

# Supporting Information

## A Low-Cost and High-Performance Microporous Metal-Organic Framework for Separation of Acetylene from Carbon Dioxide

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## EXPERIMENTAL AND ANALYSIS SECTION

### Ideal Adsorbed Solution Theory (IAST)

The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2, can be formally defined as

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$

In above equation,  $q_1$  and  $q_2$  are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacity. We calculated the values of  $q_1$  and  $q_2$  using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.

### Virial Graph Analysis: Estimation of the isosteric heats of gas adsorption ( $Q_{st}$ ).

A virial-type expression of comprising the temperature-independent parameters  $a_i$  and  $b_j$  was employed to calculate the enthalpies of adsorption for  $C_2H_2$  and  $CO_2$  (at 273 K and 298 K) on **1**. In each case, the data were fitted use equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N_i + \sum_{j=0}^n b_j N_j \quad (1)$$

Here,  $P$  is the pressure expressed in Pa,  $N$  is the amount absorbed in mmol  $g^{-1}$ ,  $T$  is the temperature in K,  $a_i$  and  $b_j$  are virial coefficients, and  $m$ ,  $n$  represent the number of coefficients required to adequately describe the isotherms ( $m$  and  $n$  were gradually increased till the contribution of extra added  $a$  and  $b$  coefficients was deemed to be statistically insignificant towards the overall fit. And the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients  $a_0$  through  $a_m$  were then used to calculate the isosteric heat of absorption using the following expression:

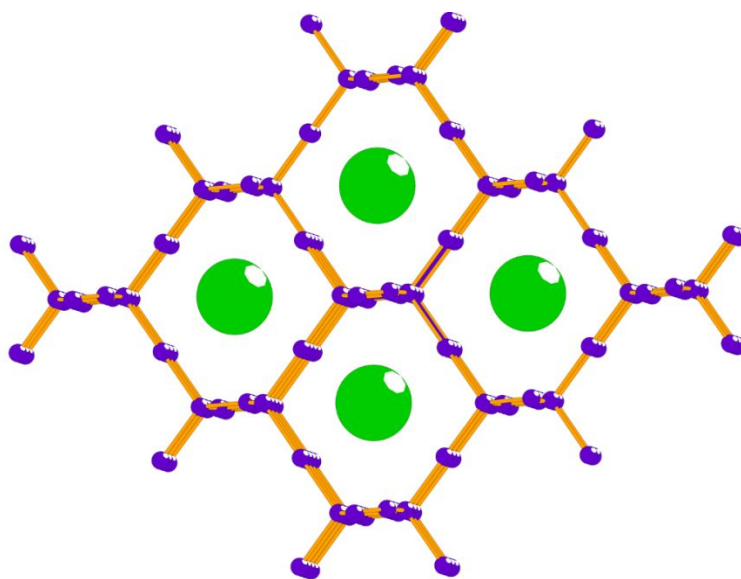
$$Q_{st} = -R \sum_{i=0}^m a_i N_i \quad (2)$$

$Q_{st}$  is the coverage-dependent isosteric heat of adsorption and  $R$  is the universal gas constant. The heat enthalpies of C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub> sorption for **1** in this manuscript are determined by using the sorption data measured in the pressure range from 0-1 bar (at 273 K and 298 K).

