



# Microporous metal-organic frameworks with suitable pore spaces for acetylene storage and purification



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## ABSTRACT

Two isostructural metal-organic frameworks (MOFs) **Cu<sub>2</sub>TPTC-Me** and **Cu<sub>2</sub>TPTC-OMe** have been synthesized and characterized. The as-synthesized MOFs show good thermal stability and hydrothermal stability. With open metal sites, suitable pore spaces and functional groups to confine acetylene molecules in frameworks, both MOFs exhibit high gravimetric acetylene storage capacities: **Cu<sub>2</sub>TPTC-Me** has a gravimetric capacity of 203 cm<sup>3</sup> g<sup>-1</sup> at 298 K and 1 bar, and **Cu<sub>2</sub>TPTC-OMe** has the highest gravimetric acetylene storage capacity ever reported with the capacity of 204 cm<sup>3</sup> g<sup>-1</sup> under the same conditions. Furthermore, **Cu<sub>2</sub>TPTC-Me** possesses both high separation selectivities of C<sub>2</sub>H<sub>2</sub>/CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> with the Henry law's selectivity of 60 and 12.7 at room temperature, respectively.

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## 1. Introduction

Acetylene (C<sub>2</sub>H<sub>2</sub>) is one of the most important raw material for various industrial productions and a promising alternative energy source for fuel cell vehicles in the future [1,2]. However, transportation of acetylene is difficult because acetylene storage is limited to <0.2 MPa in order not to cross an explosive threshold, and the current method of storing acetylene by dissolution the gas in acetone placed in a steel cylinder along with an absorbent is dangerous and easy to be contaminated. What's more, it is extremely energy consuming to separate productive acetylene from impurity gases (mainly are methane and carbon dioxide) using the traditional separation technology by cryogenic distillation based on their different vapor pressures and boiling points [3,4]. It is highly desired to discover new materials for acetylene safe storage and energy-saving purification [5–7].

As a relatively new family of porous materials, metal-organic frameworks (MOFs), which can be readily self-assembled from their corresponding metal ions or metal-containing clusters with suitable organic linkers, have been widely explored for acetylene storage [8–13] and separation [14–22]. By immobilizing specific

sites, such as open metal sites [23,24] and Lewis acidic and basic sites [25,26] into the frameworks, either high acetylene storage capacity or separation capacity has been reached in dozens of MOFs, but there are a few MOFs which exhibit both high acetylene storage capacity and separation capacity at the same time [27,28]. As for acetylene separation, optimization of both separation selectivity (mainly determined by the functional sites and size exclusive effect) and storage capacity (mainly determined by the gas storage capacities) is very important and still a challenge for researchers now. Actually, separation selectivity and storage capacity metrics do not appear to go hand-in-hand. For example, CoMOF-74 and MgMOF-74 have extraordinarily high acetylene storage capacity but low C<sub>2</sub>H<sub>2</sub>/CH<sub>4</sub> separation selectivity [6]. USTA-15 [29] and Cu<sub>3</sub>(TDPAH) (H<sub>2</sub>O)<sub>3</sub> [30] have high C<sub>2</sub>H<sub>2</sub>/CH<sub>4</sub> separation selectivity of 56 and 80.9, but low acetylene uptake amount of 34 and 155.7 cm<sup>3</sup> g<sup>-1</sup> at room temperature and 1 atm, respectively. USTA-50 [31] has high C<sub>2</sub>H<sub>2</sub>/CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation selectivity of 68 and 13.3 respectively, but the uptake amount of acetylene is only 91 cm<sup>3</sup> g<sup>-1</sup> at 296 K and 1 atm. Recently optimizing pore spaces has been known as another efficient method to confine gas molecules in frameworks and increase adsorption selectivity [32–35]. Lin and co-workers [36] have demonstrated that by introducing methyl groups into ligand to create smaller pores can enhance the isosteric heat of adsorption and improve H<sub>2</sub> adsorption. We speculate that if those important factors mentioned

