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A Hydrothermal Stable Zn(II)-based Metal-Organic Framework: Structural Modulation and Gas Adsorption

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By the solvothermal reaction of a triangular ligand, 2,4,6-tris-(4-carboxyphenoxy)-1,3,5-triazine (H_3tcpt) with $Zn(NO_3)_2$ in N,N'-dimethylacetamide/acetonitrile/H_2O (v/v/v = 1:1:1) mixed solvent, a two-fold interpenetrated three-dimensional (3D) porous metal-organic framework, $[Zn_2(tcpt)OH]$·solvents (**1**·solvents), with a rare paddlewheel second building unit (SBU) $Zn_2(COO)_3$, was synthesized and characterized. It was found that the single 3D structure of **1** forms when two-dimensional layers, which are constructed by $tcpt^{3-}$ bonding the paddlewheel SBUs, are linked by –OH group alone the axial sites of the SBUs. Compared with reported Zn(II)-based partners with this ligand, synthesis conditions, particularly used solvents clearly played a key role in the formation of different SBUs, thereby resulting distinct MOFs with the same ligand. Particularly, **1** features good water and thermal stability, and can withstand acid aqueous solution of pH values ranging from 5 to 12. In addition, **1** perfroms good adsorption ability towards H_2 (2.21 wt% at 77 K and 1 atm), and can selectively adsorb CO_2 from CH_4 and N_2, in spite of its relative low void volume (36.8%), suggesting potential application in gas storage and separation.

1. Introduction

As an emerging porous materials, metal-organic frameworks (MOFs) have been widely researched these years. Due to their interesting and various structures and excellent chemical/physical properties, MOFs could be utilized in a lot of areas, such as gas storage, separation, catalysis, magnetism, and luminescence.[1] However, to apply MOFs in practices, there are still many issues to be resolved, among them the stability of framework, especially under high temperature and water environment are particularly significant. With this purpose, some methods have been developed to enhance the stability of MOFs, such as surface carbonization,[2] fluorine modified pores,[3] and the construction of multi-interpenetrated frameworks.[4] Since MOFs are composed of organic linkers and secondary building unit (SBU), the regulation of the two parts is vital to form stable structures. Considering that the selection of organic linkers is relatively controllable, modulating the *in-situ* formed SBUs is thus a conceivable way for stability enhancing. On the other hand, the formation of a SBU depends on various factors,[5-7] e.g. reaction temperature, solvents, and pH. Under different conditions, MOFs with different structures and properties are usually obtained.

In our effort to design and synthesize new MOFs through controling reaction conditions, a tritopic ligand, 2,4,6-tris-(4-carboxyphenoxy)-1,3,5-triazine (H_3tcpt) reported by several other groups for synthesizing MOFs was used.[6,7] From the literatures, it was found that this ligand could generate a two-dimensional (2D) layer structural MOF, ($[Zn_3(L)_2(H_2O)_2]\cdot 3H_2O\cdot$TEA$\cdot$2DMF)[6] with $Zn_3(COO)_6$ SBUs in mixed DMF/EtOH/H_2O solvent. While, the 2D layers could be linked by *in-situ* produced formate species to form a three-dimensional (3D) framework (SNU-100)[7] when the used solvent was changed to pure DMF. Clearly, solvents play a key role in the formation of these MOFs.

In this work, we used different solvent of DMA/acetonitrile/ H_2O (v/v/v = 1:1:1), a new 3D MOF, $[Zn_2(tcpt)OH]$·solvents (**1**·solvents) was synthesized, in which an unusual paddlewheel SBUs $Zn_2(COO)_3$ was found. Unlike common paddlewheel SBUs[6-8] consisting of four carboxyl groups, this SBU is just three. Diffrent from above

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mentined two MOFs with this ligand, in **1** the 2D layers assembled by H_3tcpt ligands and $Zn_2(COO)_3$ SBUs are further linked by –OH groups to finally form a 3D interpenetrated framework with excellent stability. Moreover, **1** perfroms good adsorption ability towards H_2 (2.21 wt% at 77 K and 1 atm), and can selectively adsorb CO_2 from CH_4 and N_2, in spite of its relative low void volume (37.7%), suggesting potential application in gas storage and separation.

