

Electronic Supplementary Information (ESI)

Hierarchically structured metal–organic frameworks assembled by hydroxy double salt – template synergy with high space–time yield

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Experimental Section

Chemical reagents. Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, J&K, 99%), 1, 3, 5-benzenetricarboxylic acid (H_3BTC , J&K, 99%), zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, J&K, 98%), 2-methylimidazole (2Im, J&K, 99%), zinc oxide (ZnO, J&K, 99%), 1-bromohexadecane ($\text{C}_{16}\text{H}_{33}\text{Br}$, J&K, 98%), tetradecanonitrile ($\text{C}_{14}\text{H}_{27}\text{N}$, J&K, 98%), 1-bromodecane ($\text{C}_{10}\text{H}_{21}\text{Br}$, J&K, 99%), hexylamine ($\text{C}_6\text{H}_{15}\text{N}$, aladdin, 99%), *N,N*-dimethylformamide (DMF, 99.9%), and these chemical reagents were purchased and used without further purification.

Rapid synthesis of HKUST-1 with ZnO within 30 min at room temperature

In a typical synthesis,¹ 3.6 mmol of ZnO powder was dispersed in 8 mL deionized water to form nanoslurry at room temperature using sonication for 15 min, then 16 mL of DMF was added to ZnO nanoslurries to obtain solution A. Next, 7.2 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 18 mL deionized water to obtain solution B. 4 mmol of H_3BTC were dissolved in 16 mL ethanol to obtain solution C. After these solutions were stirred for 30 min. Then, solution A was added to solution B, and the mixture (solution D) was stirred for 10 min. Finally, the solution C was added to the solution D under fast magnetic stirring, and the mixture was still stirred for 30 min at room temperature, then immediately filtered. The obtained product was immersed in ethanol four times at 373 K for 32 h, then dried overnight in an oven at 393 K. The resulting product is denoted as H-HKUST-1_A1.

Rapid synthesis of HKUST-1 with 1-bromohexadecane within 30 min at room temperature

In a typical synthesis, 7.2 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added to 18 mL of deionized water to obtain solution A. Then, 4 mmol of H_3BTC and 14.4 mmol of 1-bromohexadecane were added to 16 mL of ethanol; hereafter, this mixture is named to as solution B. After both solutions were stirred

for 10 min, solution A was added to solution B, and the mixture was stirred for 30 min. However, no precipitate appearing in the control experiment.

Conventional solvothermal method synthesis of HKUST-1 within 12 h at 393K

In a typical synthesis,² 7.2 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added to 18 mL of deionized water to obtain solution A. Next, 4 mmol of H_3BTC and 14.4 mmol of 1-bromohexadecane were added to 16 mL of ethanol; hereafter, this mixture is named to as solution B. After both solutions were stirred for 10 min, solution A was added to solution B, and the mixture was stirred for 30 min. The final gel mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 393K for 12 h. After cooling to room temperature, the solid product was filtered, washed, activated, and dried. The final product is denoted as H-HKUST-1_A3.

Rapid synthesis of hierarchically structured ZIF-8 at room temperature

(Zn, Zn) hydroxy double salt was synthesized at room temperature using previously reported methods.^{1,3} 3.6 mmol of ZnO was dispersed in 5 mL of deionized water to obtain solution A, and 5 mmol of $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 5 mL of deionized water to obtain solution B. Then solution B was added to the solution A under strong magnetic stirring at room temperature. After 24 h, the formation of (Zn, Zn) hydroxy acetate HDS. Then, 9 mL of 2-methylimidazole (6 mmol) DMF and 1-bromohexadecane (3.3 mmol) solution was added to 3 mL of (Zn, Zn) HDS suspension under magnetic stirring for 30 min, then immediately filtered, washed and dried at 393 K for 12h, and the obtained product is denoted as H-ZIF-8.

2 times scaled-up synthesis of hierarchically structured HKUST-1 at room temperature

Typically, a suspension of 3.6 mmol of ZnO in 4 mL deionized water (sonicated for 15 min) was added to 8 mL of DMF with stirring for 30 min at room temperature (solution A). 7.2 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 9 mL of deionized water to obtain solution B. 14.4 mmol of 1-bromohexadecane and 4 mmol of H_3BTC were dissolved in 8 mL of ethanol to obtain solution C. After these solutions were stirred for 30 min, then mixed. After the mixture was still stirred for 30 min RTP, then filtered, activated, and dried.

