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# A Stable Amino-Functionalized Interpenetrated Metal–Organic Framework Exhibiting Gas Selectivity and Pore-Size-Dependent **Catalytic Performance**

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S Supporting Information

ABSTRACT: An amino-functionalized doubly interpenetrated microporous zinc metal-organic framework (UPC-30) has been solvothermally synthesized. UPC-30 can be stable at 190 °C and confirmed by powder X-ray diffraction. Gas adsorption measurements indicate that UPC-30 exhibits high H<sub>2</sub> adsorption heat and CO<sub>2</sub>/CH<sub>4</sub> separation efficiency. After the exchange of Me<sub>2</sub>NH<sub>2</sub><sup>+</sup> by Li<sup>+</sup> in the channels, the H<sub>2</sub> adsorption heat increased by 19.7%. Because of the existence of  $-NH_2$  groups in the channels, UPC-30 can effectively catalyze Knoevenagel condensation reactions with high yield and pore-sizedependent selectivity.

s a useful functional material for the separation of small gas Amolecules, microporous metal-organic frameworks (MOFs), which can be easily assembled from metal ions/ clusters and organic linkers, have attracted wide research interest.<sup>1-4</sup> For their easily adjustable pore size and functional pore surface, the microporous MOF can achieve efficient separation of small molecules by maximizing their size-selective sieving effects and enhancing their specific affinity. Actually, on the basis of postsynthesis ion exchange<sup>5,6</sup> and amino modification, various microporous MOFs show high performance for  $H_2$  storage and  $CO_2/CH_4$  separation.<sup>7,8</sup>

Porous MOF-based functional materials for efficient adsorption and separation of CO<sub>2</sub> have some specific characteristics and requirements:<sup>9–11</sup> (i) excellent thermal stability; (ii) accessible channels; (iii) naked nitrogen-containing heterocycles (iv) uncoordinated functional groups (e.g.,  $-NH_2$  or -OH groups); (v) open-metal sites.<sup>12,13</sup> A number of MOFs with these characteristics, such as UTSA-48,<sup>14</sup> NOTT-101,<sup>15</sup> MFM-130,<sup>16</sup> and UPC-21,<sup>17</sup> displayed a high CO<sub>2</sub>/CH<sub>4</sub> separation performance. Furthermore, some other MOFs with multifold interpenetrated frameworks<sup>18</sup> also exhibited good CO<sub>2</sub>/CH<sub>4</sub> separation efficiency. However, these types of interpenetrated MOFs for  $CO_2/CH_4$  separation are rare<sup>19</sup> because the interpenetration will reduce the porosity in the framework.

On the other hand, the functional MOF materials with highly ordered pores also show great potential for catalytic applications.<sup>20</sup> For instance, PCN-124 can catalyze the Knoevenagel condensation reactions, which was considered to be an efficient way to obtain valuable intermediate chemicals

based on the C-C coupling reaction. Conventionally, these reactions are catalyzed by homogeneous catalysts. However, it is difficult to recycle the catalysts because of the low stability and high recovery cost. Therefore, it is highly desirable to develop heterogeneous catalysts with high stability and good recyclability.

In this Communication, we present a new amino-functional 3D zinc-based MOF,  $[Zn_3(OH)(ATTCA)_2(H_2O)] \cdot C_2H_6NH_2 \cdot$  $4DMF \cdot H_2O$  (denoted as UPC-30), where  $H_3ATTCA = 2$ amino[1,1:3,1-terphenyl]-4,4,5-tricarboxylic acid. UPC-30 exhibits a doubly interpenetrated microporous framework with 1D rhombic channels. It is interesting that the material demonstrates high CO<sub>2</sub>/CH<sub>4</sub> separation efficiency and pore-size-dependent catalytic properties for Knoevenagel condensation reactions. Additionally, through the exchange of Me<sub>2</sub>NH<sub>2</sub><sup>+</sup> by Li<sup>+</sup> in the channels, the H<sub>2</sub> adsorption heat of UPC-30 increased by 19.7%.

