Supplementary information

Inducing hierarchical pores in nano-MOFs for efficient gas separation

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Additional MOF synthesis protocols:

Table 1S: Protocols of Cu-MOFs synthesized in this work.

Protocol/ Composition	***Metal salt: H_2ADC:DABCO (molar ratio)***	***Solvent (ml)***	***Temperature (℃) and duration (h)***	***BET surface area (m^2/g)***
A(Cu-MOF)	1:1:0.8	27	150 and 48	444
B	2:1:0.5	27	120 and 72	374
C	1:1:0.8	27	120 and 72	537
D(Hierarchical Cu-MOF)	1:1:0.8	90	120 and 48	607
E(Hierarchical Cu-MOF)	1:1:0.8	70	120 and 48	627.4

N_2 adsorption Isotherms

N_2 adsorption isotherms were conducted for all the compositions at 77 K and are displayed in Figure 1S. The N_2 adsorption isotherm of composition E is given in the main article.

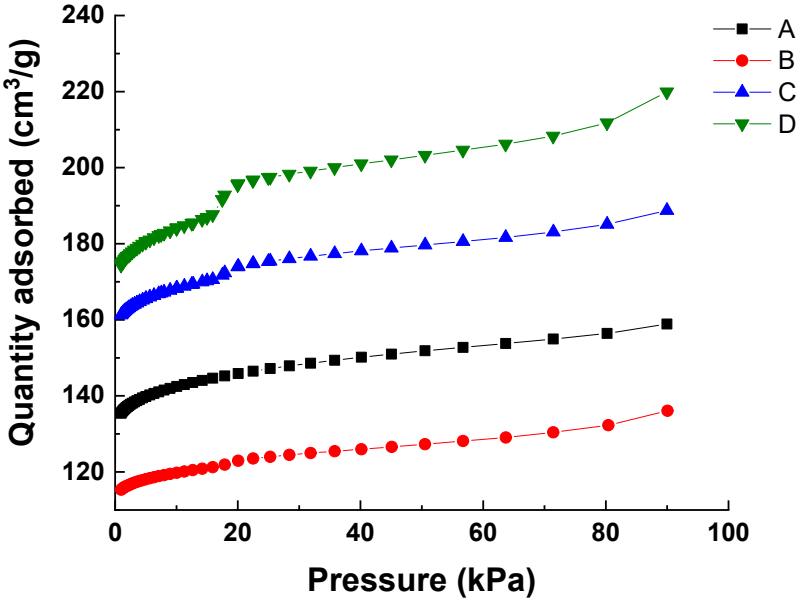

Figure 1S: N_2 adsorption isotherms for composition A (square, black), B(circle, red), C(triangle, blue) and D (inverted, olive green).

Thermal stability

Thermogravimetric analysis of Cu-MOF and hierarchical-Cu-MOF is shown in Figure 2S.

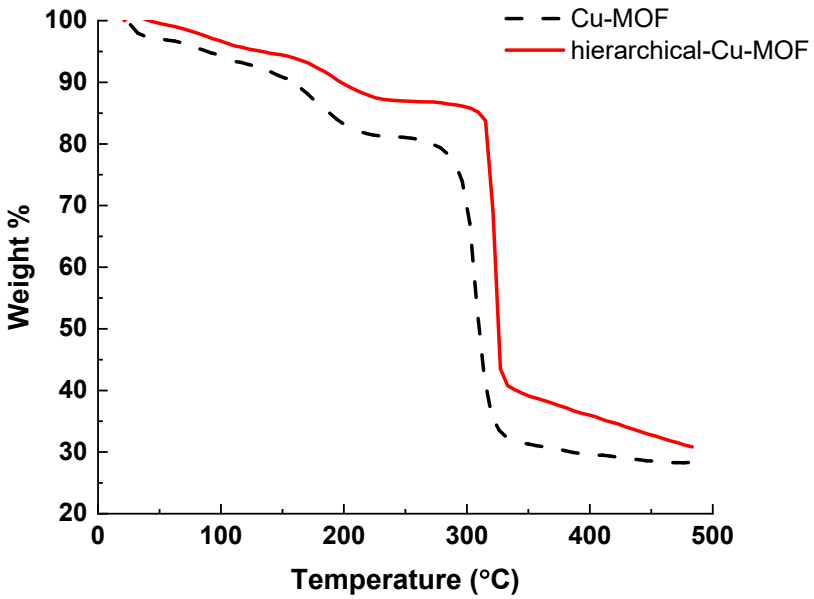

Figure 2S: Thermal gravimetric analysis of Cu-MOF, composition A (black, dashed line) and the hierarchical-Cu-MOF, composition E (red, solid line)

MOF structure

The CIF file of activated $Zn_2(adc)_2(dabco)$ MOF was obtained from the crystallographic database. The structure is simulated using Vesta software and is illustrated in Figure 3S.

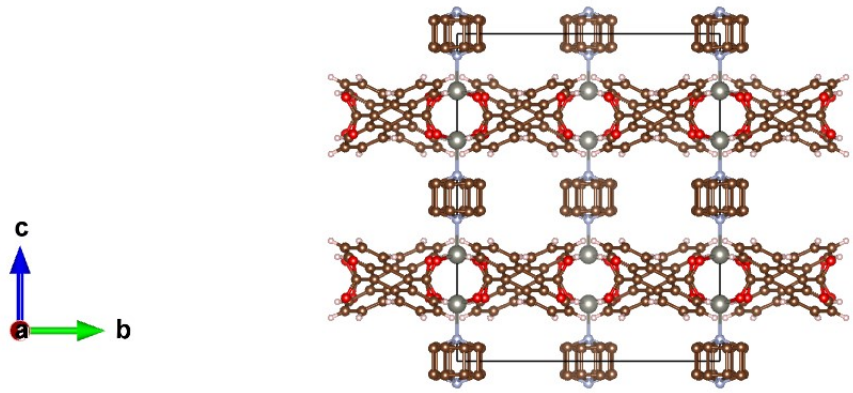

Figure 3S: Structure of $Zn_2(adc)_2(dabco)$ MOF

Table 2S: Selectivities for the separation of CO_2 from CO2/N2 and CO2/CH4 mixtures for hierarchical Cu-MOF and state-of-the art MOFs fro-m literature

MOF Name	***BET surface area (m^2/g)***	***Gas Mixture***	***Selectivity of CO2***	***CO_2 adsorption capacity***	***Tem-perature***	***Pressure***	***Reference***
Hierarchical Cu - MOF	627.4	CO_2/N_2 CO_2/CH_4	12 3	75 mg/g	295 K	1 bar	This work
IRMOF-3	2350	CO_2/N_2	18	54 mg/g	298 K	1 bar	[1]
HKUST-1	2211 1948	CO_2/CH_4 CO_2/N_2	9 36	352.1 mg/g 484 mg/g	303 K 273K	10 bar 1 bar	[2] [3]
$Cu_2(Hbtb)_2$	600	CO_2/CH_4	12.4	66 mg/g	298 K	1 bar	[4]
ZnDABCO	1725	CO_2/N_2	17	440 mg/g	298 K	15 bar	[5]
MIL-101	1007	CO_2/CH_4	6	269 mg/g	298 K	10 bar	[6]
UiO-66	1123	CO_2/N_2 CO_2/CH_4	61.5 18.3	52 mg/g	308 K	2 bar	[7]

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