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# A new meso-porous coordination polymer: synthesis, structure, and gas adsorption studies

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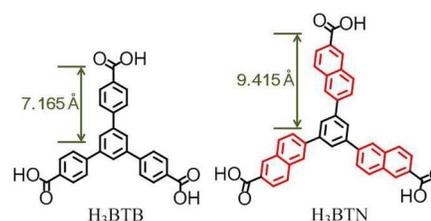
A new porous coordination framework,  $[\text{Cu}_3(\text{BTN})_2(\text{H}_2\text{O})_3] \cdot x\text{Guest}$  (NJTU-1), with large aromatic organic surface and remarkable meso-pore, was synthesized and structurally characterized. It exhibits a second high BET surface area of  $2800 \text{ m}^2 \cdot \text{g}^{-1}$  among the interpenetrated PCPs. Additionally, this PCP also demonstrates high  $\text{CH}_4$  (excess amount:  $174 \text{ cm}^3 \cdot \text{g}^{-1}$ ),  $\text{C}_2\text{H}_4$  ( $220 \text{ cm}^3 \cdot \text{g}^{-1}$ ),  $\text{C}_2\text{H}_6$  ( $299 \text{ cm}^3 \cdot \text{g}^{-1}$ ) and  $\text{CO}_2$  ( $298 \text{ cm}^3 \cdot \text{g}^{-1}$ ) uptake capacities as well as good adsorption selectivities of  $\text{C}_2\text{H}_4$  (12-145),  $\text{C}_2\text{H}_6$  (15.5-380) and  $\text{CO}_2$  (7.1-31.6) towards  $\text{CH}_4$  at 298 K.

Due to the depletion of fossil oil and the threat of global warming, a great deal of effects have been made to find the clean energy carriers, such as hydrogen, methane and  $\text{C}_2$  hydrocarbons, as well as the reduction of carbon dioxide emissions<sup>1</sup>. However, the major technical challenge for their feasible applications is how to construct an effective and economic storage system to trap the energy gas molecules. Porous coordination polymer (PCP), emerging as a new class of crystalline porous materials, has been considered as the most promising candidate<sup>2</sup>. Compared with traditional porous materials, such as activated carbons<sup>3</sup>, nanotubes<sup>4</sup>, and zeolites<sup>5</sup>, PCPs not only exhibit a large gas-uptake capacity but also structures that can be carefully tuned for trapping gas molecule in nano-space<sup>6</sup>.

Recent studies of PCPs demonstrated that besides the large surface area and pore volume, a stronger host-guest interaction is also very important for realizing higher gas uptake<sup>7</sup>. Generally, the introducing of dense and exposed metal clusters<sup>8</sup>, decorating some specific functional groups ( $-\text{NH}_2$ ,  $-\text{CONH}$ , etc.)<sup>7, 9</sup> and narrowing the pore size<sup>10</sup> were believed as the effective methods for enhanced affinity between PCP and gas molecule. Indeed, these strategies can increase the gas-binding affinity; however, they also generally lead to a decline in gas-uptake capacity because of the decreased surface area and pore volume<sup>8-10</sup>. Furthermore, the higher affinity between the host and guest will result in the higher energy consumption during the regeneration<sup>9a</sup>. Thus, to design and prepare the PCP with moderate adsorption heat for high capacity of gas storage and separation remains a challenge<sup>6g, 11</sup>.

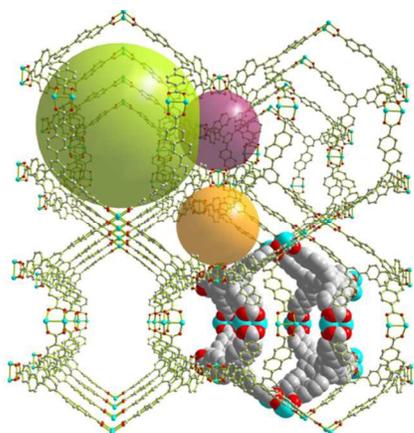
Very recently, we developed a strategy by using an organic wall to prepare porous structures,  $[\text{La}(\text{BTB})]^{12}$  and  $[\text{La}(\text{BTN})]^{13}$ , that possess high gas separation capability. The organic sites in them provide moderate binding energy to guest molecules. To continual our work, we present a mesoporous framework derived from the organic linker of

