Electronic Supplementary Information (ESI)

Template synthesis of hierarchical porous metal–organic frameworks with tunable porosity

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Experimental Section

Chemical Reagents. Copper (II) nitrate trihydrate ($Cu(NO_3)_2·3H_2O$, J&K, 99%), 1, 3, 5-benzenetricarboxylic acid (H_3BTC, J&K, 99%), zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$, J&K, 99%), 2-methylimidazole (2Im, J&K, 99%), *N*, *N*-dimethyloctadecylamine ($C_{20}H_{43}N$, J&K, 90%), *N*, *N*-dimethylhexadecylamine ($C_{18}H_{39}N$, J&K, 95%), *N*, *N*-dimethyltetradecylamine ($C_{16}H_{35}N$, J&K, 90%), *N, N*-dimethylformamide (DMF). All chemical reagents were used as-received without further purification.

Synthesis of hierarchical porous Cu-BTC by using other organic amine as template

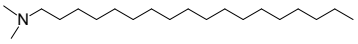
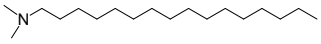
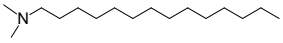
4.5 mmol of $Cu(NO_3)_2·3H_2O$ was added in 15 mL of deionized water to obtain solution A. 2.5 mmol of 1, 3, 5-benzenetricarboxylic acid (H_3BTC) and 2.25 mmol of *N*, *N*-dimethylhexadecylamine (or *N*, *N*-dimethyltetradecylamine) were added in 15 mL of anhydrous ethanol to obtain solution B. After stirring for 0.5 h, respectively. Then solution B was added in solution A, and the mixture was still stirred for 1 h. The finally obtained gel mixture was transferred into 100 mL Teflon-lined stainless steel autoclave stewing and heated to 383 K for 24 h. After being cooled naturally to room temperature, the solid product was filtered and washed with ethanol (25 mL, repeated twice). To remove the additive template and solvents trapped in the channels, the solid product was immersed by ethanol for four times at 373 K for 48 h, then dried in an oven at 423 K for 12 h. The resulting product are denoted as Cu-BTC_B and Cu-BTC_C, respectively.

Synthesis of hierarchical porous ZIF-8 by using an organic amine as template

0.67 mmol of $Zn(NO_3)_2·6H_2O$ and 2 mmol 2-methylimidazole were dissolved in 40 mL DMF while stirring. After that, 0.67 mmol of *N*, *N*-dimethyloctadecylamine was added to the mixture

solution under fast magnetic stirring, and then the mixture was still stirred for 0.5 h. The finally obtained gel mixture was transferred into 100 mL Teflon-lined stainless steel autoclave stewing and heated to 413 K for 24 h. After being cooled naturally to room temperature, the solid product was filtered and washed with ethanol. To remove the additive template and solvents trapped in the channels, the solid product was immersed by ethanol for four times at 373 K for 48 h, then dried in an oven at 423 K for 12 h. The resulting product is denoted as ZIF-8_A.

Table S1. The organic amines used in this work.

Organic amine	Molecular Formula	Structure Formula
N, *N*-dimethyloctadecylamine	$C_{20}H_{43}N$	
N,*N*-dimethylhexadecylamine	$C_{18}H_{39}N$	
N, *N*-dimethyltetradecylamine	$C_{16}H_{35}N$	

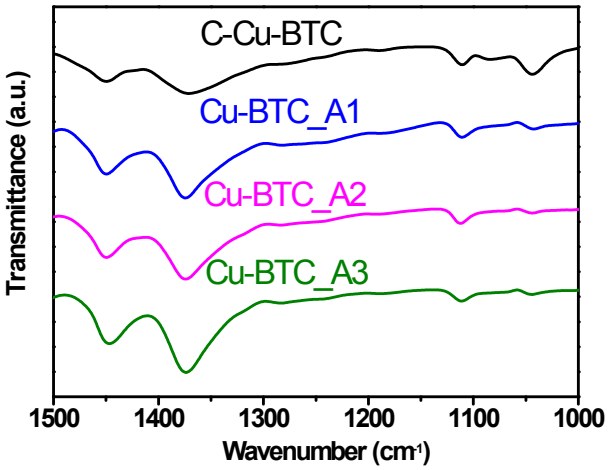


Fig. S1 FTIR spectra of Cu-BTC_A*n* (*n* = 1, 2, 3) and C-Cu-BTC samples in the narrow region of 1500–1000 cm^{-1}.