Colorless block crystals of UPC-30 were obtained by a solvothermal reaction of H<sub>3</sub>ATTCA and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in *N*,*N*-dimethylformamide (DMF)/ethanol/water (5:2:1, v/v/v) at 100 °C for 2 days. UPC-30 was characterized by single-crystal X-ray diffraction, thermogravimetric analysis (TGA), and elemental analysis. Single-crystal X-ray diffraction analysis revealed that UPC-30 crystallizes in the monoclinic system with a space group  $P2_1/c$ . The asymmetrical unit contains two deprotonated ATTCA<sup>3-</sup> ligands, three zinc ions, a coordinated water molecule, a  $\mu_3$ -hydroxyl, a protonated dimethylamine molecule, an uncoordinated water molecule, and four DMF solvent molecules. Three zinc ions possess two different coordination environments: Zn1 and Zn2 are coordinated by a  $\mu_3$ -oxygen atom and three oxygen atoms from three different TTCA<sup>3-</sup> ligands, and the average Zn-O distance is 1.966 Å; Zn3 is coordinated by a coordinated water molecule, a  $\mu_3$ -oxygen atom, and four oxygen atoms from four different ATTCA<sup>3-</sup> ligands, with an average Zn–O distance of 2.108 Å. Three zinc ions are connected through four carboxyl oxygen atoms and one  $\mu_3$ -oxygen atom to form a trinuclear  $[Zn_3(OH)(COO)_4]$ secondary building unit (Figure 1a). Structurally speaking, UPC-30 presents a 3D network constructed by the [Zn<sub>3</sub>(OH)-(COO)<sub>4</sub>] units and the tricarboxylate ligand with 1D rhombic channels (Figure 1b). The  $Me_2NH_2^+$  cations, derived from in situ decomposition of DMF molecules, are located within the accessible voids, resulting in charge equilibrium.<sup>21</sup> From a

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**Figure 1.** (a) Coordination environment of  $\mathbb{Z}n^{2+}$  ions and coordination modes of ATTCA<sup>3-</sup>. (b) 2-fold interpenetrating framework along the *b* axis. (c) 3,6-connected "sit" net.

topological point of view, the ATTCA<sup>3-</sup> ligands can be simplified into three-connected nodes and  $[Zn_3(OH)(COO)_4]$  units into six-connected nodes. Therefore, a classical "sit" architecture with a topological point symbol of  $\{4.6^2\}_2\{4^2.6^{10}.8^3\}$  was obtained (Figure 1c).

The thermal stability of UPC-30 was studied by variabletemperature powder X-ray diffraction (PXRD; Figure 2). The



Figure 2. PXRD patterns of UPC-30 at different conditions.

PXRD pattern of the samples heated at different temperatures showed similar diffraction peaks until temperatures up to 190 °C, indicating that the framework of UPC-30 was stable below 190 °C, which is consistent with the results observed from TGA. Despite the 2-fold interpenetration, UPC-30 was still porous with a free volume of 45.9%, which was calculated by PLATON after removal of the guest solvent molecule. To elucidate the permanent porosity and pore properties of UPC-30, gas-uptake experiments were performed with desolvated samples (see the Supporting Information, SI). N<sub>2</sub>-uptake (77 K) measurements gave typical I-type isotherms for a microporous solid with an adsorption of 86.2  $\text{cm}^3 \text{g}^{-1}$  (Figure 3a,b). The surface areas of Brunauer-Emmett-Teller (BET) and Langmuir calculated from the N<sub>2</sub> adsorption isotherm were 284 and 330  $m^2 \cdot g^{-1}$ , respectively. The H<sub>2</sub> adsorption experiments were carried out at 77 and 87 K with an adsorption capacity of 84.8 and 63.6  $\text{cm}^3 \cdot \text{g}^{-1}$ (0.76 and 0.57 wt %; Figure 3c). The moderate  $H_2$  absorption of UPC-30 is comparable to those of PCN-131 (0.84 wt %) and PCN-19 (0.95 wt %) at 77 K.<sup>22a</sup> In addition, the H<sub>2</sub> adsorption



**Figure 3.** (a and b) N<sub>2</sub> sorption isotherms and pore-size distribution for UPC-30 (red) and Li-UPC-30 (black) at 77 K. (c) H<sub>2</sub> sorption isotherms for UPC-30 (red and black) and Li-UPC-30 (blue and green). (d) Adsorption heat ( $Q_{st}$ ) of H<sub>2</sub> for UPC-30 (red) and Li-UPC-30 (black).

