 462 nm. The fluorescence emission can be attributed to the charge transition inside the ligand or that from the metal to ligand.

Gas adsorption properties and pore size analysis

Figure 6 shows the hydrogen storage curve of this material. At 298 K, it was activated under vacuum for 48 h and then
the hydrogen storage performance of this material was tested at 77 K. The experimental results show that the hydrogen storage capacity of the sample is 2.01 wt% at pressure of 10 bar.

Figure 7 shows the adsorption curves of carbon dioxide at 298 and 323 K. It can be seen from Figure 6 that the adsorption capacity of carbon dioxide increases with an increase of pressure. When the pressure was increased to 10 bar, the material adsorbed 4.17 mmol/g carbon dioxide at 298 K. Moreover, the adsorption capacity for carbon dioxide decreases on increasing the temperature. When the temperature was increased to 323 K, only 3.76 mmol/g of carbon dioxide was adsorbed at 10 bar. The pore structure parameters are listed in Table 1.

**Conclusion**

To sum up, the MOF, Zn(BTC)$_4$, can be synthesized by a solvothermal method using benzene-1,3,5-tricarboxylic acid as the ligand. The TG analysis shows that the material is stable up to 350 °C, then the skeleton collapses between 350~510 °C. The luminescence test shows that the material gives out strong emissions at 384 and 462 nm. The maximum hydrogen and carbon dioxide storage capacity of this MOF is 2.01 wt% (77 K, 10 bar) and 4.17 mmol/g (298 K, 10 bar) respectively, which shows that this MOF material may act as a potential material for gas adsorption. Further studies in this area toward the exploration of new structures and functions of MOFs are underway.

**Experimental**

**Reagents and instruments**

The chemical reagents used in this experiment are all commercial reagents and were used directly.

The crystal structure was solved using a Bruker SMART 1000 CCD diffractometer.
A HITACHI s4800 scanning electron microscope was employed to study the morphology. Infrared (IR) spectra were recorded using a Bruker Tensor 27 Fourier-transform infrared spectroscopy (FTIR) spectrometer in the range of 4000–400 cm\(^{-1}\) (KBr pellets). The luminescent properties were studied using an F-4500 fluorescence spectrometer at room temperature.

**Synthesis**

The main raw materials of compound \(1\) were benzene-1,3,5-tricarboxylic acid and Zn(NO\(_3\))\(_2\)•6H\(_2\)O, and the solvent was H\(_2\)O. The experimental procedures were as follows:

Zn(NO\(_3\))\(_2\)•6H\(_2\)O (6.7 mmol) was dissolved in 60 mL of H\(_2\)O, and the solution stirred. About 25 mL of methanol and benzene-1,3,5-tricarboxylic acid (7.1 mmol) were added to the solution, and the mixture was heated in an autoclave at 80 °C for 48 h. After filtration, washing, and drying, white rectangular and powdery crystals of compound \(1\) were obtained in a 75% yield. (Elemental analysis: C, 53.44; H, 2.92; Zn, 8.13%. Theoretical values: C, 53.40; H, 2.97; Zn, 8.03%.)

**Structural characterization**

Single crystals with regular shape and of appropriate size were selected to collect the diffraction data. Using Mo-K\(_\text{α}\) radiation (\(\lambda = 0.071073 \text{ nm}\)) monochromated by a graphite monochromator (\(T = 298(2)\text{K}\)), the diffraction points were collected in the range of 2.17\(^\circ\) < \(\theta\) < 25.01\(^\circ\) in the \(\omega/2\theta\) scanning mode. Data are reduced (SAINT) for absorption corrections (SADAB) after diffraction. The crystal structure was solved by direct method using SHELXL-2014 program.\(^1\) The coordinates of all n-hydrogen atoms and their anisotropic thermal parameters were corrected by the full matrix least squares method (SHELXL-2014). Crystallographic data are shown in Table 2, and bond lengths and bond angles are shown in Table 3; CCDC: 1539458.

**Gas adsorption and pore size characterization**

An intelligent gravimetric analyzer (IGA-001) was used to adsorb hydrogen and carbon dioxide under high pressure. Before the test, a 50-mg sample was activated by drying in a vacuum for several hours. The activated samples were used to adsorb carbon dioxide at 298 and 323 K, respectively. Hydrogen was adsorbed on the sample at 77 K.

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**Table 2. Crystal data of compound \(1\).**

| Property | Value |
|----------|-------|
| Empirical formula | \(C_{36}H_{24}O_{24}Zn\) |
| Formula weight | 809.67 |
| Size/mm | 0.17 × 0.15 × 0.10 |
| \(\theta\) range for data collection/(°) | 2.894–26.085 |
| Crystal system | Monoclinic |
| Space group | \(P2_1/n\) |
| a/Å | 9.5077(5) |
| b/Å | 16.3950(16) |
| c/Å | 11.6119(9) |
| \(\alpha\)/(°) | 90.00 |
| \(\beta\)/(°) | 97.2200(10) |
| \(\gamma\)/(°) | 90.00 |
| \(V/\text{nm}^3\) | 1795.7(2) |

**Table 3. Selected bond lengths (Å) and angles (°) for compound \(1\).**

| Bond | Length (Å) | Bond | Length (Å) | Bond | Length (Å) |
|------|-----------|------|-----------|------|-----------|
| Zn1-O5 | 1.939(3) | Zn1-O3 | 1.939(3) | Zn1-O2 | 1.967(3) |
| Zn1-O1 | 1.972(3) | O5-Zn1-O3 | 125.79(12) | O5-Zn1-O2 | 94.56(12) |
| O3-Zn1-O2 | 113.35(14) | O5-Zn1-O1 | 109.99(12) | O2-Zn1-O1 | 114.57(12) |
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