Calculation

Yield

The yield (%) was calculated by using the Equation (1) as follow:

$$Yield (\%) = \left(\frac{m_{actual}}{m_{theoretical}} \right) \times 100\% \quad (1)$$

Where m_{actual} represents the dried mass (g) of the obtained MOF product, and the $m_{theoretical}$ represents the theoretical mass of MOF product from stoichiometry.

Space-Time Yield (STY)

The space-time yield (STY, $\text{kg} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$) was adopted to predict the practical application value, as calculated by using the Equation (2) as follow:

$$STY = \left(\frac{m_1}{V_{solution} \tau} \right) \times 1.44 \times 10^6 \quad (2)$$

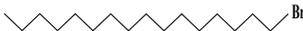
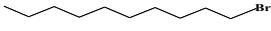
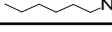
Where m_1 represents the dried mass (g) of the obtained H-HKUST-1 product, $V_{solution}$ represents the total volume (cm^3) for the mixture, and τ represents the reaction time (min).

Table S1. Porosity properties of C-HKUST-1 and the H-MOFs (H-HKUST-1_A, H-HKUST-1_B, and H-HKUST-1_C) synthesized in this work.

Sample	$S_{BET} [\text{m}^2 \cdot \text{g}^{-1}]^a$	$V_{total} [\text{cm}^3 \cdot \text{g}^{-1}]^b$	$V_{meso} [\text{cm}^3 \cdot \text{g}^{-1}]^c$	$V_{micro} [\text{cm}^3 \cdot \text{g}^{-1}]^d$
C-HKUST-1	1577	0.60	0.09	0.51
H-HKUST-1_A	869	0.58	0.21	0.37
H-HKUST-1_B	1044	0.55	0.15	0.40
H-HKUST-1_C	889	0.58	0.20	0.38

^aBET surface area; ^bTotal pore volume; ^cMesopore volume; ^dMicropore volume.

Table S2. Structure-directing agents (SDAs) used in this work for the rapid synthesis of H-MOFs.

SDA	Molecule formula	Structure formula
1-bromohexadecane	$\text{C}_{16}\text{H}_{33}\text{Br}$	
tetradecanonitrile	$\text{C}_{14}\text{H}_{27}\text{N}$	
1-bromodecane	$\text{C}_{10}\text{H}_{21}\text{Br}$	
hexylamine	$\text{C}_6\text{H}_{15}\text{N}$	

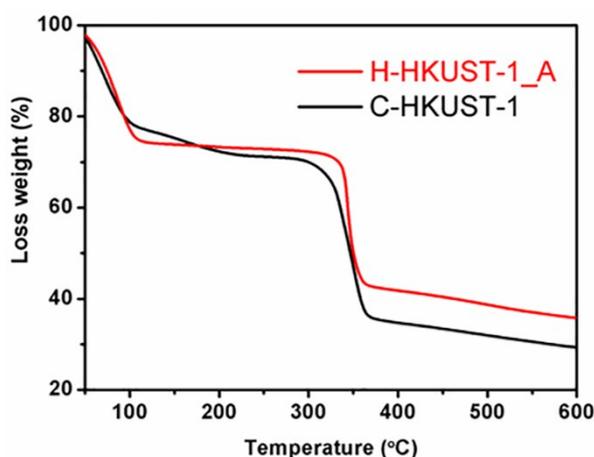


Figure S1. Thermogravimetric analysis (TGA) curves of H-HKUST-1_A and C-HKUST-1.

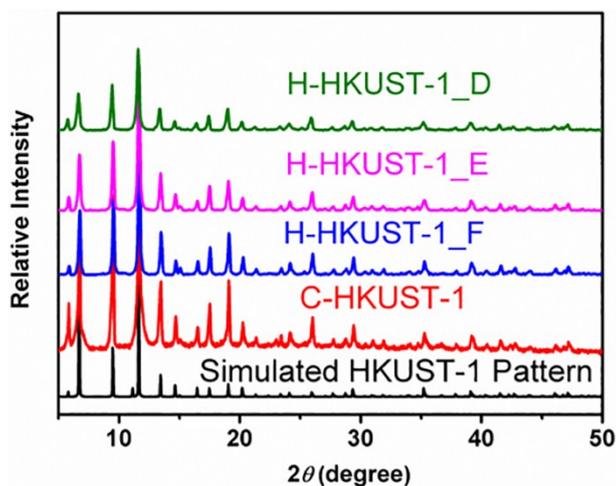


Figure S2. Powder XRD patterns of H-HKUST-1_X (X=D, E, F) and C-HKUST-1, and the simulated HKUST-1 XRD pattern.