heat is 8.6 kJ·mol<sup>-1</sup> at zero coverage and decreases slowly with increasing H<sub>2</sub> loading, calculated by the Clausius–Clapeyron equation (Figure 3d). These values are higher than those of famous MOF materials, such as NOTT-122 (6.0 kJ·mol<sup>-1</sup>),<sup>12</sup> MOF-5 (5.2 kJ·mol<sup>-1</sup>),<sup>22b</sup> and HKUST-1 (6.6 kJ·mol<sup>-1</sup>).<sup>22c</sup>

After the exchange of  $Me_2NH_2^+$  by Li<sup>+</sup> (see the SI), the surface areas of BET and Langmuir of the resultant Li-UPC-30 decreased slightly to 278 and 321 m<sup>2</sup>·g<sup>-1</sup>, and the pore size was slightly reduced by 0.05 nm (Figure 3b) based on the steric effects.<sup>23,24</sup> The adsorption amount of H<sub>2</sub> increased by 14.8% (for 97.4 cm<sup>3</sup>·g<sup>-1</sup>, 0.89 wt %) and 21.6% (for 77.3 cm<sup>3</sup>·g<sup>-1</sup>, 0.69 wt %) at 77 and 87 K, respectively (Figure 3c), and the adsorption heat of H<sub>2</sub> increased by 19.7% (for 10.3 kJ·mol<sup>-1</sup>; Figure 3d). These observations are consistent with many reports that Li<sup>+</sup> can increase the adsorption amount and Q<sub>st</sub> values for H<sub>2</sub>, which is based on the strengthened intermolecular interactions between H<sub>2</sub> and Li<sup>+</sup> in the host framework.<sup>25</sup> In addition, narrow pores can also increase the Q<sub>st</sub> value of H<sub>2</sub>, which provides more overlap potential energy fields.<sup>5</sup>

The CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>3</sub>H<sub>6</sub> adsorption isotherms for UPC-30 exhibit I-type behavior, with adsorption amounts of 41.5, 14.1, 22.7, 24.5, 30.9, 18.0, and 21.2 cm<sup>3</sup>·g<sup>-1</sup>, respectively, at 273 K (Figure 4a). The relatively higher CO<sub>2</sub> uptake capacity for UPC-30 prompted us to further investigate the ability to separate CO<sub>2</sub> from other gases by the ideal adsorbed solution theory model<sup>26</sup> with 50:50 and 10:90 binary gas mixtures, respectively. The adsorption selectivities for



Figure 4. (a)  $CO_{2'} CH_{4'} C_2H_{6'} C_2H_{4'} C_2H_{2'} C_3H_{8'}$  and  $C_3H_6$  sorption isotherms at 273 K for UPC-30. (b)  $CO_2/C4_4$ ,  $CO_2/C_3H_8$ ,  $CO_2/C_3H_6$ ,  $CO_2/C_2H_6$ ,  $CO_2/C_2H_4$ , and  $CO_2/C_2H_2$  selectivities at 273 K (50:50 and 10:90, v/v).

 $CO_2/CH_4$  are approximately 9.2 (50:50) and 10.3 (10:90) at 273 K. However, the selectivity for  $CO_2$  over  $C_3H_8$ ,  $C_3H_6$ ,  $C_2H_6$ ,  $C_2H_4$ , or  $C_2H_2$  is significantly poorer (<2 at both 50:50 and 10:90 at 273 K; Figure 4b). Although it is common to selectively capture  $CO_2$  from MOF materials,<sup>27–30</sup> UPC-30 exhibits application potential in the selective adsorption of  $CO_2$  because of its high selectivity and thermal stability.

