

## A two dimensional microporous metal-organic framework for selective gas separation



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### ABSTRACT

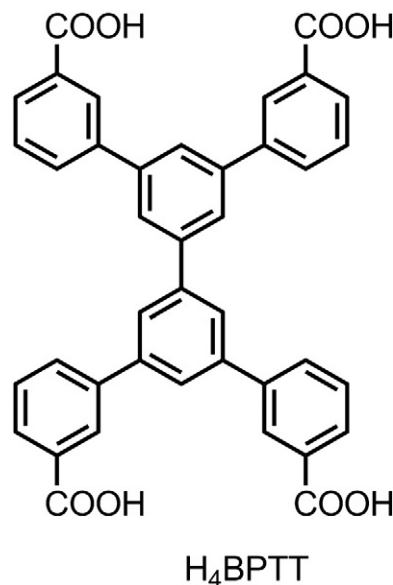
A new organic ligand of 1,1'-biphenyl-containing tetra-carboxylic acid (H<sub>4</sub>BPTT) and its first metal-organic framework [Zn<sub>2</sub>(BPTT)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>·(DMF)<sub>4.5n</sub> (**1**) was designed, synthesized and structurally characterized exhibiting two-dimensional distorted (4,4) topology. The activated **1a** exhibits permanent porosity and moderately high selectivities for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> gas separations at room temperature.

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Microporous metal-organic frameworks (MOFs) are of great interest for their diverse applications, particularly on gas storage and separation [1–8]. Compared with three-dimensional MOFs [9–12], two-dimensional MOFs are less explored for such applications because it is more challenging to stabilize the frameworks and generate the permanent porosities [13–16]. Among different types of 2D MOFs, those constructed from paddle-wheel M<sub>2</sub>(CO<sub>2</sub>)<sub>4</sub> (M = Zn<sup>2+</sup> and Cu<sup>2+</sup>) clusters and dicarboxylates, for example, Zn(BDC)(DMF) [13] and Cu(BDC-OH) [14], have attracted much attentions. Recently, we have been interested in developing new tetracarboxylic acids and realized that some of organic linkers are also favorable to assemble with paddle-wheel clusters to construct 2D frameworks. Although 2D frameworks are typically less porous than 3D ones, but the smaller pores within 2D ones might enforce their high gas separation selectivities. With this in mind, we developed a new organic linker, 3,3',3'',3'''-(1,1'-biphenyl-3,3',5,5'-tetrayl) tetrabenzoic acid (H<sub>4</sub>BPTT) (Scheme 1) and reported its first MOF of two-dimensional sheet for selective gas separation at room temperature.

This linker can be straightforwardly synthesized from the corresponding precursors. Solvothermal reaction of this organic linker with Zn(NO<sub>3</sub>)<sub>2</sub> led to the formation of new microporous MOF [Zn<sub>2</sub>(BPTT)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>·(DMF)<sub>4.5n</sub> (**1**) in which the well-known paddle wheel Zn<sub>2</sub>(COO)<sub>4</sub> clusters are bridged by BPTT tetracarboxylates to form a two-dimensional MOF (Supporting information). As shown in Fig. 1, the adjacent 2D frameworks are stacked with each other,

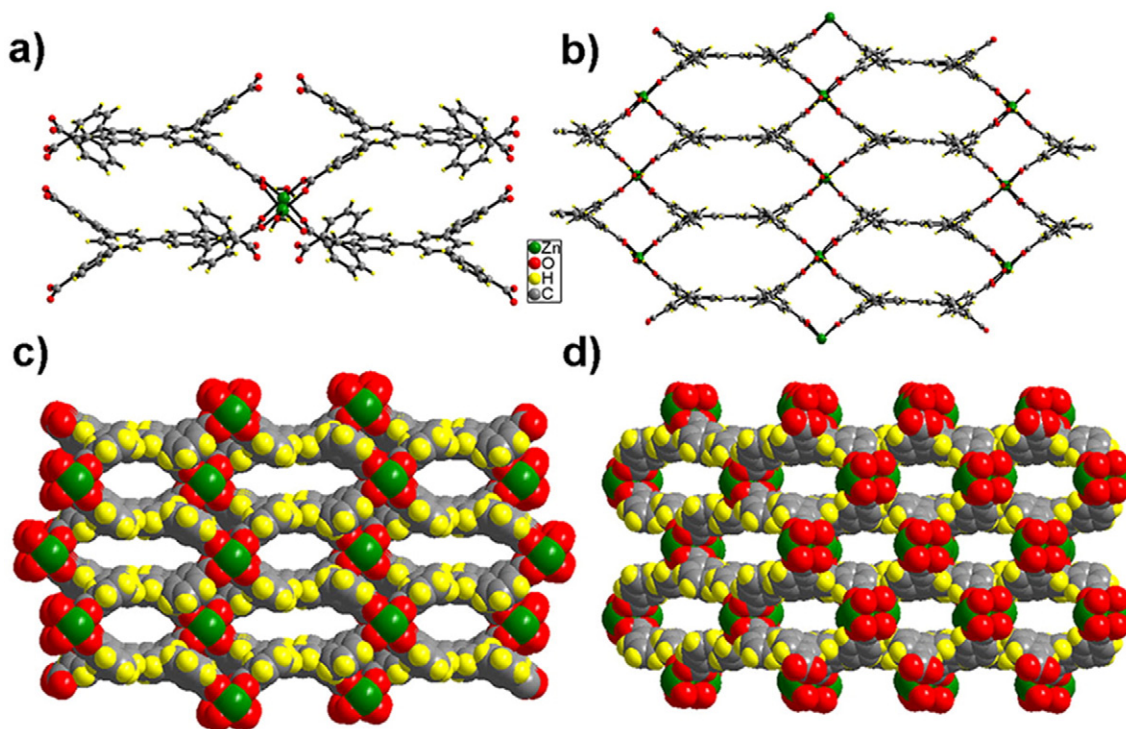
having potential accessible pores of 3.1 × 3.1 Å<sup>2</sup> and 2.9 × 6.2 Å<sup>2</sup>, respectively, without the consideration of the terminal and free solvent molecules (Fig. 1d and e). Unlike the more regular (4,4) square nets in Zn<sub>2</sub>(TBAPy) [15] and UTSA-72 [16], the one in **1** is



