

Electronic supplementary information (ESI)

Coordination modulation induced and ultrasonic-assisted synthesis of size-controlled microporous metal-imidazolate framework crystals with enhanced adsorption performance

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Materials and methods. All the chemicals and solvents are of reagent grade and were used as received without further purification. The ligand 1,4-di(1H-imidazol-4-yl)benzene (H_2L) was prepared according to the literature.^{S1} The powder X-ray diffraction (PXRD) data of the products were collected on a Bruker D8 Advance X-ray diffractometer with Cu-K α ($\lambda = 1.5418 \text{ \AA}$) radiation at room temperature. Scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 5 kV. TEM and HRTEM were carried out on a JEM-2100 high resolution transmission microscope, employing an accelerating voltage of 200 kV. Nitrogen (N_2) and carbon dioxide (CO_2) sorption experiments were carried out on a Belsorp-max volumetric gas sorption instrument. Methane (CH_4) and hydrogen (H_2) sorption experiments were carried out on Autosorb-1MP, Quantachrome. Surface areas were determined by the Brunauer-Emmett-Teller (BET) method and the mesopore size distribution was determined by using the Barrett-Joyner-Halenda (BJH) method. Prior to measurement of gas sorption, all the

samples were activated under vacuum at 160 °C for about 10 h.

Syntheses. In a typical experiment, 17 mg of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1 mmol) and 21 mg of H_2L (0.1 mmol) were dissolved in 50 mL of 1:1(v/v) mixture of ethanol and deionized water to obtain clear solution. Then 0.6 mL of aqueous ammonia (25 wt%) was introduced under ultrasonic wave conditions (40 kHz) at an ultrasonic power output of 300 W at room temperature. After 10 min, brown precipitates was collected by centrifuging, washed with deionized water and ethanol for 3 times, and then dried under vacuum at 60 °C for 5 h. The yield of particle was 49% based on the amount of ligand. In order to explore the effect of the amount of aqueous ammonia, 0, 0.1, 0.2, 0.4, 0.8, 1.0 mL of aqueous ammonia were added in the reaction system while the other conditions maintained unchanged. The yields of the particle were 46%, 47%, 66% and 58% based on the amount of ligand respectively, when 0.2, 0.4, 0.8, 1.0 mL of aqueous ammonia were added in the reaction system. When ultrasonic wave condition was removed, the reactant mixture was stirred at room temperature for 1 hour with 0.2, 0.6, 1.0 mL of aqueous ammonia in the reaction system.

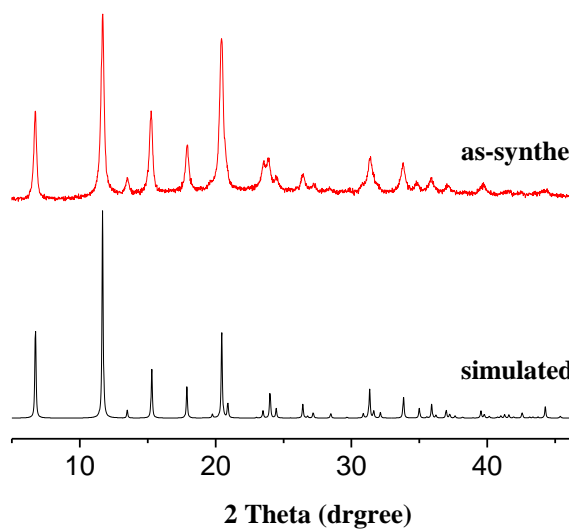


Fig. S1 Powder XRD patterns for the simulated [Cu(L)] and the as-obtained product.