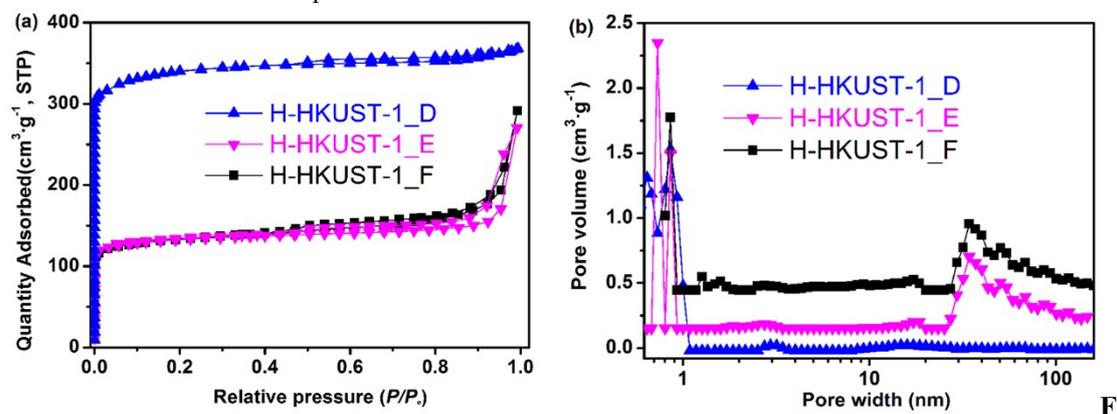


Figure S3. (a) N₂ adsorption–desorption isotherms and (b) pore size distributions of the hierarchically structured H-HKUST-1_X (X=D, E, F) samples. For show the line shapes more clearly, the isotherms of H-HKUST-1_E and H-HKUST-1_F sample are shifted upward by 0.15 and 0.5 cm³·g⁻¹, respectively.

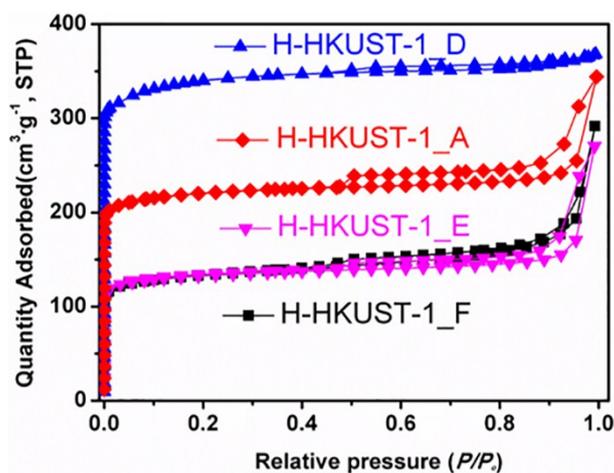


Figure S4. N₂ adsorption–desorption isotherms of the H-HKUST-1_X (X= A, D, E, F) samples.

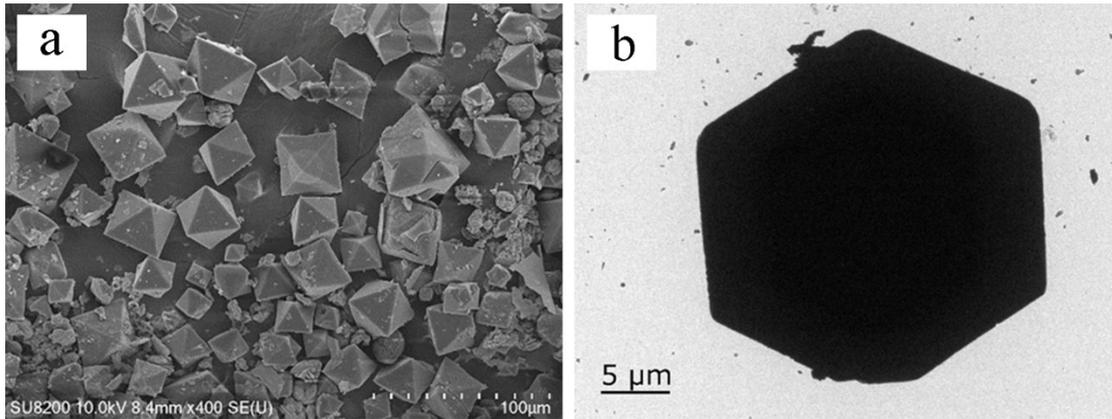


Figure S5. (a) SEM and (b) TEM images of the H-HKUST-1_A1 sample synthesized by conventional solvothermal method.