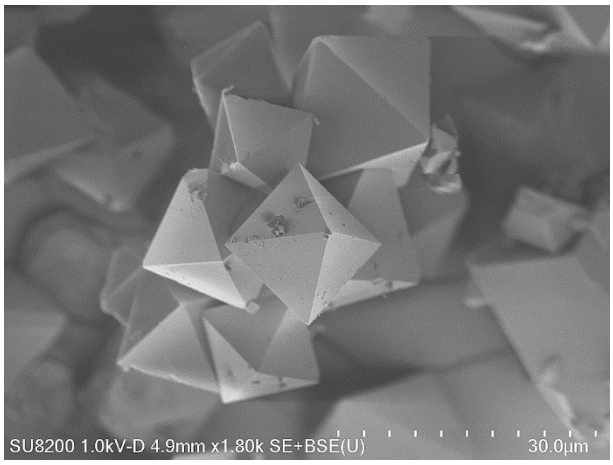


Fig. S2 SEM image of the conventional Cu-BTC (C-Cu-BTC) sample.

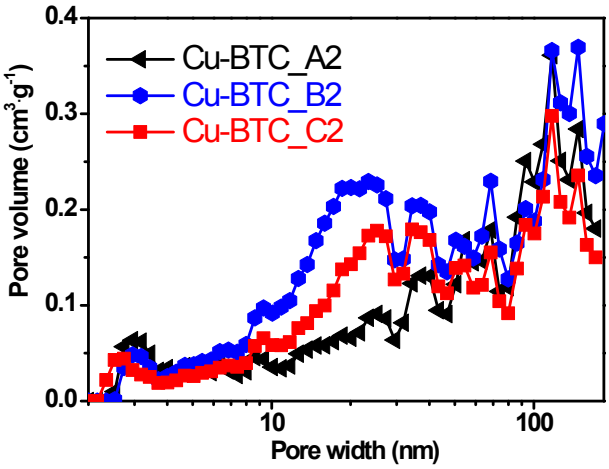


Fig. S3 Pore size distributions of hierarchical porous Cu-BTC_A2, Cu-BTC_B2 (repeated experiment), and Cu-BTC_C2 (repeated experiment).

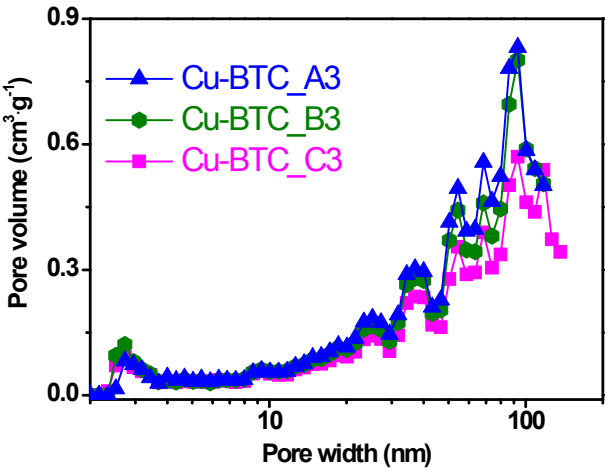


Fig. S4 Pore size distributions of hierarchical porous Cu-BTC_*X*3 (*X* = A, B, C; B means the synthesis was scaled up 5 times; C means the synthesis was scaled up 10 times).