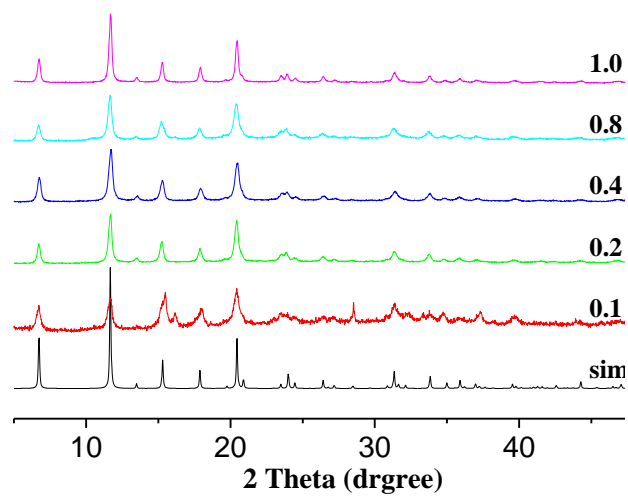


Fig. S2 Powder XRD patterns for the simulated [Cu(L)] and the products prepared with different amounts of aqueous ammonia.

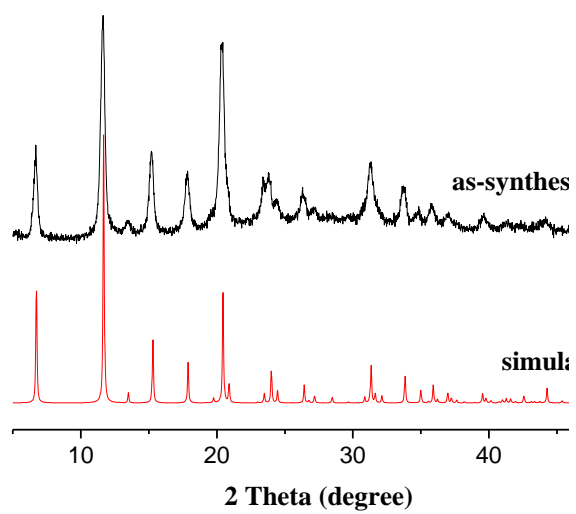


Fig. S3 Powder XRD patterns for the simulated [Cu(L)] and the sample prepared without ultrasonic-assisted synthesis.

