Electronic Supplementary Information (ESI)

Ultrafast room-temperature synthesis of hierarchically porous metal–organic frameworks with high space–time yields

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Experimental section

Ultrafast room-temperature synthesis of hierarchical porous HKUST-1

In a typical synthesis, 525 mg of 1, 3, 5-benzenetricarboxylic acid (H_3BTC, 2.5 mmol) was dissolved in 15 mL anhydrous methanol, and 1093 mg of copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, 4.5 mmol) was dissolved in 15 mL deionized water, respectively. Then mixed and stirring. After that, 6.75 mmol of organic amines (protonation-templating agent, see Table S1) was added into the mixture under fast magnetic stirring at room temperature. After stirring for various reaction time *t* (min), the obtained glaucous precipitate was immediately filtered and washed with methanol, the obtained product was immersed in ethanol at 373 K for 48 h (4 times) and then dried overnight in an oven at 393 K. The resulting products HKUST-1 were labeled as HKUST-1_*Xt* (*X*= A, B, denotes the type of organic amines (Table S1); *t* = 1, 10, 30, denotes synthesis time (min)). No glaucous product was obtained in the control experiment without adding organic amines after the same synthesis time. For comparison, the conventional HKUST-1 was also prepared through solvothermal synthesis approach at 393 K according to a previous report,[1] which was denoted as C-HKUST-1.

Ultrafast room-temperature synthesis of hierarchical porous ZIF-8

In a typical synthesis, 670 mg of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 2 mmol) and 167 mg of 2-methylimidazole (2Im, 2 mmol) were dissolved in 40 mL anhydrous methanol, then stirring 5 min. After that, 3 mmol organic amine (*N*,*N*,*N*,*N*-tetramethyl-1, 6-hexanediamine) was added into the mixture solution under fast magnetic stirring at room temperature. After stirring for 1 min, the

white product was immediately filtered and washed with methanol (50 mL, 2 times), and then dried overnight in an oven at 393 K. The resulting product ZIF-8 was denoted as ZIF-8_A1.

Ultrafast room-temperature synthesis of hierarchical porous ZIF-61

In a typical synthesis, 200 mg of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 0.67 mmol), 111 mg of 2-methylimidazole (2Im, 1.35 mmol) and 275 mg of imidazole (Im, 4.04mmol) were dissolved in 20 mL anhydrous methanol, then stirring for 10 min. After that, 0.67 mmol organic amine (*N*,*N*,*N*,*N*-tetramethyl-1, 6-hexanediamine) was added into the mixture solution. After continue stirring for 1 min, the mixture solution was immediately filter and washed with methanol (10 mL, 2 times). The obtained product was immersed in ethanol at 373 K for 48 h (4 times) and then dried overnight in an oven at 393 K. The resulting product ZIF-61 was denoted as ZIF-61_A1.

Ultrafast room-temperature synthesis of hierarchical porous ZIF-90

In a typical synthesis, 480 mg of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 2.0 mmol) and 290 mg of imidazole-2-carboxyaldehyde (ICA, 3.0 mmol) were dissolved in 30 mL methanol, then stirring for 10 min. After that, 3.0 mmol organic amine (*N*,*N*,*N*,*N*-tetramethyl-1, 6-hexanediamine) was added into the mixture solution under fast magnetic stirring at room temperature. After stirring for 1 min, the canary suspension was immediately filtered and washed with methanol (10 mL, 2 times), and then dried overnight in an oven at 393 K. The resulting product was denoted as ZIF-90_A1.

Calculation

Yield calculation

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

Where m_{actual} is representative the dried mass (g) for the obtained MOF powder in this work, and $m_{\text{theoritical}}$ is representative the theoretical mass of MOF product from stoichiometry.

Space-time yields (STYs) calculation

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

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

where m1 is representative the dried mass (g) for the hierarchical porous HKUST-1 powder prepared from the rapid synthesis, $V_{solution}$ is the total volume (cm^3) for the water and methanol mixed solution, and τ is the residence time (min).

Computational methods

We adopted density functional theory (DFT) to calculate molecular properties of organic amine. The geometry optimization of molecule was performed at the DFT B3LYP level theory using 6-311+G(d, p) basis set with GAUSSIAN 09 program.[2] This basis set provided a wide range of organic compounds in accurate geometry and electronic properties.[3] The molecular electrostatic potential (MEP) of organic amine was calculated by using DFT-B3LYP/6-31G* method that based on optimized geometry. And the frontier molecular orbitals were also calculated at the B3LYP/6-31G* level of theory.

