

Electronic supplementary information (ESI)

Facile fabrication and adsorption property of nano/microporous coordination polymer with controllable size and morphology

Qing Liu, Li-Na Jin Wei-Yin Sun*

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China

Materials and methods. All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. The btc triethylammonium salt was synthesized by dissolving H₃btc (2.1 g, 0.01 mol) in triethylamine (10 ml, 30 wt% in water) and dried under reduced pressure. Then the salt was dissolved in distilled water to form a solution with with 0.1 M btc triethylammonium salt. 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. FT-IR spectra were recorded in the range of 400 - 4000 cm⁻¹ on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Nitrogen sorption experiments at 77 K were carried out on a Belsorp-max volumetric gas sorption instrument. Surface areas were determined by the Brunauer-Emmett-Teller (BET) method. Prior to measurement of nitrogen sorption, all samples were activated under vacuum

at 453 K for about 5 h. The mesopore size distribution was determined by using the Barrett-Joyner-Halenda (BJH) method.

Syntheses. In a typical experiment, the surfactant of CTAB (0-9.11 g, 0-25 mmol) was dissolved in 50 mL of 1:1 (v/v) mixture of ethanol and deionized water and stirred vigorously for 5 min at room temperature until a transparent solution was obtained. Then 0.15 mL of a 0.1 M $\text{Cu}(\text{NO}_3)_2$ aqueous solution and 0.1 mL of a 0.1 M btc triethylammonium salt aqueous solution were added respectively and the reaction mixture was stirred vigorously for an additional 5 min at room temperature. The resulted blue powder was isolated by centrifugation, washed with ethanol for 3 times and dried under vacuum for 5 h at room temperature. In order to explore the effect of the concentration of reactant, Cu(II) salt and ligand btc^{3-} keep in a 3:2 molar ratio on the basis of crystal composition. For a given concentration of CTAB (0, 0.005 M, 0.01 M, 0.05M, 0.1M), only the concentration of reactants changes while other conditions like temperature, solvent, and reaction time remain unchanged. The concentrations of Cu^{2+} are 0.1, 0.2, 0.3, 0.6, 1.2 and 3 mM respectively when 0.05, 0.1, 0.15, 0.3, 0.6, 1.5 mL of 0.1 M $\text{Cu}(\text{NO}_3)_2$ aqueous solution are added.

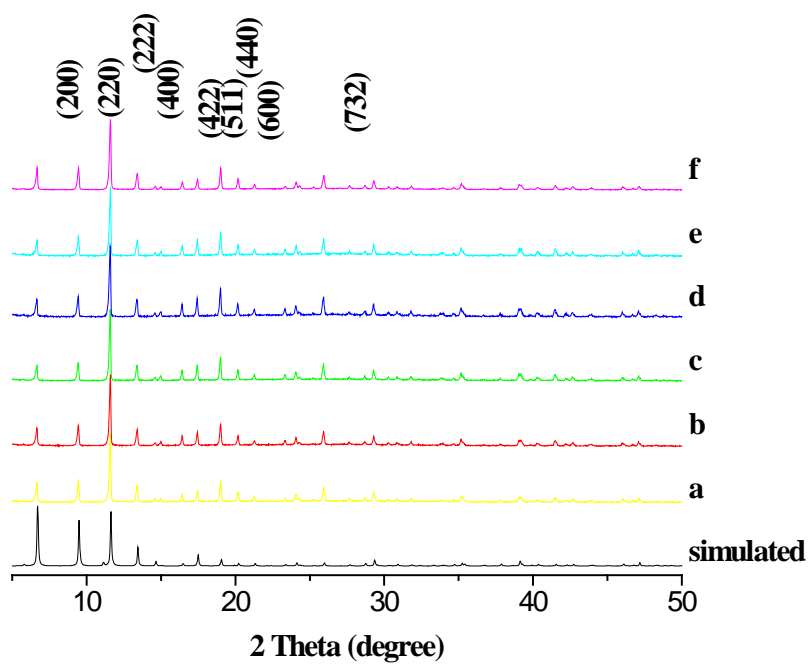


Fig. S1 Powder XRD patterns for simulate [Cu₃(btc)₂] and samples prepared with different concentrations of CTAB: (a) 0; (b) 0.005; (c) 0.01; (d) 0.05; (e) 0.1 and (f) 0.5 M.