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above could be incorporated into MOFs simultaneously and then collaboratively utilized to maximize acetylene storage and separation capacity, we could realize some more promising MOFs for acetylene safe storage and energy-saving purification. Herein we designed and synthesized two isostructural NbO-type microporous MOFs **Cu<sub>2</sub>TPTC-Me** (TPTC-Me = 2',5'-dimethyl-[1,1':4',1''-terphenyl]-3,3'',5,5''-tetracarboxylate) and **Cu<sub>2</sub>TPTC-OMe** (TPTC-OMe = 2',5'-dimethoxy-[1,1':4',1''-terphenyl]-3,3'',5,5''-tetracarboxylate) for acetylene storage and purification. With open metal sites, suitable pore spaces and functional groups to confine acetylene molecules, both MOFs exhibit exceptionally high gravimetric capacities of 203 cm<sup>3</sup> g<sup>-1</sup> and 204 cm<sup>3</sup> g<sup>-1</sup> at 298 K and 1 bar respectively, which are moderately higher than the previously reported highest value of 201 cm<sup>3</sup> g<sup>-1</sup> in HKUST-1 [37]. What's more, **Cu<sub>2</sub>TPTC-Me** exhibits high selectivities of C<sub>2</sub>H<sub>2</sub>/CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> with the Henry law's selectivity of 60 and 12.7 at room temperature, respectively.

## 2. Experimental

### 2.1. Materials and measurements

All chemical reagents and gases were obtained from commercial sources and used without further purification. Nitrogen (N<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), acetylene (C<sub>2</sub>H<sub>2</sub>), methane (CH<sub>4</sub>), and argon (Ar) were obtained from Jinggong Special Gas Company (Hangzhou, China). Organic solvents 1,4-dioxane, acetonitrile, N,N-dimethylformamide (DMF), trichloromethane (CHCl<sub>3</sub>), tetrahydrofuran (THF), toluene, ethylacetate, petroleum ether, and other relevant inorganic compounds (HCl, NaOH, K<sub>2</sub>CO<sub>3</sub>, and MgSO<sub>4</sub>) were purchased from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). Bis(pinacolato)diboron, and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> were obtained from Energy Chemical (Shanghai, China). Cupric nitrate was purchased from Aladdin Chemistry Co., Ltd., (Shanghai, China). 1,4-Dibromo-2,5-dimethyl-benzene and 1,4-dibromo-2,5-dimethoxy-benzene were obtained from Alfa Aesar (Tianjin, China). Dimethyl 5-aminoisophthalate was purchased from Shanghai Demo Medical Technology Co., Ltd., (Shanghai, China). Elemental analyses for C, H, and N were performed on an EA1112 microelemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ = 5–50° range on an X'Pert PRO diffractometer with Cu K<sub>α</sub> radiation (λ = 1.542 Å) at room temperature. Thermogravimetric analyses (TGA) were conducted on a Netzsch TGA 209 F3 thermogravimeter with a heating rate of 10 K min<sup>-1</sup> in N<sub>2</sub> atmosphere. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> on a 500 MHz Bruker Advance DMX500 spectrometer with tetramethylsilane (TMS) as an internal standard.

### 2.2. Gas sorption measurements

Gas adsorption was measured by a Micromeritics ASAP 2020 surface area analyzer. In order to remove guest solvent molecules in the framework, both MOFs were exchanged with dry acetone 12 times and then activated at 373 K under high vacuum for 12 h until the outgas rate was <5 μmHg min<sup>-1</sup> prior to measurements. N<sub>2</sub> sorption isotherms were measured at 77 K with liquid nitrogen. C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> sorption isotherms were measured at 273 K with ice-water bath (slush), and at 298 K with a water bath of 25 °C, respectively.