Materials characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE diffractometer system equipped with Ni filtered Cu target Kα radiation (40 kV, 40 mA, wave length λ = 0.15418 nm) at room temperature. MOF powder diffraction patterns (XRD) were simulated by using Materials Studio package 5.0, and the crystal structure files were obtained from the Cambridge Crystallographic Data Centre (CCDC-112954 for HKUST-1, CCDC-602542 for ZIF-8, CCDC-671069 for ZIF-61, CCDC -693596 for ZIF-90). Scanning electron microscopy (SEM) images were obtained on a Carl Zeiss, ZEISS Ultra 55 at a low landing energy (5.0 kV). Transmission electron microscopy (TEM) was performed on a JEM- 2100HR electron microscope operated at 200 kV. Thermogravimetric analysis (TGA) of samples was carried out with a TG 209 instrument (Netzsch) and heated from 298 to 873 K in nitrogen atmosphere at a rate of 5 K /min. Elemental analysis was performed on an Elemental Vario EL-III analyzer. Nitrogen adsorption–desorption data were measured on an ASAP 2020 or ASAP 2460 (Micromeritics) system at 77 K. All of samples were outgassed for 8 h at 393 K before measurements. The specific surface areas of samples were calculated by applying the Brunauer–Emmett–Teller (BET) equation, and the pore size distribution was analyzed from the desorption branch of the isotherm using the DFT method. The micropore volume (V_{micro}) was determined employing t-plot micropore analysis. The total pore volume (V_{total}) was obtained via the single point adsorption branch of the isotherm.

Table S1. Chemical structure of the protonation-templating agent used in this work and the corresponding abbreviations.

Organic amine (Protonation-templating agent)	Structure formula	Abbreviation

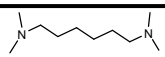
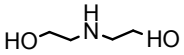
N, *N*, *N*, *N*-tetramethyl-1, 6-hexanediamine		A
diethanolamine		B

Table S2. The product hierarchical porous HKUST-1_*X*1 (*X* = A and B) were characterized by elemental microanalysis calculated for $Cu_3(BTC)_2(H_2O)_3$.

Sample	C (wt. %)	H (wt. %)	N (wt. %)
C-HKUST-1	32.79	1.82	0.00
HKUST-1_A	31.86	4.69	1.36
HKUST-1_B	33.82	6.79	1.37

Table S3. Space-time yields of ZIF-8, ZIF-61, and ZIF-90, respectively.

Sample	ZIF-8	ZIF-61	ZIF-90
Space-time yields [$kg \cdot m^{-3}d^{-1}$]	1.02×10^4	9.22×10^3	1.85×10^4