2. Experimental section

2.1 Materials and measurements

The ligand 2,4,6-tris(4-carboxyphenoxy)-1,3,5-triazine (H_3tcpt) was synthesized according to the literature method.[9] All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. The IR spectra were recorded on a Thermo Nicolet IR200 FT-IR spectrometer as KBr pellets (4000–400 cm^{-1}). Thermogravimetric analyses (TGA) were carried out on a SHIMADZU DTG-60 thermoanalyzer under nitrogen with a heating rate of 5 ^oC min^{-1} from room temperature to 700 ^oC. Powder X-ray diffraction (PXRD) measurements were performed on a SHIMADZU XRD-6000 X-ray diffractometer using Cu-*K*α radiation (λ = 0.1542 nm), in which the X-ray tube was operated at 40 kV and 40 mA at room temperature. The temperature-dependent X-ray powder diffraction patterns were recorded in a Bruker D8 diffractometer at 40 kV and 40 mA with a Cu-target tube and a graphite monochromator. The elemental analysis for C, H and N were performed on an Elementar Vario Micro Cube analyzer. N_2, H_2, CO_2 and CH_4 adsorption measurements (up to 1 bar) were performed on an Autosorb-3.0 (Quantachrome) volumetric analyzer. All these gases are extra pure quality (99.999% purity).

2.2 Synthesis of 1·solvents

$Zn(NO_3)_2·6H_2O$ (0.2 mmol, 59.4 mg) and H_3tcpt (0.1 mmol, 48.9 mg) were added to a mixed solvent of N,N'-dimethylacetamide (DMA)/ acetonitrile (ACN)/H_2O (v/v/v = 1:1:1, 6 mL) with two drops of tetrafluoroboric acid (HBF_4, 48%) in a sealed glass vial. Then the obtained mixture was ultrasonicated to dissolve and then heated at 90 ^oC for 48 h. After cooling to room temperature, prism colorless crystals were collected by filtration, and washed with H_2O and DMA (Yield: 43.5% based on H_3tcpt). Anal. calcd (%) for the activated sample (see below) $C_{24}H_{13}N_3O_{10}Zn_2$ (%): C, 45.46; H, 2.07; N, 6.63. Found: C, 45.51; H, 2.01; N, 6.57.

2.3 X-ray crystallography

Diffraction intensity data of the single crystal of complex was collected on a Agilent Technologies SuperNova diffractometer at 100 K equipped with a mirror monochromated Cu-Kα radiation (λ= 1.54184 Å) by using a *ω*-scan mode. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.[10] All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program *SHELXL-2014*.[11] The single suite *WINGX*[12] and *Olex2 1.2-alpha*[13] were used as integrated systems for the crystallographic programs. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations, and their positions and thermal parameters were fixed during the structure refinement. For this compound, the volume fractions of disordered solvent in the pores could not be modeled in terms of atomic sites and were treated using the *MASK* routine in the *Olex2* software package. The coordination O atoms of hydroxy in **1**·solvents were disordered, and treated by occupancies refinement of the disordered atoms. Crystallographic data and refinement parameters are listed in Table S1, and selected bond lengths and angles are listed in Table S2. CCDC–1414115 contains the supplementary crystallographic data of **1**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

2.4 Water stability test

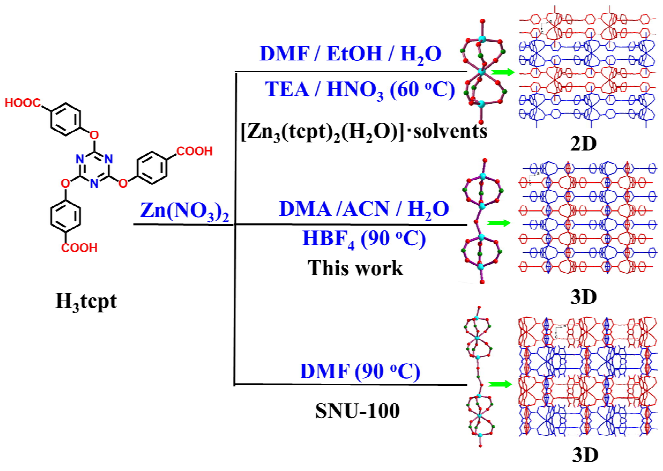
Seven as-synthesized bulk samples in the same batch (45 mg) were soaked in pH = 5, 6, 7, 8, 9, 11, and 12 aqueous solutions for 48 h, respectively. After that, the samples were collected by decanting and dried in air, then the structural integration were checked.