For the Lewis basic  $-NH_2$  group present in the channel, UPC-30 was used to catalyze the Knoevenagel condensation reaction.<sup>31</sup> As a demonstration, because of possible clathration within the MOF channel, the aromatic aldehyde was selected as the substrate. The catalytic results of different substrates are summarized in Table 1. As a control experiment, the reaction was completely stopped after the removal of UPC-30, and this was supported by gas chromatography (GC)–mass spectrometry (Figure S5).

|  | Table 1. | Knoevenagel | Reactions | Catalyzed | l by | UPC-30 |
|--|----------|-------------|-----------|-----------|------|--------|
|--|----------|-------------|-----------|-----------|------|--------|

| ួ   | CN UPC-30 (1                 | 0 wt%)       | CN                     |
|---|------------------------------|--------------|------------------------|
| <sub>R</sub> ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,, | + $\langle CH_2CI_2 \rangle$ | , RT         |                        |
| entry <sup>a</sup>                                | R                            | <i>t</i> (h) | yield (%) <sup>b</sup> |
| 1   | Ph                           | 5            | 94.1                   |
| 2   | 4-NO <sub>2</sub> Ph         | 5            | 74.4                   |
| 3   | 4-MePh                       | 5            | 71.4                   |
| 4   | $4-C(CH_3)_3Ph$              | 5            | 21.5                   |
| 5   | 1-naphthyl                   | 5            | 18.9                   |
| 6   | 4-FPh                        | 5            | 18.4                   |
| 7   | 4-PhOPh                      | 5            | 16.6                   |
| 8   | 4-MeOPh                      | 5            | 5.1                    |
| 9   | 4-PhPh                       | 5            | 0                      |

<sup>*a*</sup>Reaction conditions: activated sample UPC-30 (10 wt %), malononitrile (1.0 mmol, 0.066 g), an aldehyde (1.0 mmol),  $CH_2Cl_2$  (3 mL), room temperature. <sup>*b*</sup>GC yield.

UPC-30 can be recovered from the reaction system by centrifugation and reused three cycles without significant loss of activity. The PXRD pattern of the recovered catalyst was found to be unchanged after three cycles (Figure 2), indicating its excellent chemical stability. A pore-size-dependent catalytic capacity was observed for UPC-30. The yield for Knoevenagel condensation of benzaldehyde and malononitrile can reach 94.1% after 5 h at room temperature. It should be noted that these values are lower than those for PCN-124 (99%)<sup>32a</sup> and Cz-MOF  $(99\%)^{32b}$  but still comparable to that of PCP-1  $(96\%)^{32c}$ and higher than that of  $1_{Cu'}$  (90%),<sup>32d</sup> making these MOFs qualified considerable candidates for C-C coupling reaction. As a comparison, the yield decreased with an increase in the bulk of the substituent on the aldehyde substrate. When a bulky aldehyde of 1,1'-biphenyl-4-carbaldehyde was selected as the substrate, the reaction does not proceed (Table 1).

In conclusion, using tricarboxylic acid  $H_3ATTCA$  as the ligand, a doubly interpenetrated microporous zinc MOF (UPC-30) was synthesized, which incorporates pendent  $-NH_2$  groups. In UPC-30, the  $[Zn_3O(COO)_4]$  subunits are linked by the tricarboxylic acid ligand to form a microporous framework possessing a 1D channel. After the exchange of  $Me_2NH_2^+$  by Li<sup>+</sup> in the channels, the  $H_2$  adsorption heat increased by 19.7%. UPC-30 exhibit selective adsorption of CO<sub>2</sub> over CH<sub>4</sub> at 273 K, providing some benefit for the major challenges of gas separation. In addition, the presence of Lewis basic  $-NH_2$  groups allows UPC-30 to act as a catalyst for size-selective Knoevenagel

condensation reactions. A further study on the synthesis of other porous MOF materials with this ligand is underway in our laboratory.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02148.

Synthesis and activation of UPC-30, crystal data, TGA curves, IR pattern, room-temperature emission spectra,  $CO_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $C_3H_8$ , and  $C_3H_6$  sorption isotherms and  $CO_2/CH_4$ ,  $CO_2/C_3H_8$ ,  $CO_2/C_3H_6$ ,  $CO_2/C_2H_4$ , and  $CO_2/C_2H_2$  selectivities at 273 K for Li-UPC-30, evidence of the heterogeneous nature of catalysis in the Knoevenagel reaction of benzaldehyde, and GC spectrum (PDF)

# Accession Codes

CCDC 1543307 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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