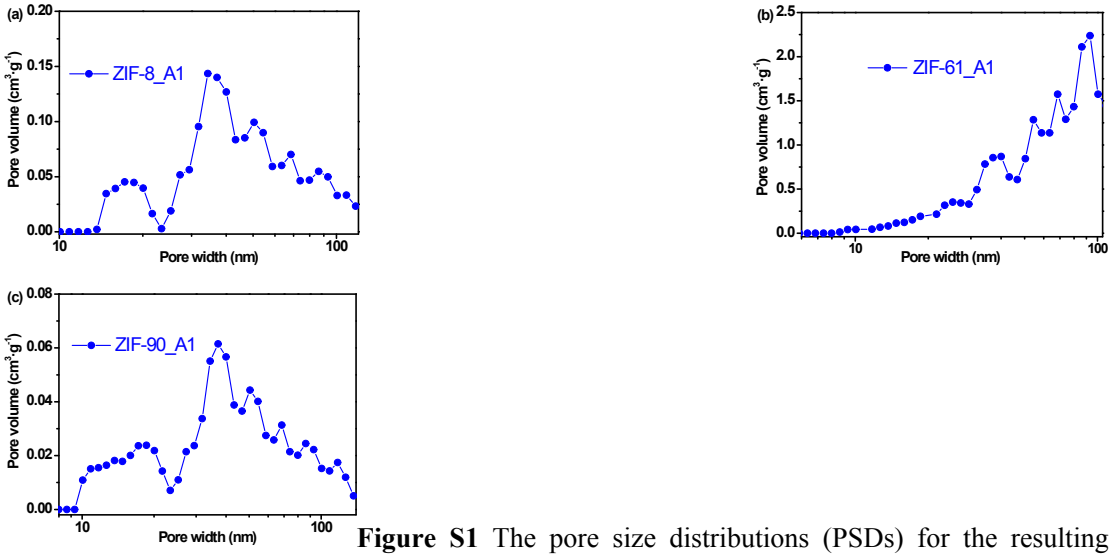


Figure S1 The pore size distributions (PSDs) for the resulting hierarchical porous MOFs: (a) ZIF-8_A1; (b) ZIF-61_A1; and (c) ZIF-90_A1.

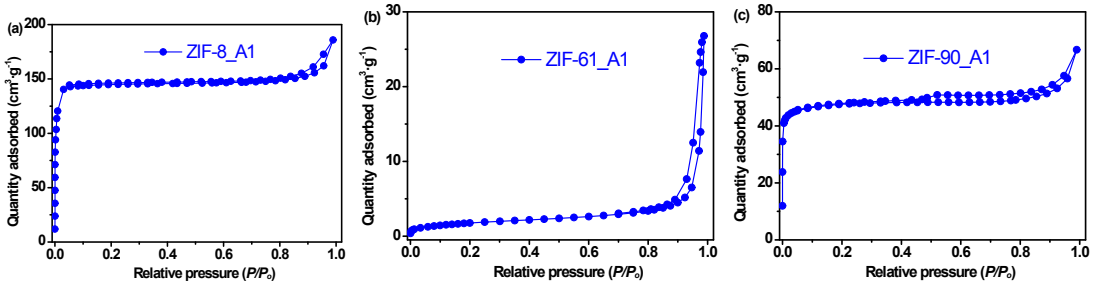


Figure S2 N_2 adsorption-desorption isotherms for the resulting hierarchical porous MOFs: (a) ZIF-8_A1; (b) ZIF-61_A1; and (c) ZIF-90_A1.

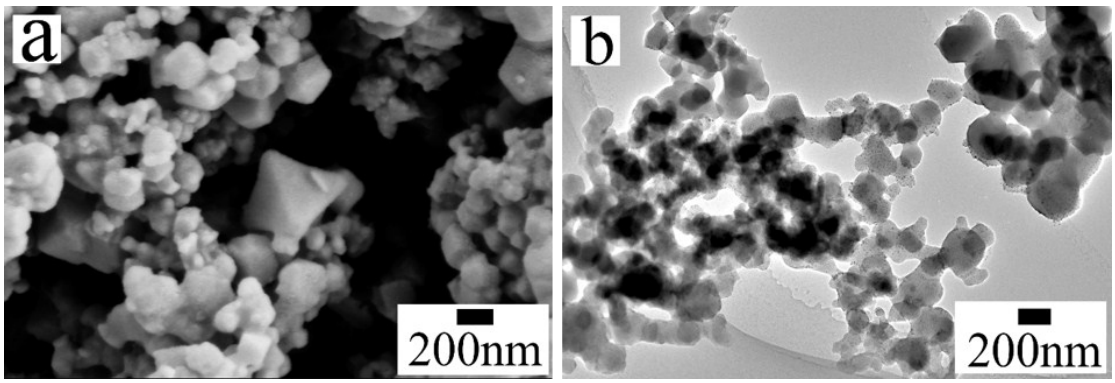


Figure S3 (a) SEM and (b) TEM images of hierarchical porous HKUST-1_B1 sample synthesized within 1 min with diethanolamine as protonation-templating agent.