2.5 Gas adsorption measurement

Before gas adsorption measurements, as-synthesized **1**·solvents was soaked in methanol for 3 days to exchange the involved solvents (DMA, ACN and H_2O). Subsequently, the sample was soaked in anhydrous dichloromethane for more than 3 days, during that time fresh dichloromethane was exchanged every day to completely remove methanol solvent. The sample was collected by decanting and dried in air. Before the gas adsorption tests, the dry sample was loaded in a sample tube and further activated under high vacuum at an optimized temperature of 100 ^oC for 6 h. Finally, 68 mg of degassed sample was used for gas sorption measurements. The gas adsorption isotherm measurements were proceeded at 77 K in a liquid nitrogen bath, at 87 K in a liquid argon bath, at 195 K in a dry ice-acetone bath, at 273 K in an ice-water bath and at 298 K in a water bath.

3. Results and discussion

3.1 Synthesis and crystal structure



Scheme 1 Synthetic procetures and structures of three MOFs with H_3tcpt ligand obtained under different reaction conditions.

We all know that there are a lot of factors which can affect the formation of MOFs, such as reaction solvent, temperature and pH. As shown in Scheme 1, three different MOFs were synthesized by using H_3tcpt ligand under different reaction conditions. $[Zn_3(tcpt)(H_2O)_2]\cdot 3H_2O\cdot TEA\cdot 2DMF$ obtained by Han[6] is an *AB* packing 2D structure with 41.4% void volume while SNU-100 obtained by Suh[7] possesses an interpenetrated 3D frameworks with 38.1% solvent accessible volumes. In our work, **1** with a new structural type different from those of above mentioned two MOFs was obtained through a solvothermal reaction of $Zn(NO_3)_2$ and H_3tcpt in a mixed solvent of DMA/ACN/H_2O with two drops of HBF_4 at 90 °C.

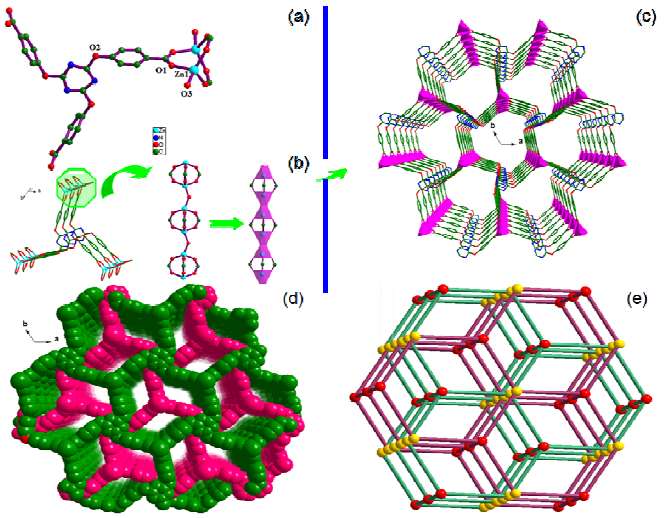


Fig. 1 (a) Coordination environment of the Zn^{2+} in **1**. (All H atoms omitted for clarity). (b) The localized geometry of the $(Zn_2(COO)_3)$ SBU in **1** and polyhedral views of the SBU. (c) View of the hexagonal one-dimensional (1D) channels in a single 3D framework of **1**. (e) Space-filling view of 1D channels in **1** (after interpenetration). (e) Schematic representation of the (3,5) topological net in **1**; the golden balls represent three-connected ligand $tcpt^{3-}$, and the red balls represent the five-connected SBUs.