$\text{H}_3\text{BTN}$  (Scheme 1),  $[\text{Cu}_3(\text{BTN})_2(\text{H}_2\text{O})_3] \cdot x\text{Guest}$  (NJTU-1: NJTU denotes Nanjing Tech University), with a second high BET surface area of  $2800 \text{ m}^2 \cdot \text{g}^{-1}$  among the interpenetrated PCPs. Additionally, this PCP also demonstrates high  $\text{CH}_4$  (excess amount:  $174 \text{ cm}^3 \cdot \text{g}^{-1}$ ),  $\text{C}_2\text{H}_4$  ( $220 \text{ cm}^3 \cdot \text{g}^{-1}$ ),  $\text{C}_2\text{H}_6$  ( $299 \text{ cm}^3 \cdot \text{g}^{-1}$ ) and  $\text{CO}_2$  ( $298 \text{ cm}^3 \cdot \text{g}^{-1}$ ) uptake capacities as well as good adsorption selectivities of  $\text{C}_2\text{H}_4$  (12-145),  $\text{C}_2\text{H}_6$  (15.5-380) and  $\text{CO}_2$  (7.1-31.6) towards  $\text{CH}_4$  at 298 K.



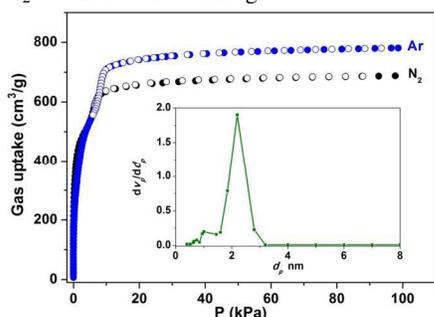
**Scheme 1.** Molecular structures of the ligands  $\text{H}_3\text{BTB}$  and  $\text{H}_3\text{BTN}$

Solvothermal reaction of  $\text{H}_3\text{BTN}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  in  $\text{DMF}/\text{H}_2\text{O}$  under acidic conditions at  $65 \text{ }^\circ\text{C}$  affords block-shaped pale-blue single crystals of  $[\text{Cu}_3(\text{BTN})_2(\text{H}_2\text{O})_3]$  (NJTU-1) with high yield. A single-crystal structure determination revealed that NJTU-1 crystallizes in the Im-3 space group. Each square  $[\text{Cu}_2(\text{COO})_4]$  paddlewheel was bridged by four branched  $\text{BTN}^{-3}$  ligands, and  $\text{BTN}^{-3}$  ligand was connected by three paddlewheels, resulting in a 3, 4-connected net which is same as the prototypical  $\text{Pt}_3\text{O}_4$  framework, MOF-14<sup>14</sup>. Strong  $\pi$ - $\pi$  interactions between the adjacent aromatic rings of the BTN ligands, displaced each other by  $3.79 \text{ \AA}$ , hold the interpenetrated BTN units together. The overall structure of NJTU-1 is packed by three types of cages (Fig. 1), however, despite interpenetration, the tailored diameter ( $\sim 25 \text{ \AA}$ ) in two integrated pore still makes NJTU-1 to be the rare interpenetrated PCP with mesopores, and which can't be realized by MOF-14. The total accessible volume of the fully desolvated NJTU-1 is ca. 74.6% (calculated by the PLATON program), reflecting a high porosity. In addition, the PXRD profile of NJTU-1 indicates that the framework retains its crystallinity after activation (Fig. S3), and which was also confirmed by the photo of the desolvated sample (Fig. S4). The further leball analysis of the PXRD demonstrated that the cell parameter ( $a = 33.389 \text{ \AA}$ ) of desolvated NJTU-1 increased a little than that of the single crystal data ( $33.175 \text{ \AA}$ ). Therefore, we can conclude that the desolvated NJTU-1 maintained the structural integrity.