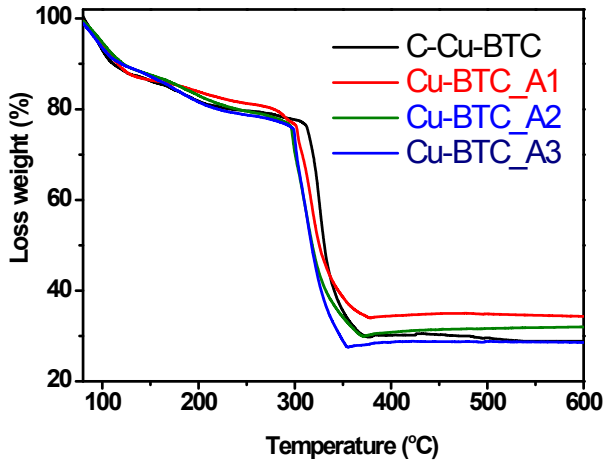


Fig. S5 The thermogravimetric analysis (TGA) of hierarchical porous Cu-BTC_A*n* (*n* = 1, 2, 3) and C-Cu-BTC.

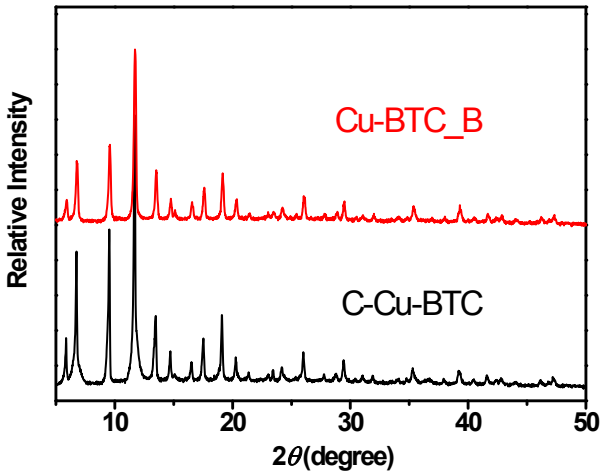


Fig. S6 Power XRD patterns of hierarchical porous Cu-BTC_B and C-Cu-BTC samples.

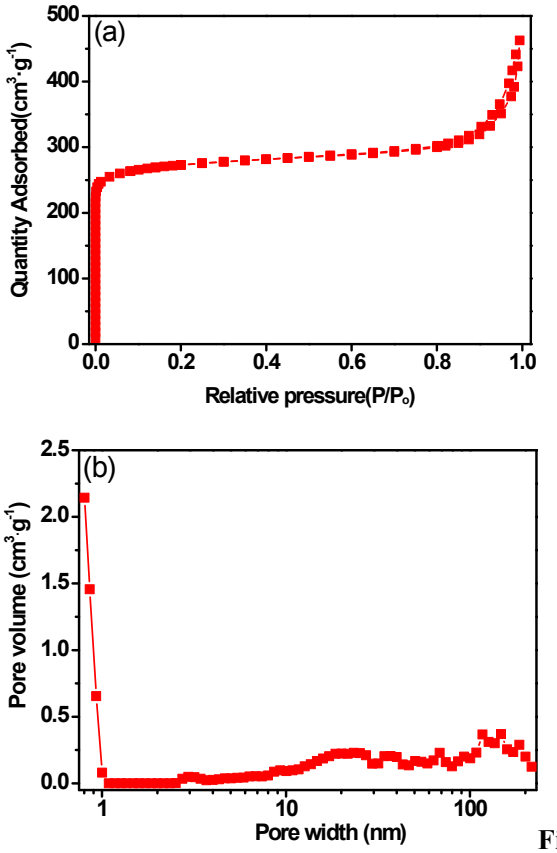


Fig. S7 (a) N_2 adsorption-desorption isotherms and (b) pore size distributions of the hierarchical porous Cu-BTC_B sample.