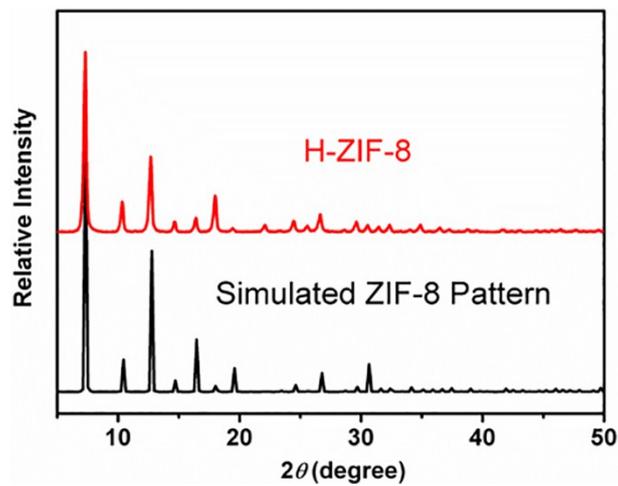


Figure S6. Powder XRD pattern of the H-ZIF-8 sample and the simulated ZIF-8 pattern.

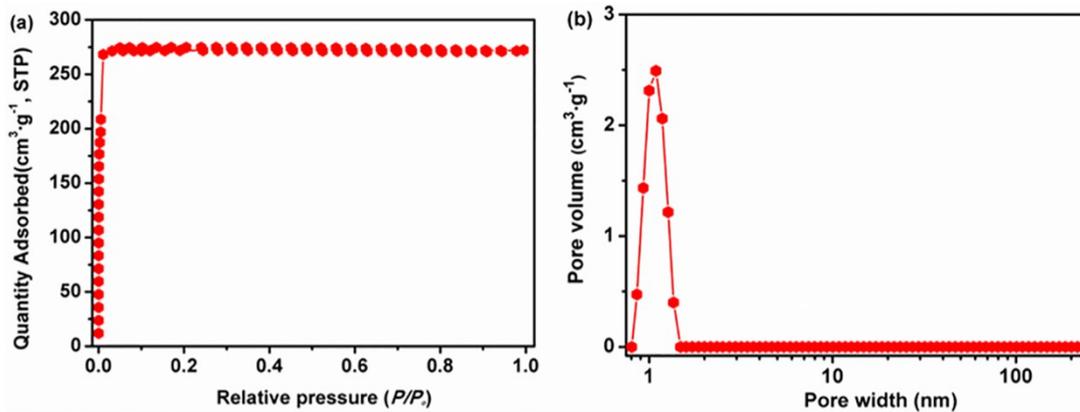


Figure S7. (a) N₂ adsorption–desorption isotherms and (b) pore size distributions of the conventional ZIF-8 sample.

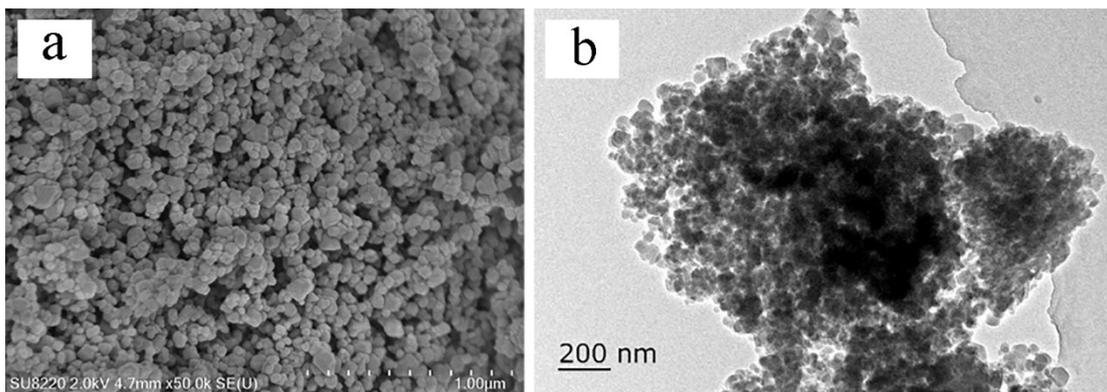


Figure S8. (a) SEM and (b) TEM images of H-ZIF-8 sample synthesized with cooperative template strategy.

References

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