**Fig. 1** The packing view of three type cages in NJTU-1.

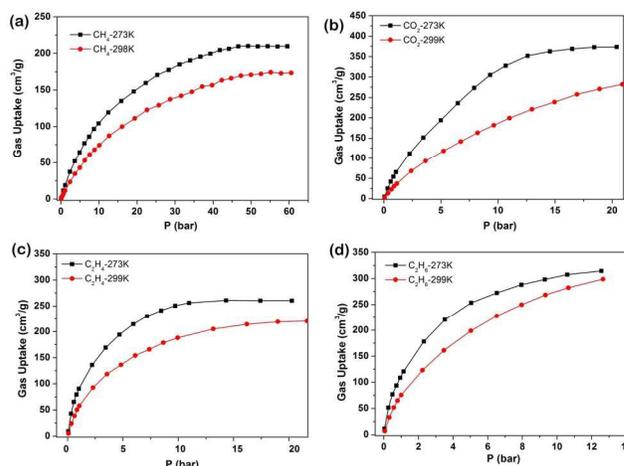
To confirm the rigidity and permanent porosity of NJTU-1, the as-synthesized sample was treated with supercritical carbon dioxide (SCD) and then degassed under high vacuum at room temperature to obtain the desolvated framework. The  $N_2$  and Ar adsorption of NJTU-1 (77 and 87 K) exhibit reversible isotherms with stepwise adsorption behavior (Fig. 2), which are the characteristic for PCPs with meso-pores. Remarkably, NJTU-1 can take up a large amounts of  $N_2$  ( $688 \text{ cm}^3 \cdot \text{g}^{-1}$ ) at 77 K, 1 bar, which is higher than that of HKUST-1 ( $450 \text{ cm}^3 \cdot \text{g}^{-1}$ )<sup>14</sup> and MOF-14 ( $440 \text{ cm}^3 \cdot \text{g}^{-1}$ )<sup>15</sup>. Thus, the estimated apparent Brunauer-Emmett-Teller surface area (BET:  $2800 \text{ m}^2 \cdot \text{g}^{-1}$ ; Langmuir surface  $3030 \text{ m}^2 \cdot \text{g}^{-1}$ ) is almost two times higher than that of MOF-14 (Langmuir surface  $1502 \text{ m}^2 \cdot \text{g}^{-1}$ ), even the size of the ligand just extended very a little ( $2.3 \text{ \AA}$ ). More importantly, to the best of our knowledge, NJTU-1 possesses the second high surface area among the interpenetrated PCPs reported to date (NJU-Bai9:  $4258 \text{ m}^2 \cdot \text{g}^{-1}$ )<sup>16</sup>. The calculated pore size distributions according to the  $N_2$  isotherm are distributed around 11-15 and 17-30  $\text{\AA}$ , indicating that the multiple pore size distributions are consistent with the dimensions of the cages in the crystal structure. In addition, the total pore volume calculated from the maximum amount of adsorbed  $N_2$  reached to  $1.08 \text{ cm}^3 \cdot \text{g}^{-1}$ .



**Fig. 2** Low pressure gas adsorption isotherms of  $N_2$  and Ar in NJTU-1 at 77 and 87 K. The insert figure shows the pore size distribution (DFT model) based on the calculation of the  $N_2$  adsorption isotherms.

High surface area and functional aromatic rings of NJTU-1 prompted us to investigate its gas storage capacities. High pressure adsorption isotherms of  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$  and  $CO_2$  were collected at 273 and 298 K, respectively (Fig. 3). The excess  $CH_4$  uptake of NJTU-1 achieved to  $174 \text{ cm}^3 \cdot \text{g}^{-1}$  at 55 bar and 298 K ( $210 \text{ cm}^3 \cdot \text{g}^{-1}$  at 50 bar and 273 K) (Fig. 3b),

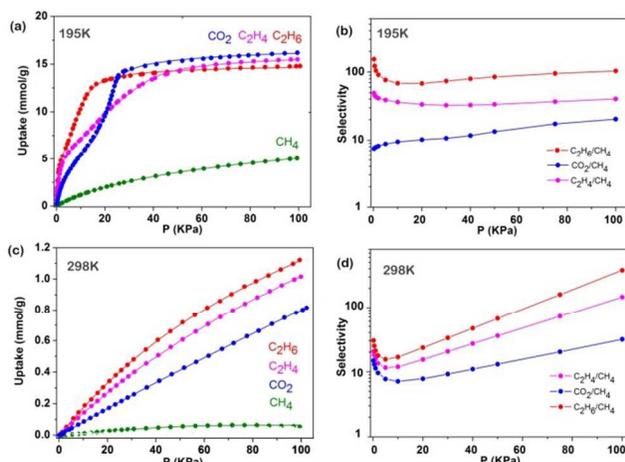
which is comparable with that of some well-known materials, such as, PCN-14 (total uptake:  $252 \text{ cm}^3 \cdot \text{g}^{-1}$  at 35 bar and 290 K)<sup>17</sup> and USTA-20 (total uptake:  $195 \text{ cm}^3 \cdot \text{g}^{-1}$  at 35 bar and 300 K)<sup>18</sup>. In addition, the  $C_2H_4$  and  $C_2H_6$  uptake amounts ( $220$  and  $299 \text{ cm}^3 \cdot \text{g}^{-1}$  at 298 K) of NJTU-1 make it a good candidate for C2 hydrocarbons storage. Taking the consideration of compressed  $C_2H_6$  within the void pore in NJTU-1, the total  $C_2H_6$  uptake of it can reach to  $400 \text{ mg} \cdot \text{g}^{-1}$  at 13 bar and 298 K. Thus, a container filled with NJTU-1 can store about 12.6 times the amount of  $C_2H_6$  in an empty container at 13 bar and 298 K. In addition, the functional pore environment of NJTU-1 have also enabled high excess  $CO_2$  uptake ( $298 \text{ cm}^3 \cdot \text{g}^{-1}$  at 298 K and 25 bar and  $373 \text{ cm}^3 \cdot \text{g}^{-1}$  at 273 K and 20 bar), and which is very close to the performance of MOF-210 ( $358 \text{ cm}^3 \cdot \text{g}^{-1}$ )<sup>6c</sup> and MOF-200 ( $330 \text{ cm}^3 \cdot \text{g}^{-1}$ )<sup>6c</sup> at 20 bar and 298 K with much larger surface areas. Therefore, these series of values reflect that NJTU-1 is a good and efficient adsorbent for gas fuels.