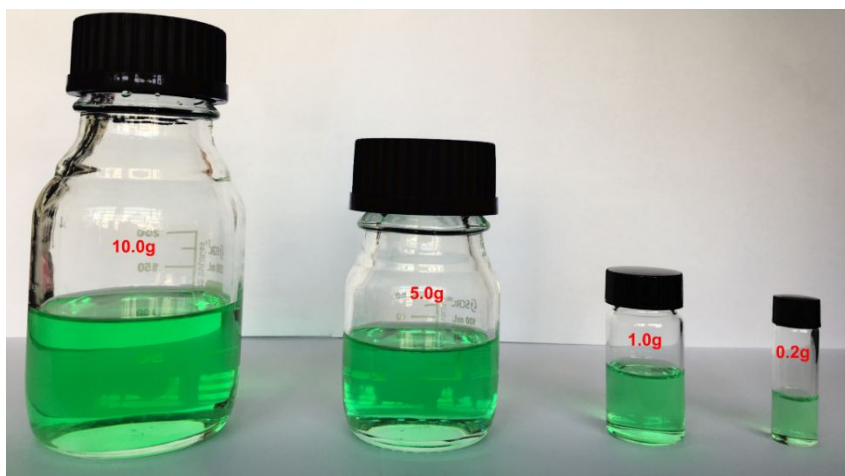
### **Breakthrough Tests.**

Before the breakthrough experiments, the collected crystal material was washed with fresh DMF for several times to wipe off the residuum and then was exchanged by acetone for about 3 days. After solvent-exchange, the crystal material was evaluated from the Micromeritics ASAP 2020 surface area analyzer at 353 K for 10 h and then at 403 K for 14 h under high vacuum until the outgas rate was 5 µmHg min<sup>-1</sup> to yield the activated [Ni<sub>3</sub>(HCOO)<sub>6</sub>]. The breakthrough experiments were conducted in a packed column (4.6 mm × 100 mm) filled with the activated **1** samples under a C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> dynamic feed gas with a flow of 0.5 mL min<sup>-1</sup> at 298 K. The column was first purged with He (15 mL min<sup>-1</sup>) for 12 h at 298 K with packed sample. The mixed gas (C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub>, 50/50, v/v) flow was then introduced at 0.5 mL min<sup>-1</sup> and outlet gas from the column was monitored using gas chromatography (GC-2010 plus, SHIMADZU) with a flame ionization detector (FID). The adsorption bed can be regenerated by He flow (20 mL/min) for 6 to 10 hours at 313 K.

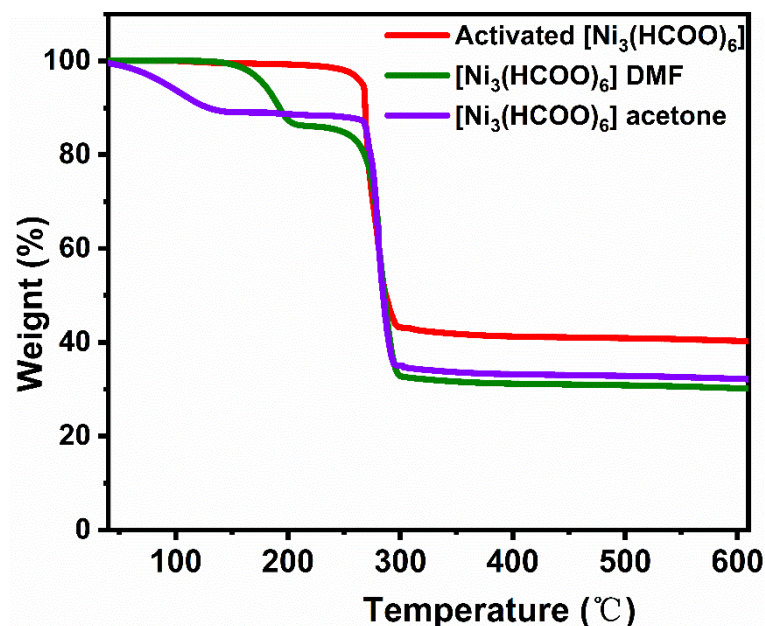
## Supporting Figures.