Single-crystal X-ray structure analysis reveals that **1**·solvents crystallizes in the hexagonal $P6_3/m$ space group and possesses a two-fold interpenetrated 3D framework structure. In the structure of **1**, there exists one crystallographic independent Zn(II) center which is coordinated by three O atoms of carboxylate from three $tcpt^{3-}$ ligands and one O atom of hydroxy (Fig. 1a), and the angle between the triazine ring and benzene ring in $tcpt^{3-}$ ligand is 90°. As shown in Fig. 1b, the two adjacent Zn(II) are bonded together by three carboxylate groups to generate a paddlewheel SBU $(Zn_2(COO)_3)$, which is linked by two hydroxy groups to give a five-connected node, as cofirmed by solid state ^{1}H NMR (Fig. S7). This node is different from the six-connected SBU node $(Zn_3(COO)_6)$ in SNU-100[7] and $[Zn_3(tcpt)(H_2O)_2]\cdot 3H_2O\cdot TEA\cdot 2DMF$ MOFs.[6] The Zn–O1 bond length is 1.921(4) Å, which is close to those reported in other zinc-carboxylate compounds.[5a,6,7,8b,8c] In **1**, each SBU links to three $tcpt^{3-}$ ligands, and each $tcpt^{3-}$ ligand binds three SBUs to form a 2D layer with an irregular hexagonal lattice, which run parallel to the *ab* plane. Interestingly, these 2D layers are linked by O atoms of hydroxy along the *c* axis, which gives rise to a 3D framework (Fig. 1c). Due to the large void, two 3D networks mutually interpenetrate (Fig. 1d), reinforced with each other via intermolecular π···π (3.4490 Å) interactions between the nearly coplanar central triazine rings. As a result, the stability of the whole frameworks is further enhanced (as discussed below), and the porosity of this MOF is tuned owning to the hexagonal channels being parted into three smaller rhombic channels with the dimensions of about 4.0 × 6.4 Å (*a* × *b*, taking into account the *van der Waals* radii). By simplifing the organic ligand and the SBU as 3-connected and 5-connected nodes, respectively, the overall structural framework of **1** can be described as a (3,5)-connected infinite 3D *hms* topology (Schlafli symbol $(6^3)(6^9\cdot 8)$) (Fig. 1e). In addtion, the effective free void volume of **1** estimated is about 36.8% (617.4 $Å^3$ out of the 1678.3 $Å^3$ per unit cell volume).

3.2 Stability

Framework stability is one of restrictive factors for the practical application of MOFs. To examine the thermal and water stability of **1**, TGA and PXRD experiments were carried out. The TGA curve of the as-synthesized **1**·solvents reveals a total weight loss of 19.4% before 400 °C, corresponding to the loss of the guest ACN, H_2O and DMA solvent molecules (calculated, 18.7%) following by the decomposition of the compound (a significant weight loss is observed) (Fig. S2b). The TGA curve of solvent (MeOH and CH_2Cl_2) exchanged sample of **1** exhibits the weight loss of 20% from 25 to 140 °C indicating the removal of the new solvent molecules and the framework could remain stable up to 400 °C, followed by the compound decomposition. Compared with the 2D structural $[Zn_3(tcpt)(H_2O)_2]\cdot 3H_2O\cdot TEA\cdot 2DMF$[6] with a thermal stability up to 360 °C, SNU-100[7] and **1** seemed to be more stable. This might be caused by the SBU stabilization[28,29]. In the SBU, Zn(II) is four-coordinated in a tetrahedral environment, which is generally a stable configuration for Zn(II) complexes. Moreover, both the discrete SBUs in SNU-100 and **1** were connected to form an infinite chain of linked SBUs, further improving the stability of the SBU and the whole frameworks.