**Fig. 3** High pressure  $CH_4$  (a),  $CO_2$  (b),  $C_2H_4$  (c) and  $C_2H_6$  (d) isotherms for NJTU-1 at 273 (black line) and 298 K (red line), respectively. All desorption data (fully reversible) are omitted for clearly.

In order to explore the function ability of pores in NJTU-1, the low pressure adsorption isotherms of different gases at 195 and 298 K were further investigated (Fig. 4a and c). The gas uptakes of it exhibit significant chance for the selective capture of  $C_2H_4$ ,  $C_2H_6$  and  $CO_2$  from natural gases. Ideal adsorbed solution theory (IAST)<sup>19</sup> was employed to predict multi-component adsorption behaviors from the experimental pure-gas isotherms. The predicted adsorption selectivity for equimolar  $CO_2$  and C2 towards  $CH_4$  mixtures in NJTU-1 as a function of bulk pressure presented in Fig. 4a and c. As expected, the selectivity of  $C_2H_6$  to  $CH_4$  is very high (ca. 154-68) in the range of 100kPa at 195K. In addition, at 298K, the predicted selectivities of  $C_2H_4/CH_4$  (12-145),  $C_2H_6/CH_4$  (15.5-380) and  $CO_2/CH_4$  (7.1-31.6) are sensitive to the loading, and which can be divided into two parts: a quick decrease of selectivity at the low pressure region, and a gradually increase at high pressures. Importantly, the predicted values of them are larger than 8, indicates the practically feasible<sup>20</sup>. Therefore, compared with some important porous materials, such as MOF-177<sup>21</sup>, MOF-210<sup>6c</sup> and NU-100<sup>6d</sup> et al, (high storage, but low selectivity) and MOF-74<sup>22</sup>, SIFSIX-3-Cu/Zn<sup>10b</sup> (high

selectivity, but low storage), the integrated two characters of higher storage and higher selectivity make NJTU-1 as an excellent candidate for CO<sub>2</sub> capture.



**Fig. 4.** Low pressure gas adsorption isotherms (points) and the dual-site Langmuir–Freundlich fit lines (line) of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and CO<sub>2</sub> at 195 and 298 K, respectively (a and c). The IAST predicted selectivity of C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and CO<sub>2</sub> toward CH<sub>4</sub> (b and d).

To better understand these observations, the adsorption enthalpies of these series gases were calculated by virial method<sup>23</sup>. As shown in Fig. S15, the adsorption heat of CO<sub>2</sub> (25.1 kJ·mol<sup>-1</sup>) at zero coverage is significant lower than that of the frameworks with functional amide groups and open metal site<sup>24</sup>, reflecting a moderate CO<sub>2</sub>-framework interaction. Taking the structure into consideration, we attribute such moderate  $Q_{st}$  value to the weak dipole moment of the organic sites from ligands<sup>25</sup> as well as its significant large mesopore (~25 Å)<sup>26</sup>. Thus, the potential energy consumption for regeneration of NJTU-1 will be lower than that of series important materials for gas separation, such as, MgMOF-74, NiMOF-74, Cu-TDPAT, CuBTC, PCP-1 (La-BTN) or NaX zeolite (Fig. S15b)<sup>13, 24</sup>. Additionally, due to the similar structure of NJTU-1, HKUST-1, and MOF-14, their CO<sub>2</sub> adsorption heats were further compared. The reported  $Q_{st}$  value of CO<sub>2</sub> in HKUST-1 varied from 29.2 to 35.0 kJ·mol<sup>-1</sup><sup>14, 27</sup>, meanwhile, the calculated  $Q_{st}$  of CO<sub>2</sub> in MOF-14 reached to 26.3 kJ·mol<sup>-1</sup> (Fig S20). The increased adsorption heats should be explained as the narrower pore size effect and also the higher density of open metal site in HKUST-1 and MOF-14<sup>10,26</sup>, even the smaller organic sites were found in their corresponding structure. In addition, NJTU-1 shows moderate affinity to C<sub>2</sub>H<sub>4</sub> (19.7 kJ·mol<sup>-1</sup>) and C<sub>2</sub>H<sub>6</sub> (20.0 kJ·mol<sup>-1</sup>), and has the relatively low CH<sub>4</sub> adsorption enthalpies (14.9 kJ·mol<sup>-1</sup>). Here, we can conclude that different host-guest interactions is the reason for managing the selectivities in NJTU-1<sup>8a, 9</sup>.