Isotherm data were analyzed using the virial equation [36]:

$$\ln(n/p) = A_0 + A_1 n + A_2 n^2 + \dots \quad (1)$$

where the *p* is pressure, *n* is total amount adsorbed, and A<sub>0</sub>, A<sub>1</sub>, etc., are virial coefficients. A<sub>0</sub> is related to adsorbate–adsorbent

interactions, whereas A<sub>1</sub> describes adsorbate–adsorbate interactions. At low surface coverage A<sub>2</sub> and higher terms can be neglected and A<sub>0</sub>, A<sub>1</sub> can obtain from the linear fitting equation between ln(*n/p*) and *n*. The Henry's Law constant (K<sub>H</sub>) is equal to exp(A<sub>0</sub>), and the Henry's law selectivity for C<sub>2</sub>H<sub>2</sub> over CH<sub>4</sub> and CO<sub>2</sub> is calculated based on the equation S<sub>ij</sub> = K<sub>H</sub>(i)/K<sub>H</sub>(j).

The isosteric heat of adsorption, Q<sub>st</sub>, defined as

$$Q_{st} = RT^2 \left( \frac{\partial \ln P}{\partial T} \right) \quad (2)$$

were determined using the pure component isotherm fits. The calculations of Q<sub>st</sub> are based on the use of the Clausius–Clapeyron equation [36].

### 2.3. X-ray collection and structure determination

Crystallographic measurements were taken on a Bruker APEX-II diffractometer with an CCD detector using graphite-monochromatic Mo K<sub>α</sub> radiation (λ = 0.71073 Å) at 296 K for **Cu<sub>2</sub>TPTC-Me** and 293 K for **Cu<sub>2</sub>TPTC-OMe**. The determination of the unit cell and data collection of both MOFs was performed with CrysAlisPro. The data reduction was carried out with Bruker SAINT. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm [38]. The structure of both MOFs were determined by direct methods and refined by the full-matrix least-squares method with the SHELX-97 program package [39]. All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropically. The H atoms on the ligands were placed in idealized positions and refined using a riding model. The dimethyl phenyl (dimethoxy phenyl) unit of ligands are disordered, which are split into two parts during structural refinement. The disordered lattice DMF, MeCN and water molecules could not be located successfully from Fourier maps in the refinement cycles. The scattering from the highly disordered lattice guest molecules were removed using the SQUEEZE procedure implemented in the PLATON package [40]. Crystallographic data are summarized in Table S1 and S2. CCDC 1400652 for **Cu<sub>2</sub>TPTC-Me** and CCDC 1400653 for **Cu<sub>2</sub>TPTC-OMe** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### 2.4. Synthesis of Cu<sub>2</sub>TPTC-Me and Cu<sub>2</sub>TPTC-OMe

**Cu<sub>2</sub>TPTC-Me** and **Cu<sub>2</sub>TPTC-OMe** were solvothermally synthesized similarly to the literatures [36,41]. Organic linkers H<sub>4</sub>TPTC-Me and H<sub>4</sub>TPTC-OMe were synthesized via Suzuki coupling reaction followed by hydrolysis and acidification (Scheme S1).

**Synthesis of Cu<sub>2</sub>TPTC-Me.** H<sub>4</sub>TPTC-Me (15 mg, 0.035 mmol) and Cu(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2.5</sub> (30 mg, 0.129 mmol) were dissolved in DMF/H<sub>2</sub>O/ acetonitrile (10 mL, v/v/v = 3:1:1) in a screw-capped vial. After adding HCl (100 μL) (37%, aq.) to the mixture, the vial was capped and then heated at 80 °C for 48 h in an oven. Then green rhombicprism shaped crystals were harvested after cooling down the mixture to room temperature and washing it several times with DMF. Elemental analysis: Calcd (Found) For Cu<sub>2</sub>(TPTC-Me)(H<sub>2</sub>O)<sub>2</sub>·(DMF)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>MeCN: C, 47.39 (46.90); H, 5.56 (5.43); N, 7.27 (7.64)%.

**Synthesis of Cu<sub>2</sub>TPTC-OMe.** H<sub>4</sub>TPTC-OMe (15 mg, 0.032 mmol) and Cu(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2.5</sub> (30 mg, 0.129 mmol) were dissolved in DMF/H<sub>2</sub>O (8 mL, v/v = 3:1) in a screw-capped vial. After adding HCl (50 μL) (37%, aq.) to the mixture, the vial was capped and then heated at 80 °C for 48 h in an oven. Then green rhombicprism

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