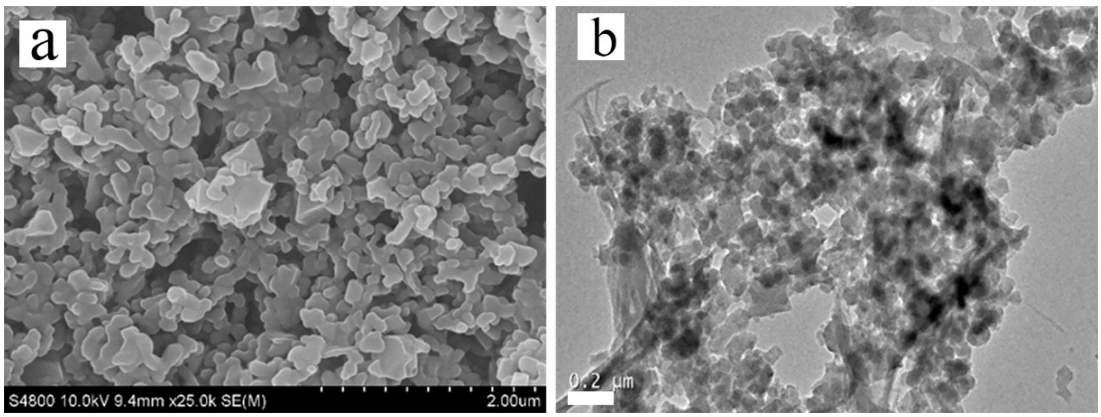


Fig. S8 (a) SEM and (b) TEM images of hierarchical porous Cu-BTC_B sample.

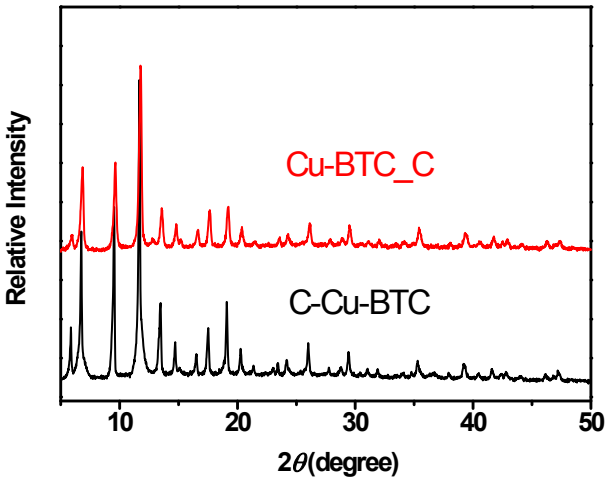
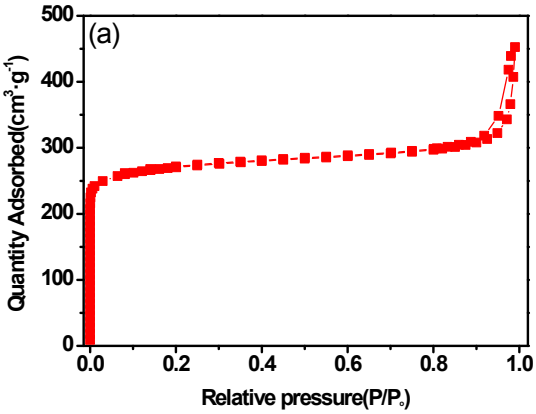


Fig. S9 Power XRD patterns of hierarchical porous Cu-BTC_C and C-Cu-BTC samples.



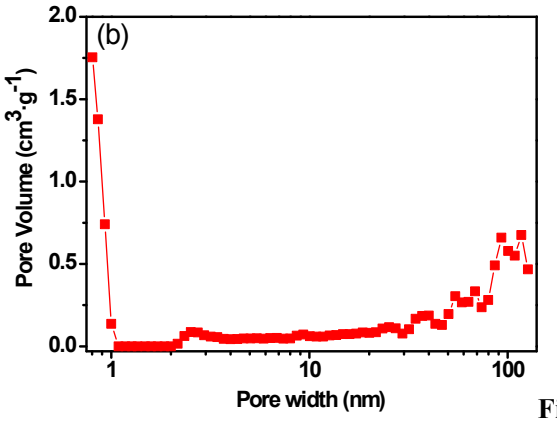


Fig. S10 (a) N_2 adsorption-desorption isotherms and (b) pore size distributions of the hierarchical porous Cu-BTC_C sample.