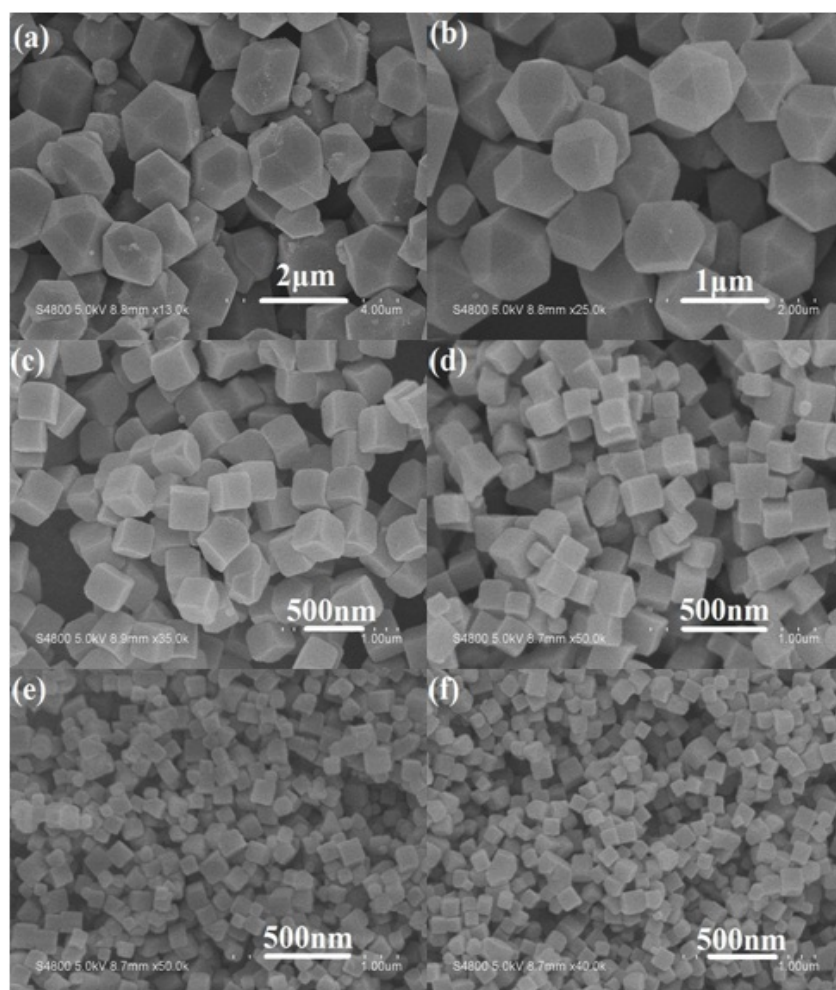


Fig. S2 SEM images of [Cu₃(btc)₂] samples prepared with different concentrations of Cu²⁺ without CTAB: (a) 0.1; (b) 0.2; (c) 0.3; (d) 0.6; (e) 1.2 and (f) 3 mM.