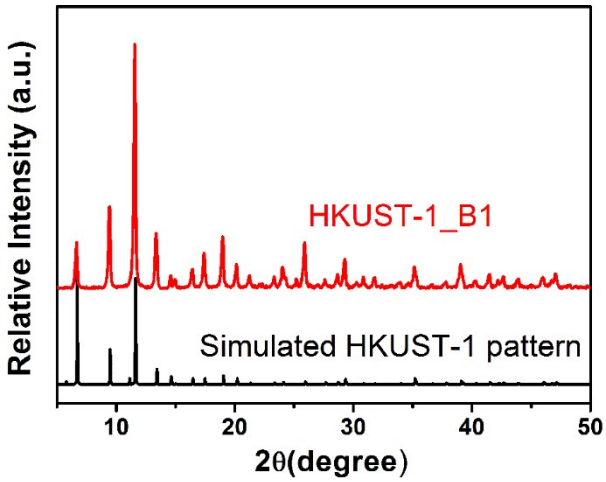


Figure S4 Powder XRD patterns of the HKUST-1_B1 sample (red) and the simulated HKUST-1 pattern (black).

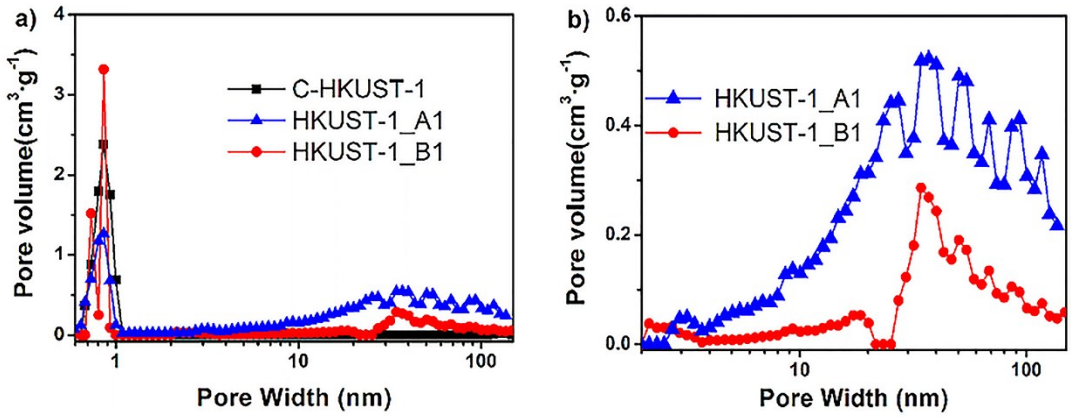


Figure S5 The pore size distributions (PSDs) of the C-HKUST-1sample and the as-synthesized hierarchical porous HKUST-1_*X*1 (*X* = A, B) samples.

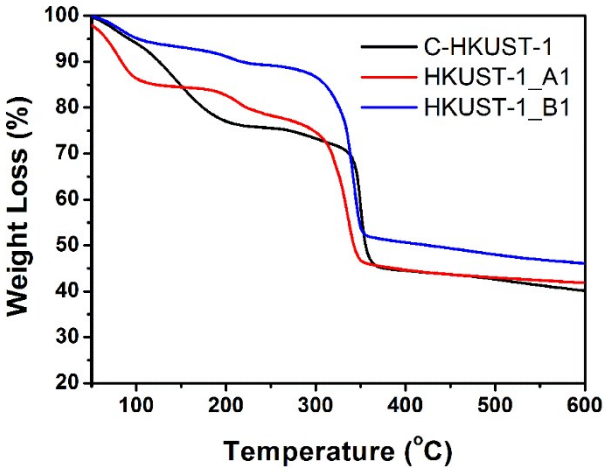


Figure S6 The thermogravimetric analysis (TGA) of the hierarchical porous HKUST-1_*X*1 (*X* = A and B) and C-HKUST-1 samples.

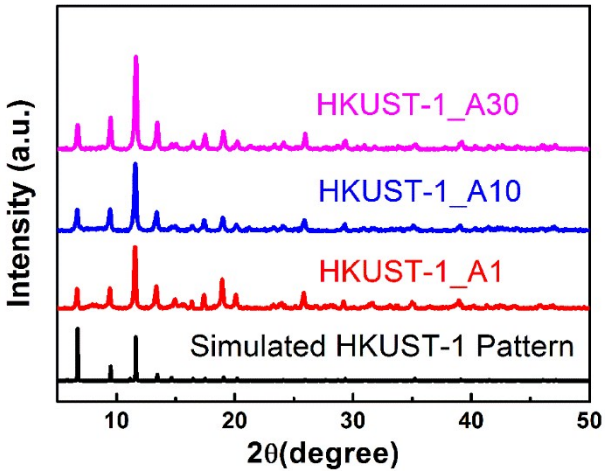


Figure S7 Powder XRD patterns for the as-synthesized HKUST-1_A*t* (*t* = 1, 10, 30) samples produced from different synthesis time and simulated HKUST-1 pattern.