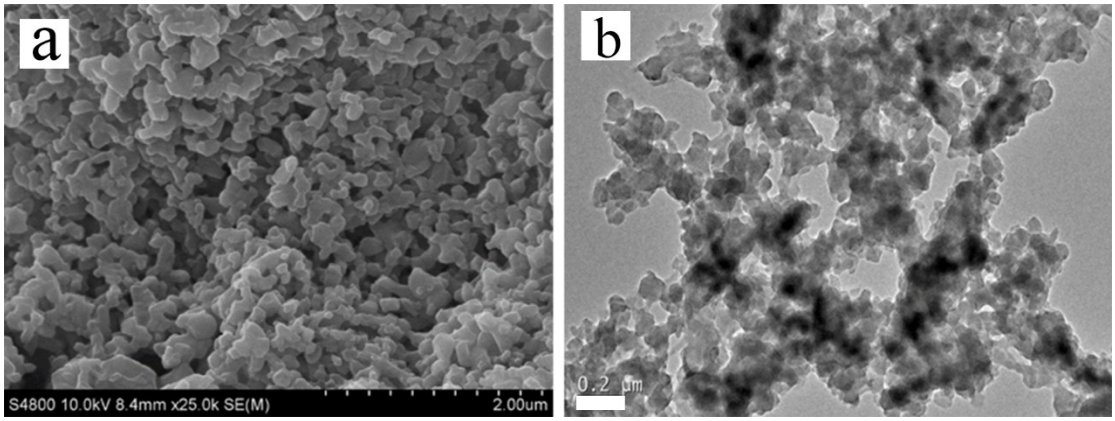


Fig. S11 (a) SEM and (b) TEM images of hierarchical porous Cu-BTC_C sample.

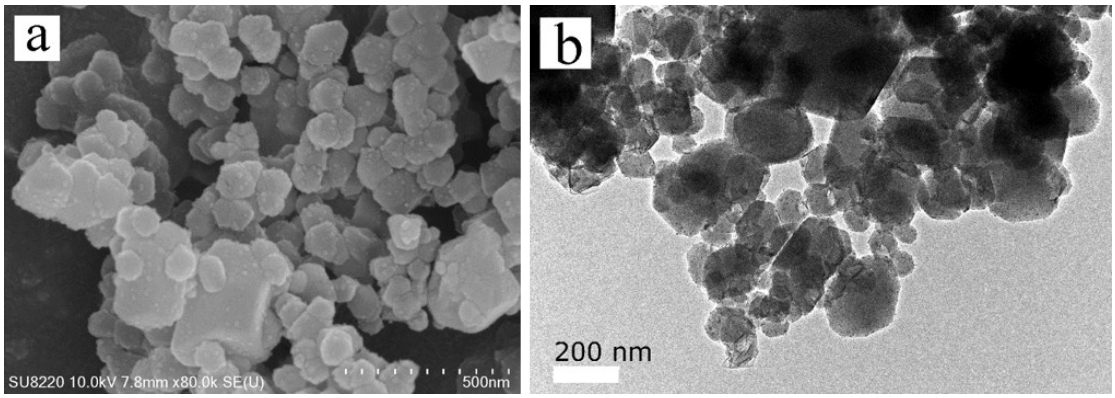


Fig. S12 (a) SEM and (b) TEM images of hierarchical porous ZIF-8_A sample.

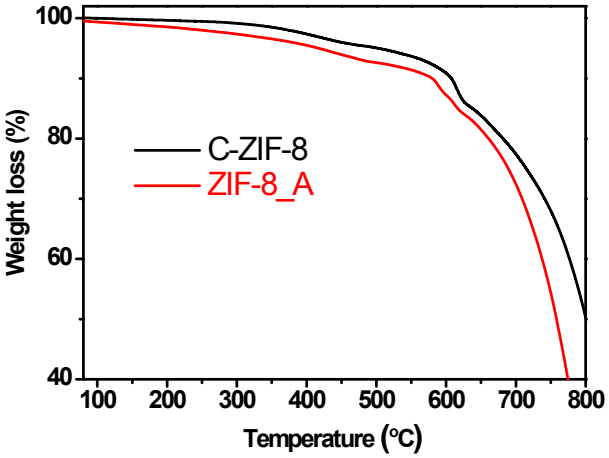


Fig. S13 Thermogravimetric analysis (TGA) of hierarchical porous ZIF-8_A and C-ZIF-8.