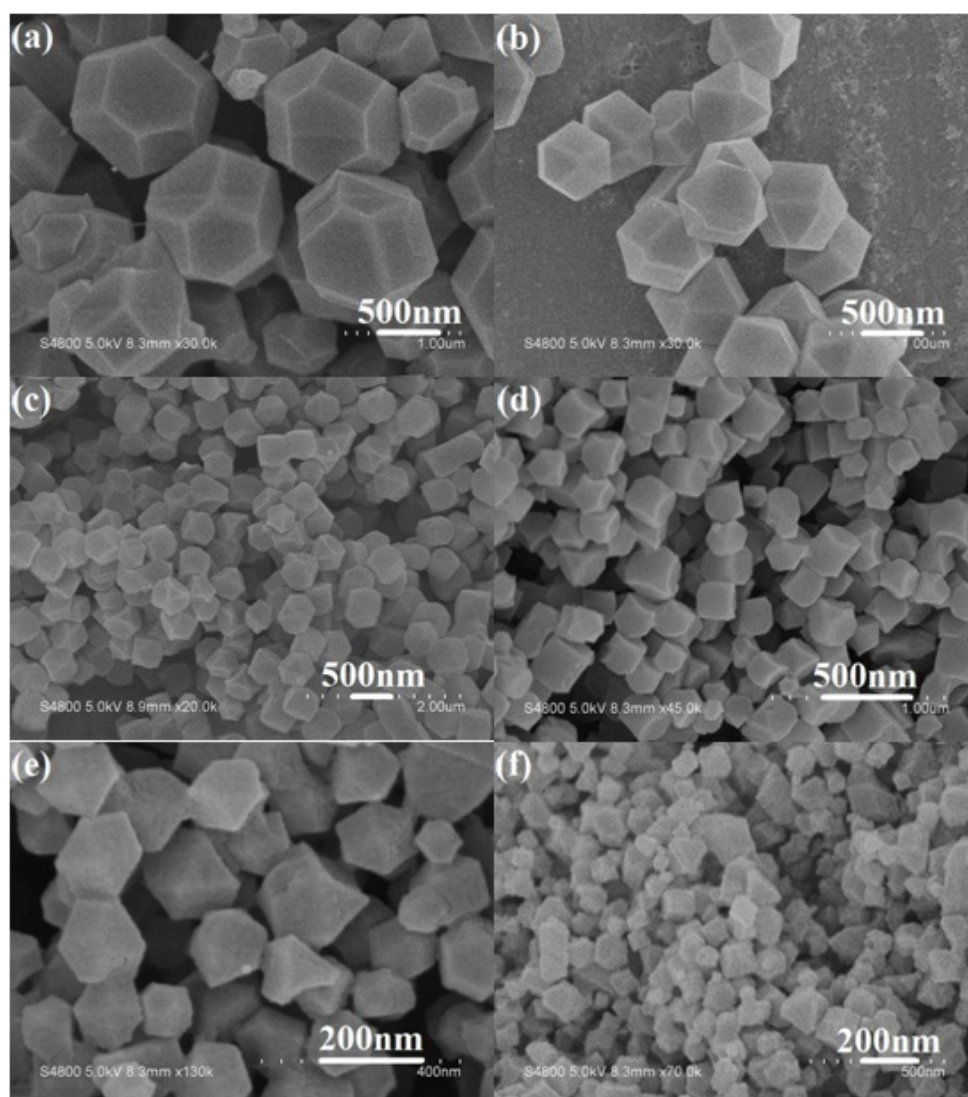


Fig. S3. SEM images of [Cu₃(btc)₂] samples prepared with different concentrations of Cu²⁺ when the concentration of CTAB is 0.005 M: (a) 0.1 mM; (b) 0.2 mM; (c) 0.3 mM; (d) 0.6 mM; (e) 1.2 mM and (f) 3 mM.