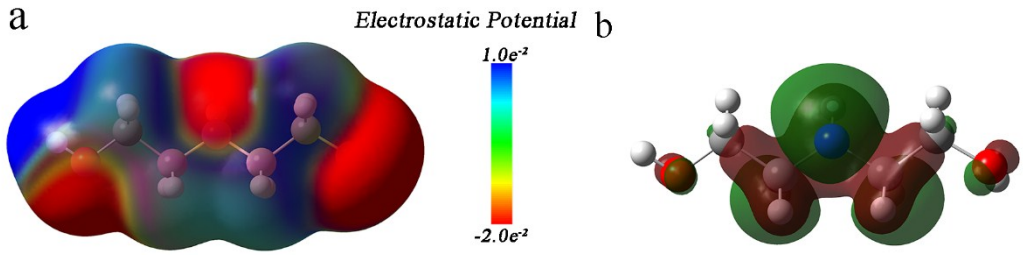


Figure S8 (a) Molecular electrostatic potential map (MEP); (b) Molecular orbital surfaces of diethanolamine (white ball = hydrogen atom; gray ball = carbon atom; blue ball = nitrogen atom).[4]

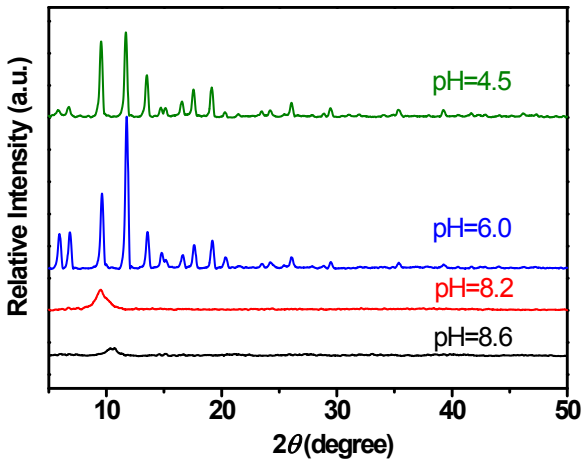


Figure S9 XRD patterns for the obtained products synthesized with different pH conditions.

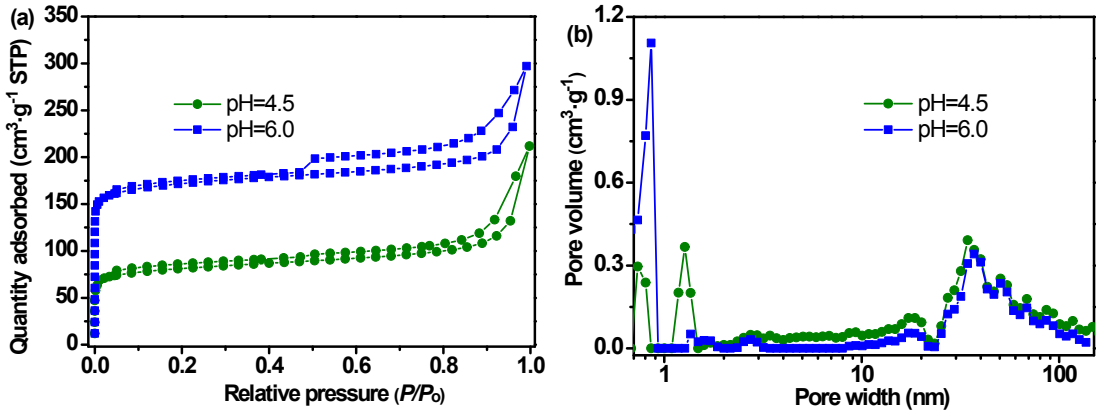


Figure S10 (a) N_2 adsorption-desorption isotherms and (b) pore size distributions of the obtained products synthesized with different pH conditions.

References

1. S. S.-Y. Chui, S. M.-F. Lo, J. P. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, 283, 1148-1150.
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3. B. Liu, Q. Duan, C. Li, Z. Zhu, H. Xi and Y. Qian, *New J. Chem.*, 2014, 38, 4380-4387.
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