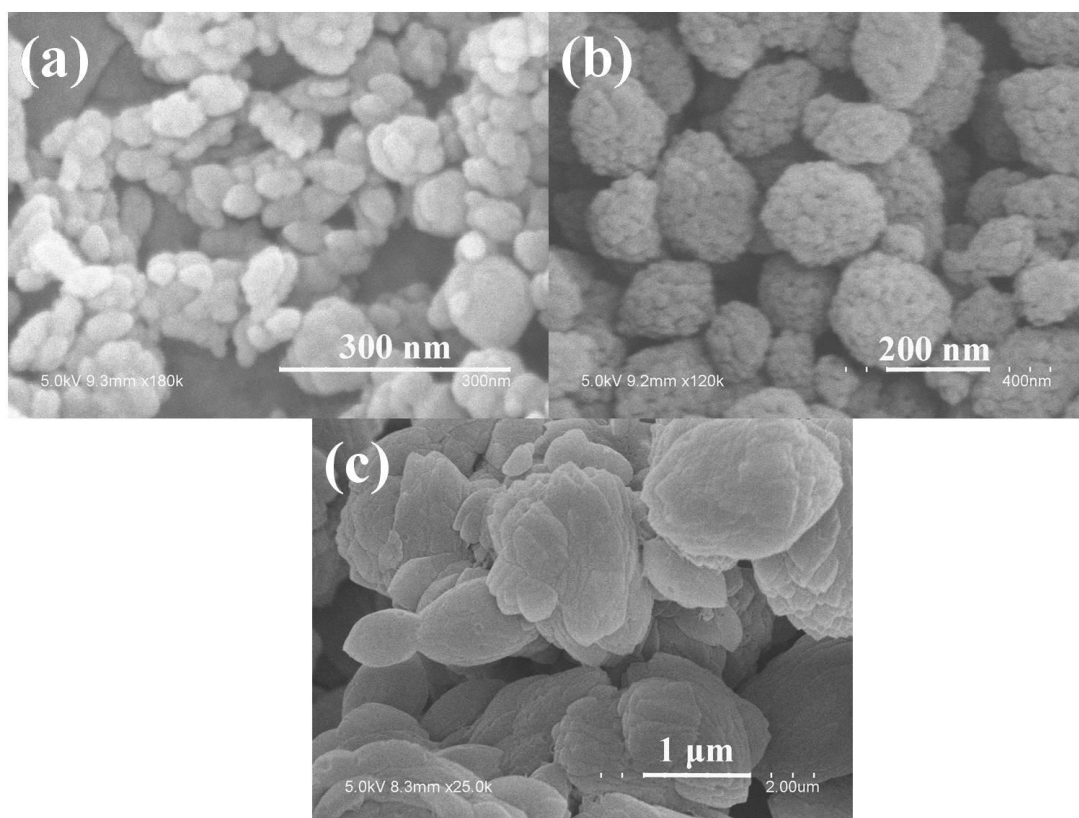


Fig. S4 SEM images of the products prepared with different amounts of aqueous ammonia: (a) 0.2, (b) 0.6, (c) 1.0 mL when ultrasonic-assisted synthesis is removed.

Hydrogen isotherms at 77 K and 87 K for the product fit to the virial equation of the form given in Equation 1.^{S2} The heat of adsorption is then calculated from the fitting parameters using Equation 2.

$$\ln p = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad (1)$$

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

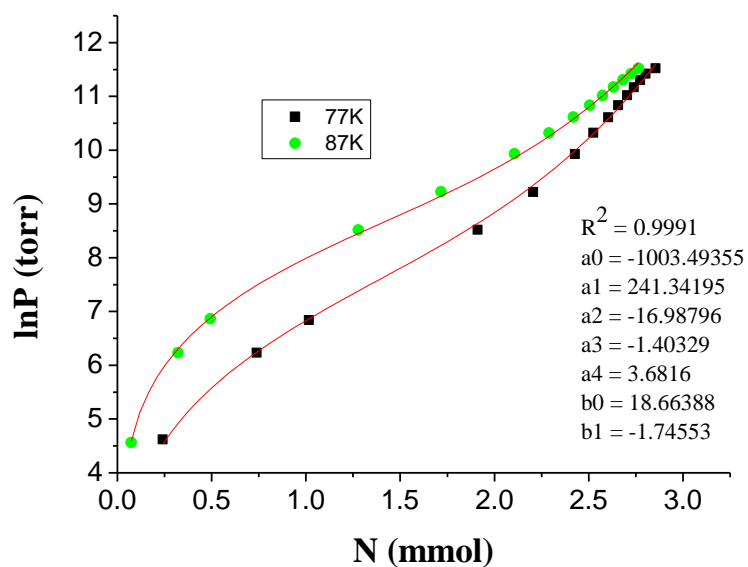


Fig. S5 Details of fitting and calculation of isosteric heat of adsorption for bulk-[Cu(L)].

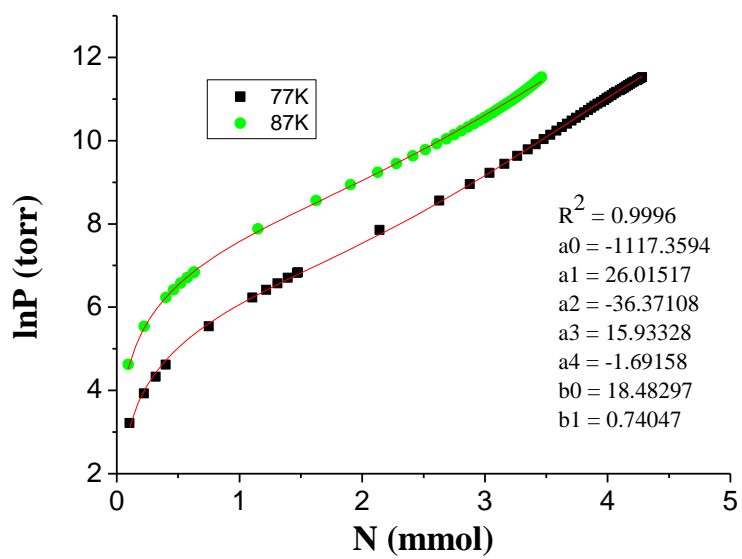


Fig. S6 Details of fitting and calculation of isosteric heat of adsorption for nano-[Cu(L)].