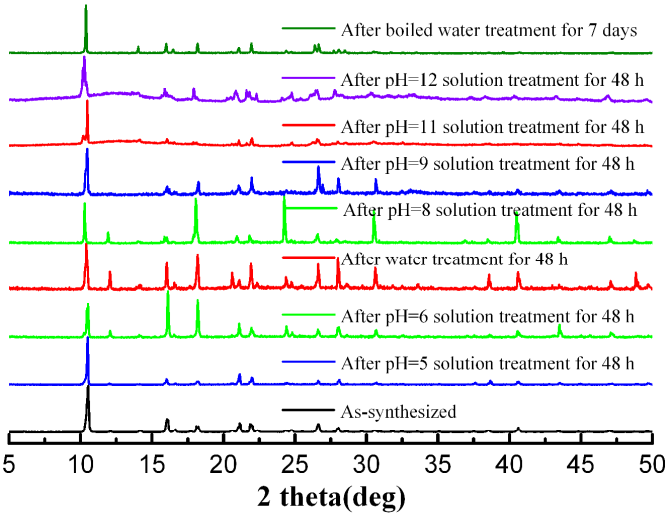


Fig. 2 PXRD patterns of **1** after treated by soaking its samples in pH = 5, 6, 7, 8, 9, 11 and 12 aqueous solutions, respectively for 48 h and boiled water for 7 days.

It should be pointed out that a lot of MOFs can not preserve their framework structues under water environment, because the relative weak coordination bonds could not stand the attack from water molecule, particularly in acid/base conditions, which limits their applications in a lot of fields. Therefore, the stable MOFs are urgent

pursuit.[14] For **1** in this work, firstly it was found that the PXRD patterns of the as-synthesized bulk product, the solvent exchanged sample and the after gas-sorption sample are closely coincident with the simulated pattern derived from the X-ray single crystal data (Fig. S2a), suggesting a good stability against organic solvents and vacuum of this MOF. Then, the PXRD patterns of samples of **1** which were treated by soaking in pH = 5, 6, 7, 8, 9, 11 and 12 aqueous solution, respectively for 48 h were collected (Fig. 2). Interestingly, the resulting patterns still match well with the simulated one, indicating the high water stability, even if in the presence of acid. However, the samples of **1** dissolved aqueous solution with the pH over 13. Another tough condition, soaking the samples of **1** in boiled water, was tested. Surprisingly, this MOF could be stable in boiled water for at least 7 days, as proved by the PXRD (Fig. 2 and Fig. S2e). Furthermore, the CO_2 uptakes of the samples of **1** treated by aqueous solutions with different pH values have no obvious changes when compared with original sample (Fig. 5d), also confirming the excellent framework stability of **1**. The excellent water/acid stability of this MOF may be attributed to the specific SBU and interpenetrated nature in its structure, being beyond a lot of Zn(II)-based MOFs.

3.3 Gas adsorption

Encouraged by the porous structure, the high stability and structural rigidity, N_2 adsorption experiment at 77 K was performed to evaluate the porosity of **1**. The uptake amount of N_2 is 252 $cm^3\ g^{-1}$ (STP) at 77 K and 1 atm, and the adsorption shows a reversible type I isotherm (Fig. 3), which is characteristic of the microporous material. The calculated H-K (Horvath-Kawazoe)[15] pore size distributions range from 3.2 to 7.8 Å, being corresponding to the pore sizes evaluated form single-crystal X-ray structure. Based on the N_2 adsorption isotherm, the Brunauer-Emmett-Teller (BET) and Langmuir surface areas of this MOF are estimated to be 905 and 1076 $m^2\ g^{-1}$, respectively, and the pore volume is 0.306 $cm^3\ g^{-1}$, both higher than those for $Zn_3(tcpt)(H_2O)_2$.

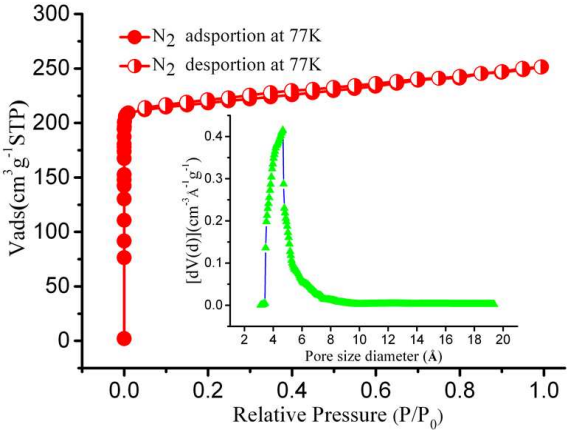


Fig. 3 N_2 sorption isotherms of **1** at 77K (inset, pore size distribution plot).