In summary, we have synthesized a new porous coordination polymer by using a 3-connected ligand with large aromatic ring. NJTU-1 represents a significant mesopore and second high BET surface area of 2800 m<sup>2</sup>·g<sup>-1</sup> among the interpenetrated PCPs. Additionally, it also shows high CH<sub>4</sub> (excess capacity: 174 cm<sup>3</sup>·g<sup>-1</sup>), C<sub>2</sub>H<sub>4</sub> (220 cm<sup>3</sup>·g<sup>-1</sup>), C<sub>2</sub>H<sub>6</sub> (299 cm<sup>3</sup>·g<sup>-1</sup>) and CO<sub>2</sub> (298 cm<sup>3</sup>·g<sup>-1</sup>) adsorption capacities as well as good adsorption selectivities of C<sub>2</sub>H<sub>4</sub> (12-145), C<sub>2</sub>H<sub>6</sub> (15.5-

380) and CO<sub>2</sub> (7.1-31.6) towards CH<sub>4</sub> at 298 K. This work demonstrates that the ligand expansion, especially through large aromatic rings, is an effective method to boost the surface area and gas uptake, thereby enhancing adsorption selectivity with moderate energy. Therefore, the promising future of the fine construction for functional porous materials would be expected.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: X-ray crystallographic file (CIF), experimental details, IR, TGA, PXRD and gas adsorption isotherms of them. See DOI: 10.1039/b000000x/

‡ Crystal data for NJTU-1: C<sub>26</sub>H<sub>15</sub>CuO<sub>5</sub>·xguest, M = 470.92, cubic, *Im*-3, *a* = 33.175(4) Å, *V* = 36512(13) Å<sup>3</sup>, *Z* = 24, *D<sub>c</sub>* = 0.514 g·cm<sup>-3</sup>, GOF = 1.16 based on *F*<sup>2</sup>, *R*<sub>(int)</sub> = 0.089, *wR*<sub>2</sub> = 0.3554 [for 5191 data *I* > 2σ(*I*)]. CCDC number: 1030658.

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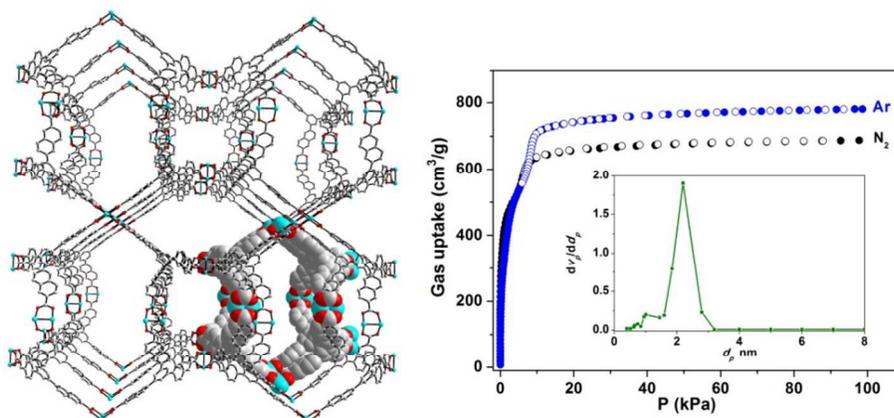
# A new meso-porous coordination polymer: synthesis, structure, and gas adsorption studies

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A new porous coordination framework, NJTU-1, with low binding energy and remarkable meso-pore, exhibits high surface area and excellent gas adsorption behaviors at 298 K.