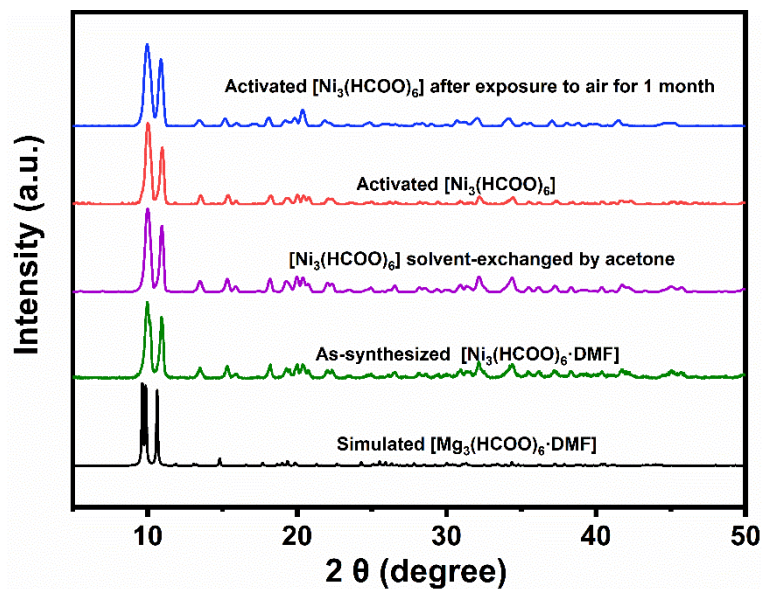
**Figure S1.** The interconnection of Ni atoms of  $[\text{Ni}_3(\text{HCOO})_6]$  viewed from b axis.



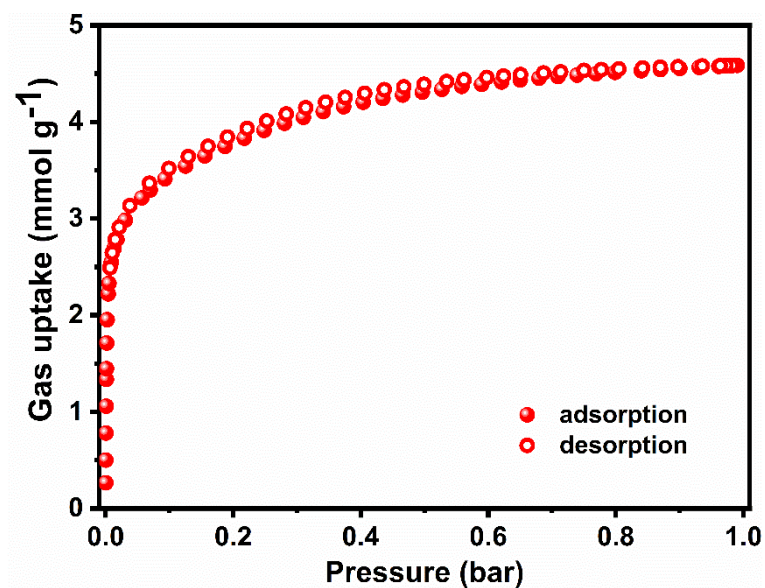
**Figure S2.** Investigating the scalability of  $[\text{Ni}_3(\text{HCOO})_6]$  synthesis by using different content raw materials, but keeping the same concentration.