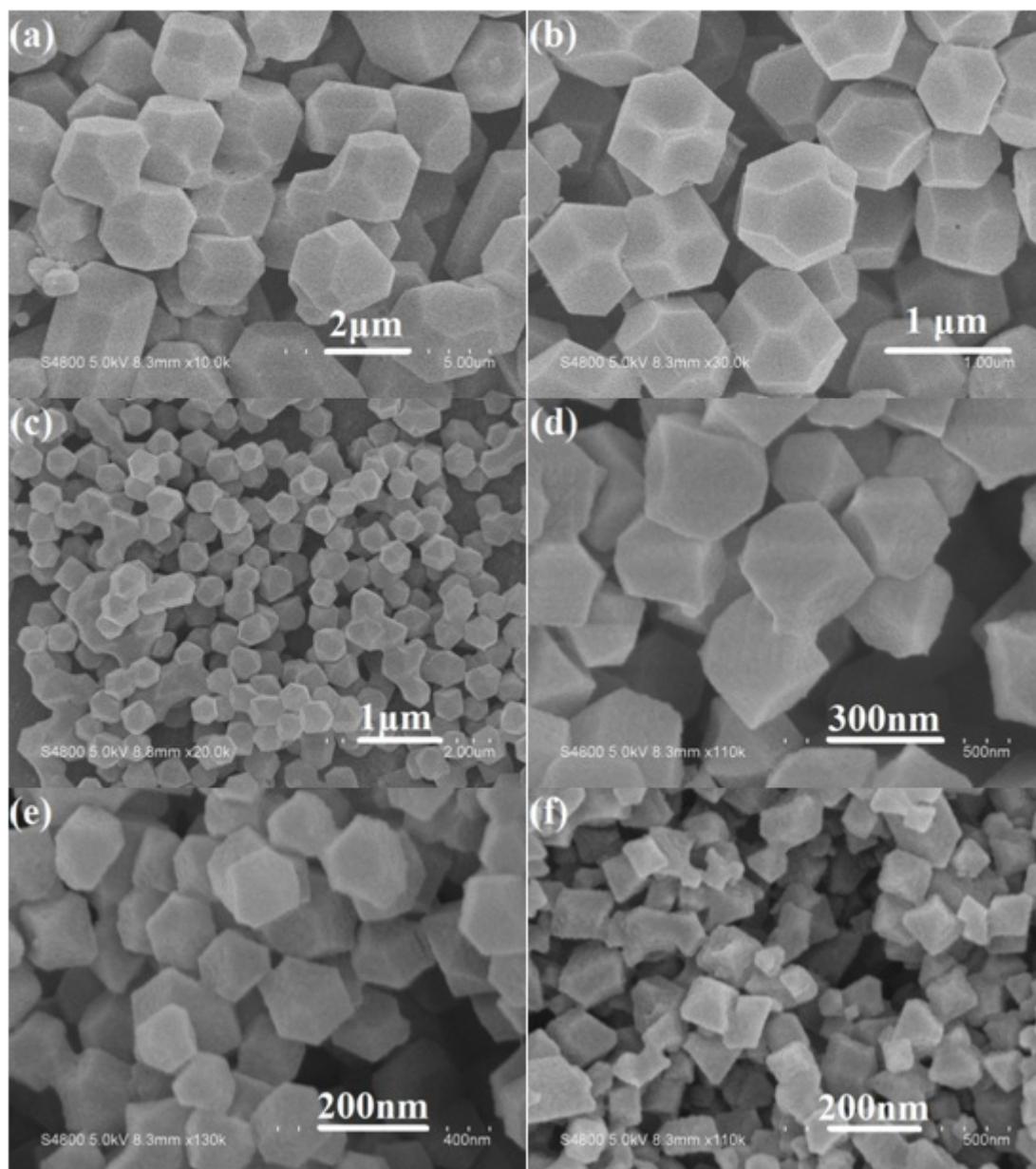


Fig. S4. SEM images of $[\text{Cu}_3(\text{btc})_2]$ samples prepared with different concentrations of Cu^{2+} when the concentration of CTAB is 0.01 M: (a) 0.1 mM; (b) 0.2 mM; (c) 0.3 mM; (d) 0.6 mM; (e) 1.2 mM and (f) 3 mM.