The permanent porosity and suitable pore size in **1** prompt us to investigate its H_2 storage ability. The adsorption isotherms of H_2 at 77 and 87 K under the pressure up to 1 atm are shown in Fig. 4. It reveals that **1** can adsorb a large amount of H_2 up to 2.21 wt% and 1.52 wt%, respectively at 1 atm. It should be pointed out that the H_2 uptake of **1** is comparable with many reported MOFs like MOF-177,[S6] MOF-650,[S13] SNU-100'-M',[7] and Cu_2(TPPC-O^{n}Pr)[S14] in spite of its relative lower void volume (37.7%) and BET surface areas (Table S3). It is noteworthy that the micropore size distributions of **1** is around 5 Å just close to the size about two H_2 molecules (2 × 2.8 Å), which may help enhancing the interaction forces between the H_2 molecules and the framework, thereby benefiting the H_2 adsorption. Moreover, as shown in Fig. S6, interpenetration brought rhombic channels with small open windows (3.66 Å, Fig. S6), which might benefit for the H_2 adsorption.[7,29,30] Some studies have proved that small pore size is necessary to achieve high H_2 uptake, since the small pore enables the overlap of energy potentials between the opposing walls, leading to higher interaction energy with the H_2 molecules.[31-34] For example, PCN-6 exhibits a higher H_2 uptake than PCN-6', indicating a substantially stronger interaction in the interpenetrated PCN-6, than that in the non-interpenetrated PCN-6'.[35] To evaluate the interaction between the adsorbed H_2 molecules and the host framework of **1**, the isosteric heats of adsorption (Q_{st}) of H_2 adsorption were calculated, to be 8.0~6.8 kJ mol^{-1} depending on the degree of H_2 loading (Fig. S3b), estimated by fitting the H_2 isotherms at 77 and 87 K using a Virial method (Fig. S3a)[16]. The initial Q_{st} (8.0 kJ mol^{-1}) is higher than those for some common MOFs such as MOF-5 (4.8 kJ mol^{-1}), because of the small pore size resulting from the structural interpenetration.

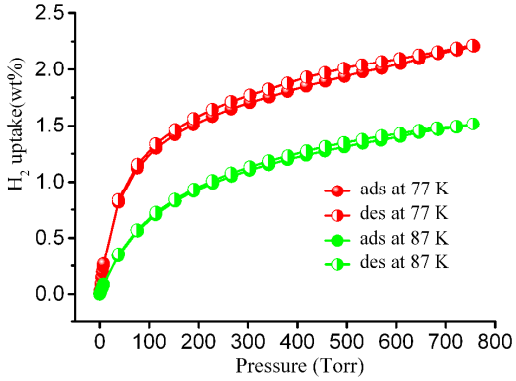


Fig. 4 H_2 sorption isotherms of **1**.

Although non-interpenetrated frameworks usually have large pores and high surface areas suitable for a lot of adsoption-based applications,[8a,S6,S13] the interpenetrated networks have been proven to be useful in some cases, such as in selective guest captures.[4b,17-20] Therefore, **1** was further checked for CO_2, CH_4 and N_2 captures. The adsorption isotherm of CO_2 at 195 K is shown in Fig. 5a. Clearly, significant amounts of CO_2 were adsorbed and the isotherm presents typical type I curve, with no obvious change upon repeated cyclings. The adsorption amounts increase abruptly at the low pressure range, up to 150 $cm^3\ g^{-1}$ (STP) at 50 torr, and finally up to 205 $cm^3\ g^{-1}$ (40.3 wt%) at 1 atm. Approximately 11.6 CO_2 molecules are adsorbed for per cell volume of **1**. Moreover, as shown in Fig. 5b and c, gas adsorptions of **1** exhibit significantly different uptakes towards CO_2, CH_4 and N_2 at both 273 and 298 K. **1** can uptake a moderate amount of CO_2 up to 110.5 $cm^3\ g^{-1}$ (273 K) and 71.3 $cm^3\ g^{-1}$ (298 K), while the uptake amounts of CH_4 are 45.8 $cm^3\ g^{-1}$ (273 K) and 19.9 $cm^3\ g^{-1}$ (298 K) at 1 atm. However, at the two temperatures, the uptake amounts of N_2 are only 17.7 and 3.5 $cm^3\ g^{-1}$, respectively at 1 atm.