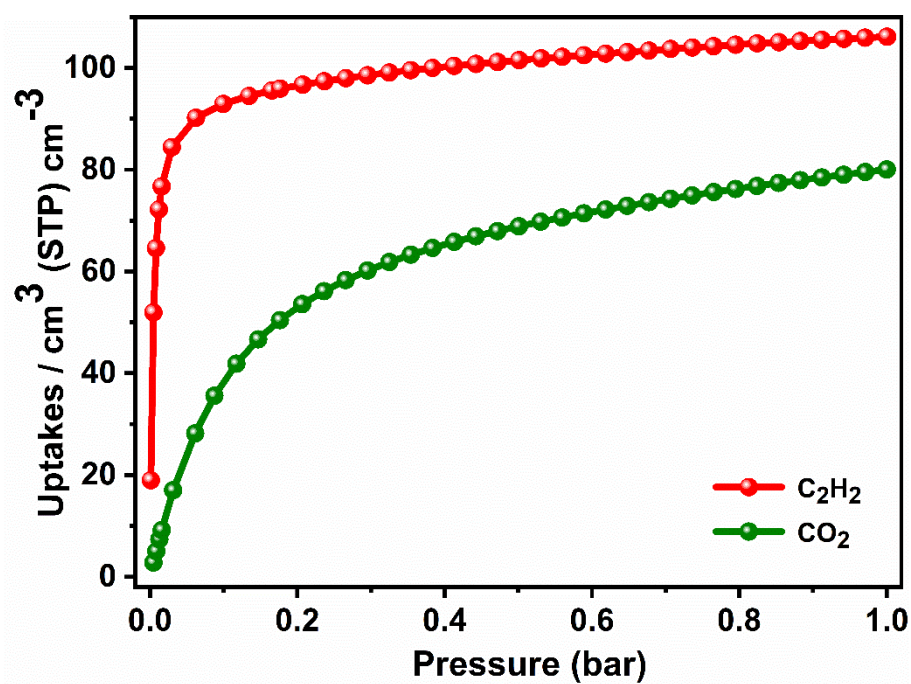
**Figure S3.** Thermogravimetric analysis (TGA) curves of the as-synthesized  $[\text{Ni}_3(\text{HCOO})_6 \cdot \text{DMF}]$ , solvent-exchanged by acetone, and activated sample, which were evaluated in  $\text{N}_2$  atmosphere with a heating rate of  $10^\circ\text{C}/\text{min}$ .



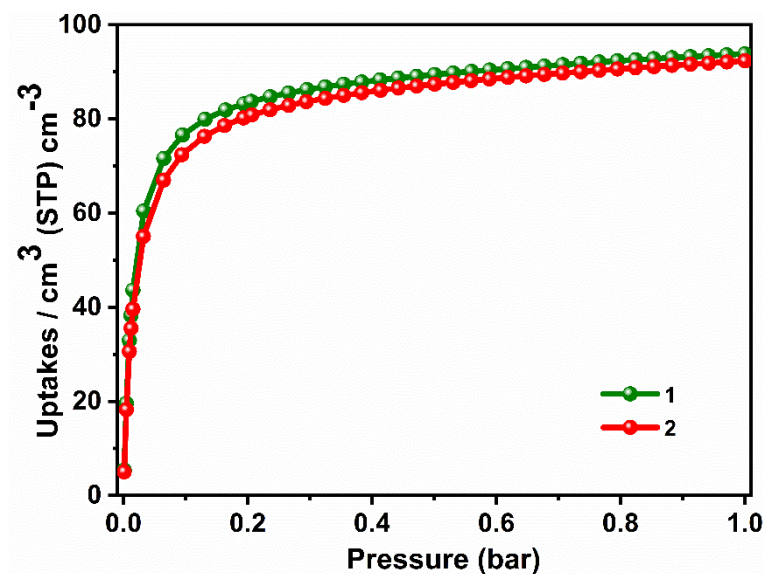
**Figure S4.** The PXRD patterns for  $[\text{Ni}_3(\text{HCOO})_6]$  as-synthesized in DMF (olive green), solvent-exchanged by acetone (purple), activated (red), activated after exposure to air for 1 month (blue) along with the simulated XRD pattern  $[\text{Mg}_3(\text{HCOO})_6]$  (black) from the reference<sup>1</sup>.