The methods are applied to estimate the CO₂/N₂ selectivity according to the literature.^{S3} The ratios of these initial slopes of the CO₂ and N₂ adsorption isotherms were applied to estimate the adsorption selectivity for CO₂ over N₂.

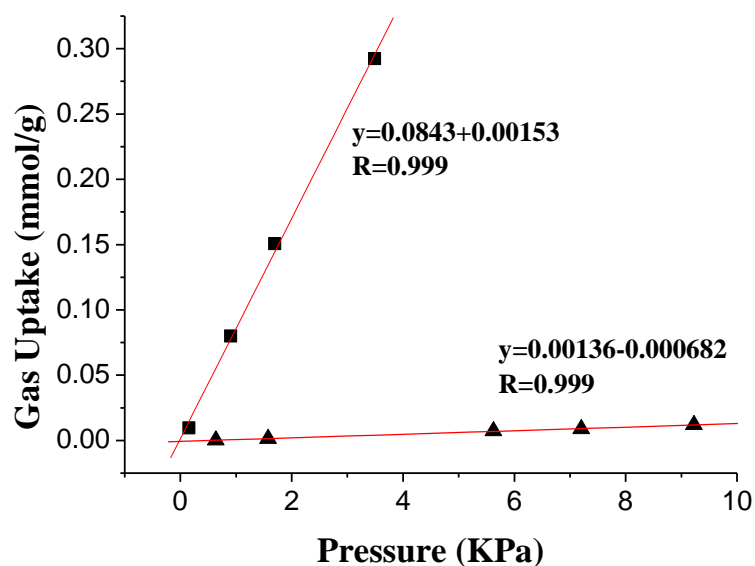


Fig. S7 The fitting initial slope for CO₂ and N₂ isotherms collected at 273K (CO₂: squares; N₂: triangles).

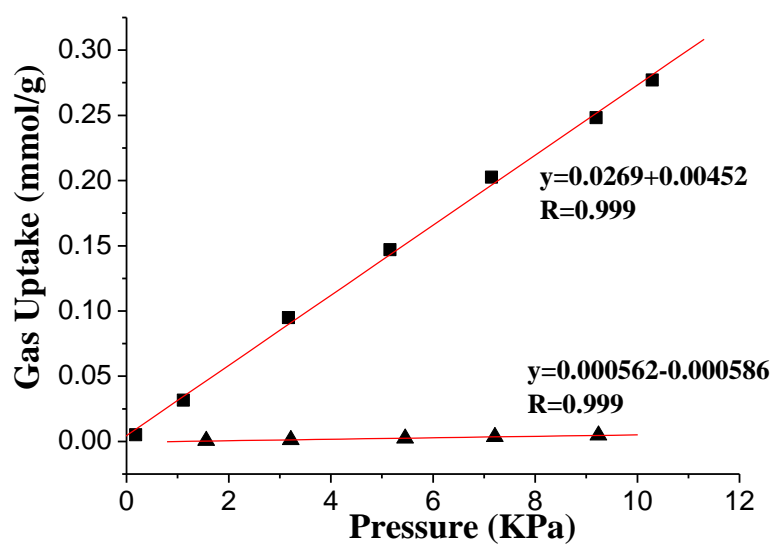


Fig. S8 The fitting initial slope for CO₂ and N₂ isotherms collected at 298K (CO₂: squares; N₂: triangles).

Reference:

- S1 (a) R. ten Have, M. Huisman, A. Meetsma and A. M. van Leusen, *Tetrahedron*, 1997, **53**, 11355; (b) S. S. Chen, J. Fan, T.-a. Okamura, M. S. Chen, Z. Su, W. Y. Sun and N. Ueyama, *Cryst. Growth Des.*, 2010, **10**, 812.
- S2 K. L. Mulfort and J. T. Hupp, *Inorg. Chem.*, 2008, **47**, 7936.
- S3 J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 38.