In order to estimate the adsorption selectivities of **1** towards CO_2, CH_4 and N_2, the initial slopes of their adsorption isotherms were calculated at very low pressure ranges (Fig. S5a and b).[21] The calculated CO_2/CH_4 selectivity is 5.2:1 at 273 K and 5.0:1 at 298 K. Using the same method, the CO_2/N_2 selectivities were calculated to be 19.4:1 at 273 K and 33.6:1 at 298 K, respectively. The selectivity for CO_2 over N_2 at 298 K is indeed comparable to some reported MOFs (Table S4), and higher than BPL carbon which is widely applied in industry for gas separations.[36] In addition, to evaluate the interaction between the CO_2 molecules and the host framework, the CO_2 isosteric heats of adsorption (Q_{st}) in **1** was calculated based on the respective adsorption isotherms at 273 K and 298 K. Employing the Clausius-Clapeyron equation,[22,23] the calculated Q_{st} values range from 31.2 to 40.9 kJ mol^{-1} depending on the gas loading (Fig. S4). The observed selective sorption behaviors of CO_2 over CH_4 and N_2 may be attributed to the stronger host-guest interaction between the CO_2 molecules with large quadrupole moment and the framework, than other two gases.[24-27] On the other hand, the framework interpenetration leads to narrow rhombic channels with a size of 4.0 × 6.4 Å. However, the height of rhombic channels is only 3.66 Å (Fig. S6). Given the dynamic radius of these gas molecules, CO_2 (3.3 Å), N_2 (3.64 Å), CH_4 (3.8 Å), dimensional effect may also play an important role for the selective adsorption.

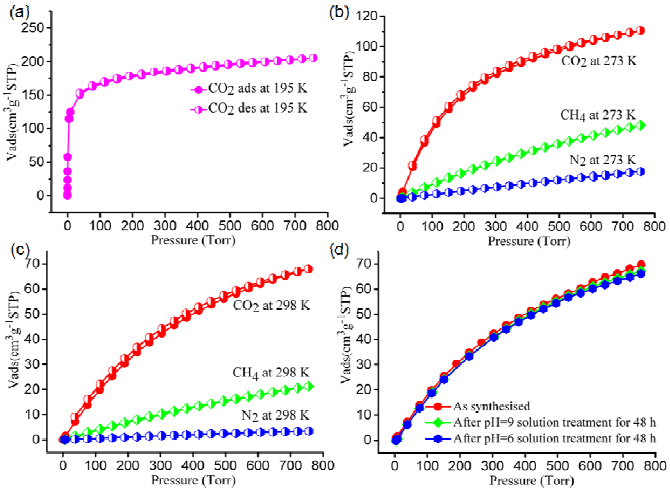


Fig. 5 Gas sorption isotherms for **1**: (a) CO_2 at 195 K. (b) CO_2, CH_4 and N_2 at 273 K. (c) CO_2, CH_4 and N_2 at 298 K. (d) CO_2 at 298 K.

Conclusions

A novel two-fold interpenetrated 3D MOF with rare Zn(II)-based SBU, ($Zn_2(COO)_3$) has been synthesized under a solvothermal reaction conditions and structurally characterized. Compared with reported Zn(II)-based partners with the same ligand, the synthesis conditions, particularly used solvents played a key role in the formation of different SBUs, thereby distinct MOFs in this system. Particularly, **1** has good thermal and excellent water stability, even if in acid aqueous solution with the pH ranging from 5 to 12. In addition, **1** performs pretty good gas sorption capabilities for H_2 and CO_2, and high adsorption selectivities towards CO_2 over N_2 and CH_4, suggesting its potential applications in gas storage and separation.

Acknowledgement

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Graphical Abstract

A Hydrothermal Stable Zn(II)-based Metal-Organic Framework: Structural Modulation and Gas Adsorption

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A hydrothermal stable MOF, $[Zn_2(tcpt)OH]$·solvents (**1**·solvents) was synthesized, in which an unusual paddlewheel SBUs $Zn_2(COO)_3$ was found. Furthermore, **1** can adsorb considerable amounts of H_2 and displays high selective adsorption of CO_2 over N_2.