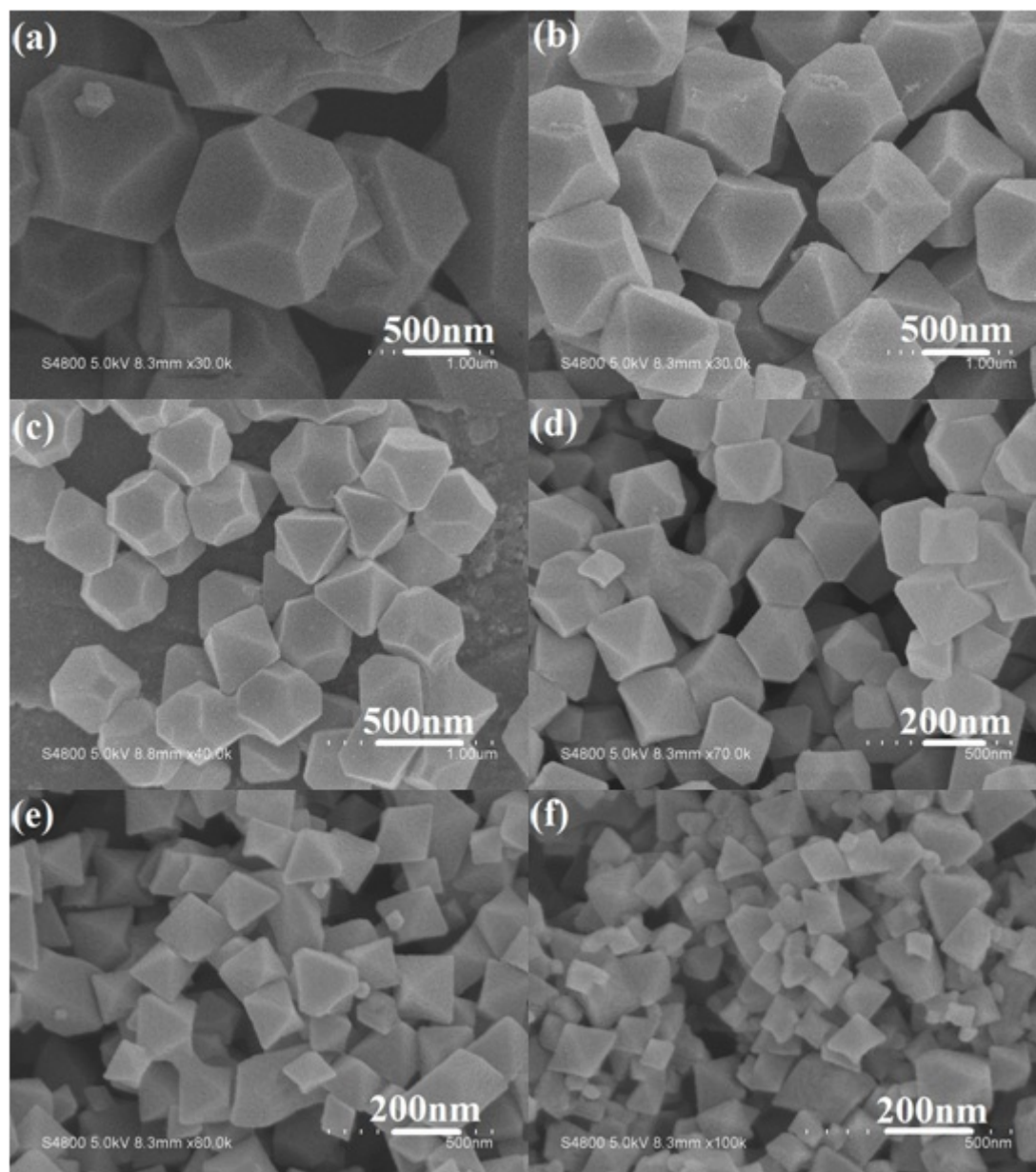


Fig. S5. SEM images of [Cu₃(btc)₂] samples prepared with different concentrations of Cu²⁺ when the concentration of CTAB is 0.05 M: (a) 0.1 mM; (b) 0.2 mM; (c) 0.3 mM; (d) 0.6 mM; (e) 1.2 mM and (f) 3 mM.