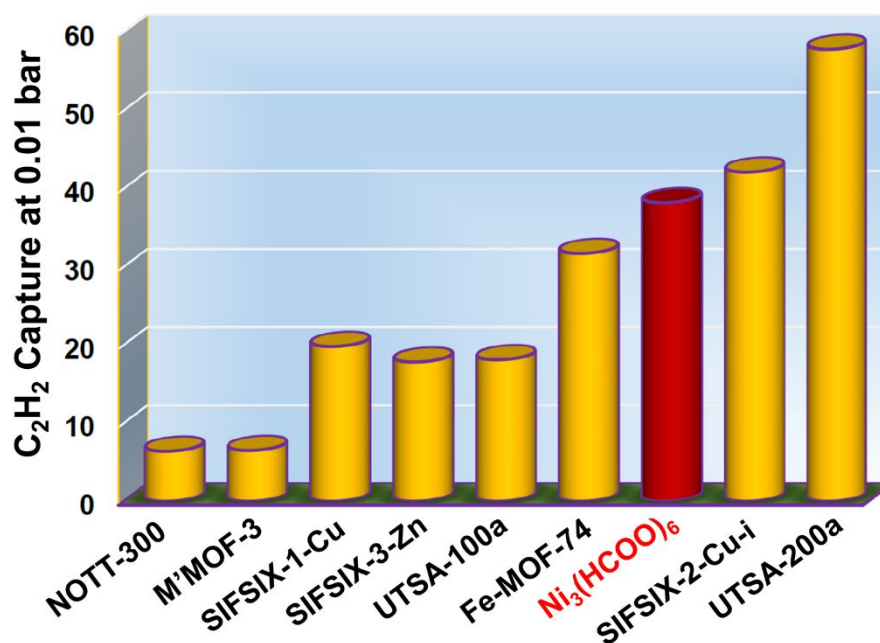
**Figure S5.** The CO<sub>2</sub> sorption isotherms for activated [Ni<sub>3</sub>(HCOO)<sub>6</sub>] at 196 K (closed symbols, adsorption; open symbols, desorption).



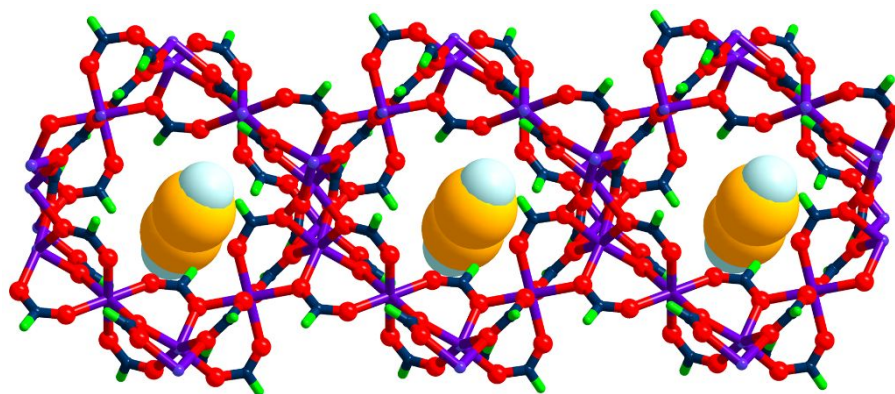
**Figure S6.** Single component adsorption isotherms of activated [Ni<sub>3</sub>(HCOO)<sub>6</sub>] for C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub> at 273 K.