Scheme 1.

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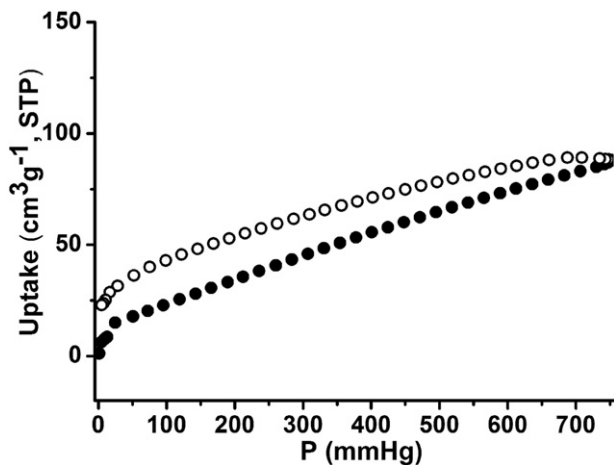


**Fig. 1.** X-ray crystal structure of **1** indicating (a) the coordination geometry for Zn(II) atoms, (b) 2D framework with the distorted (4,4) topology, (c) the framework packing of **1** along (d) *a* and (e) *c* axis, respectively.

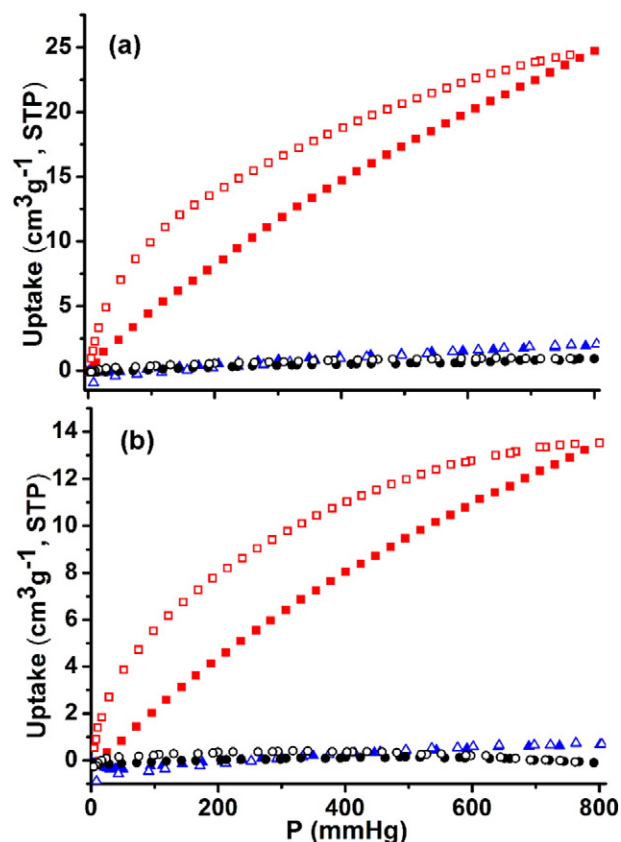
heavily distorted, leading to its different packing from  $\text{Zn}_2(\text{TBAPy})$  [15] and **UTSA-72** [16] as well.

The phase purity of the material in bulk amount was confirmed by powder X-ray diffraction (PXRD) (Fig. S2). Thermogravimetric analysis (TGA) studies reveal that **1** gradually loses the free DMF and coordinated water molecules (obsd. 31.4%, calcd. 31.7%) in the temperature range from 25 °C to 400 °C to form the desolvated framework. The activated **1a** still exhibits crystalline nature as shown in its PXRD pattern. The acetone-exchanged **1** was activated under high vacuum at room temperature for 24 h and then 80 °C for 20 h to generate the activated **1a**. The  $\text{CO}_2$  gas sorption isotherm at 196 K (Fig. 2) clearly indicates its microporous nature. **1a** has Brunauer–Emmett–Teller (BET) surface area of  $143 \text{ m}^2 \text{ g}^{-1}$ , which is smaller than  $173 \text{ m}^2/\text{g}$  in **UTSA-72a** [16].

The small pore spaces and the establishment of its permanent porosity within **1a** motivated us to examine its  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2$  gas sorption



**Fig. 2.**  $\text{CO}_2$  sorption isotherm of **1a** at 196 K (solid symbols: adsorption, open symbols: desorption).



**Fig. 3.**  $\text{CO}_2$  (red),  $\text{CH}_4$  (blue), and  $\text{N}_2$  (black) sorption isotherms of **1a** at (a) 273 K and (b) 296 K (solid symbols: adsorption, open symbols: desorption).

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