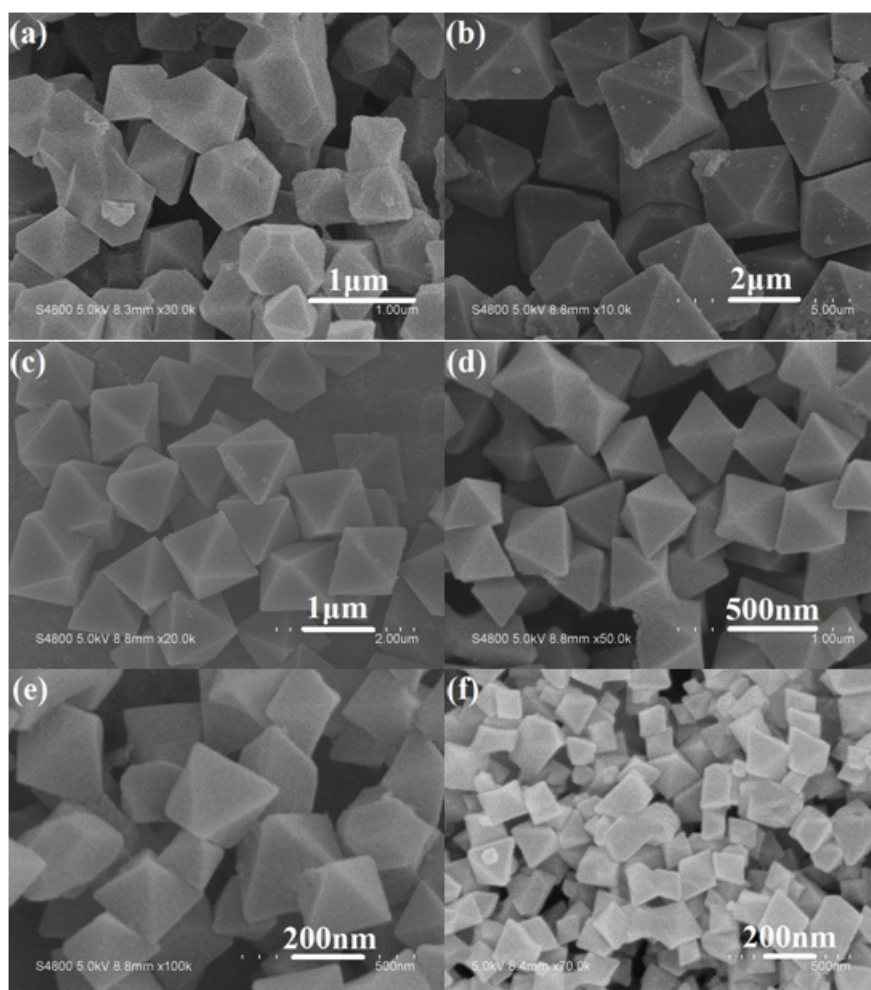


Fig. 6. SEM images of [Cu₃(btc)₂] samples prepared with different concentrations of Cu²⁺ when the concentration of CTAB is 0.1 M: (a) 0.1; (b) 0.2; (c) 0.3; (d) 0.6; (e) 1.2 and (f) 3 mM.

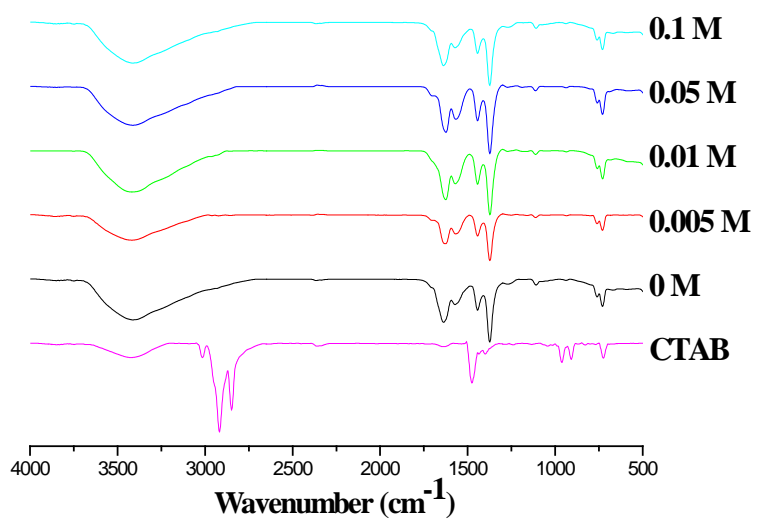


Fig. S7 IR spectra of CTAB and [Cu₃(btc)₂] samples prepared with different concentrations of CTAB.

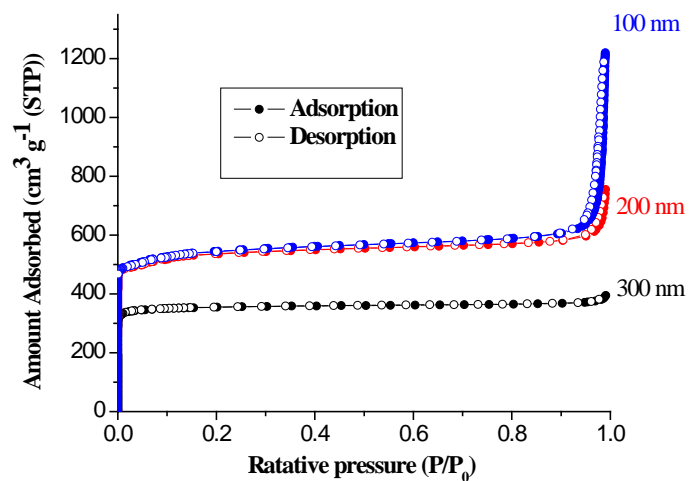


Fig. S8 Adsorption and desorption isotherms for nitrogen (at 77 K) of cubic samples with different sizes.