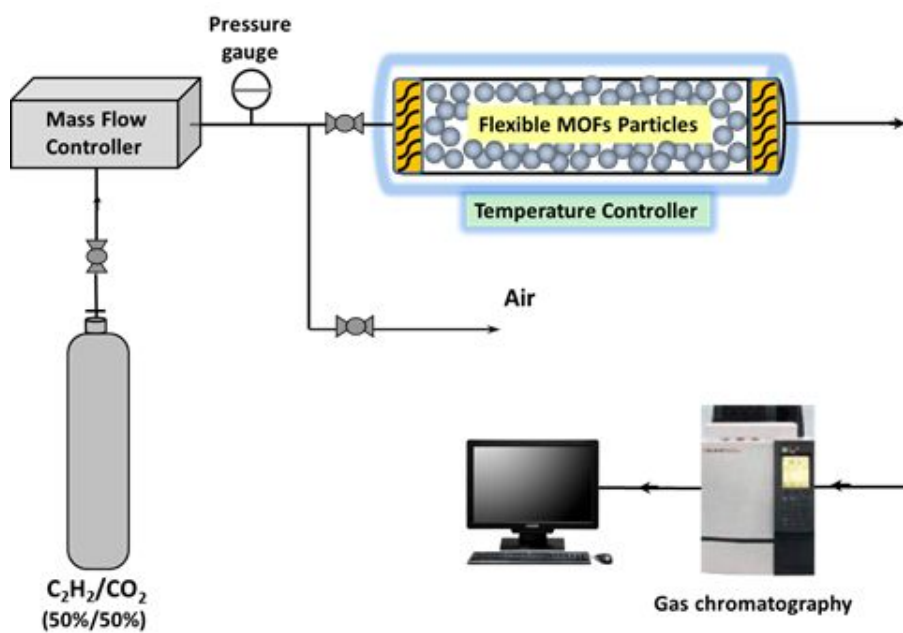
**Figure S7.** The  $\text{C}_2\text{H}_2$  adsorption isotherms at 298 K of the fresh activated  $[\text{Ni}_3(\text{HCOO})_6]$  (1) and activated  $[\text{Ni}_3(\text{HCOO})_6]$  after air exposure (70% humidity) for one month (2).



**Figure S8.** Comparison of the capture capacities of  $\text{C}_2\text{H}_2$  among representative MOFs<sup>2-6</sup>.



**Figure S9.** The illustration of the overall aspects of  $\text{C}_2\text{H}_2$  molecules within the framework of  $[\text{Ni}_3(\text{HCOO})_6]$  viewed from b axis



**Figure S10.** The procedures for the breakthrough test of activated  $[\text{Ni}_3(\text{HCOO})_6]$  for  $\text{C}_2\text{H}_2/\text{CO}_2$  (v : v, 50 : 50) at room temperature.

**Table S1.** Comparison of the capture capacities of C<sub>2</sub>H<sub>2</sub> and the selectivity of C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> among representative MOFs.

| MOFs                                   | Framework Density [g cm <sup>-3</sup> ] | C <sub>2</sub> H <sub>2</sub> Uptakes [cm <sup>3</sup> cm <sup>-3</sup> ] at 0.01 bar | C <sub>2</sub> H <sub>2</sub> Uptakes [cm <sup>3</sup> cm <sup>-3</sup> ] at 1.0 bar | IAST selectivity of C <sub>2</sub> H <sub>2</sub> /CO <sub>2</sub> at 1.0 bar | Ref       |
|----------------------------------------|-----------------------------------------|---------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|-----------|
| [Ni <sub>3</sub> (HCOO) <sub>6</sub> ] | 1.756                                   | 38.2                                                                                  | 93.8                                                                                 | 22.0                                                                          | This work |
| NOTT-300                               | 1.062                                   | 6.4                                                                                   | 150.8                                                                                | \                                                                             | 3         |
| Fe-MOF-74                              | 1.126                                   | 31.7                                                                                  | 171.5                                                                                | \                                                                             | 6         |
| SIFSIX-3-Zn                            | 1.578                                   | 17.8                                                                                  | 141.3                                                                                | \                                                                             | 2         |
| TIFSIX-2-Cu-i                          | 1.269                                   | \                                                                                     | 116.5                                                                                | 6.5                                                                           | 8         |
| JCM-1                                  | 1.331                                   | \                                                                                     | 99.8                                                                                 | 13.7                                                                          | 9         |
| NUMOF-1-Ni                             | 1.731                                   | 70.9                                                                                  | 105.6                                                                                | 25.0                                                                          | 10        |
| UTSA-74                                | 1.34                                    | \                                                                                     | 145.0                                                                                | 9.0                                                                           | 7         |
| UTSA-100a                              | 1.146                                   | 18.1                                                                                  | 109.6                                                                                | \                                                                             | 5         |
| UTSA-200a                              | 1.417                                   | 57.8                                                                                  | 116.0                                                                                | \                                                                             | 2         |

## Reference

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