Electronic Supplementary Information

Investigation of Prototypal MOFs Consisting of Polyhedral Cages with Accessible Lewis-Acid Sites for Quinoline Synthesis

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Commercially available reagents were purchased in high purity from Fisher Scientific or Sigma Aldrich and used without further purification. The powder X-ray diffraction was performed on a Bruker D8 Advance, CuKα, λ = 1.54178 Å (40 kV, 40 mA). Temperature-programmed desorption of NH_3 (NH_3-TPD) was carried out on FINESORB-3010 equipped with a thermal conductivity detector. The samples were first outgassed under 373 K for 12 h before the measurement. After cooling to 298 K, the samples were saturated in an NH_3 stream (5% in Ar) for 30 minutes and consequently treated in Ar (30 mL/min) for 1 h for removing physisorbed NH_3. Finally, the TPD profile was determined by increasing temperature from 298 K to 523 K with ramping rate of 10 K/min while recording NH_3 desorption with a thermal conductivity detector.

MOF Synthesis

HKUST-1,[1] MOF-505[2] and MMCF-2[3] were prepared using the procedures reported in the literature. The phase purity was confirmed by the powder X-ray diffraction, illustrated in Fig. S1-S3.

Catalysis experiments

The Friedlander condensation reaction was conducted in a 5 mL round bottom flask equipped with a condenser and a magnetic stirrer at a stirring rate of 120 r/min. In a typical procedure, 2-aminoaryl ketones (1mmol), ketone compounds (2 mL) were added into the flask with loading catalyst (0.01mmol on basis of $Cu_2(CO_2)_4$ unit, MOF-505, 6.7 mg; HKUST-1, 6.3 mg and MMCF-2, 17.1 mg) and the resulting mixture was stirred at 358 K for 24 hours. The products were monitored by GC-MS (HP-5MS column, 5% phenyl methyl siloxane, 30 m × 0.25 mm × 0.25 μm; injector temperature 250 °C). All products were identified by the comparison of GC retention times and mass spectra with those of the authentic samples.

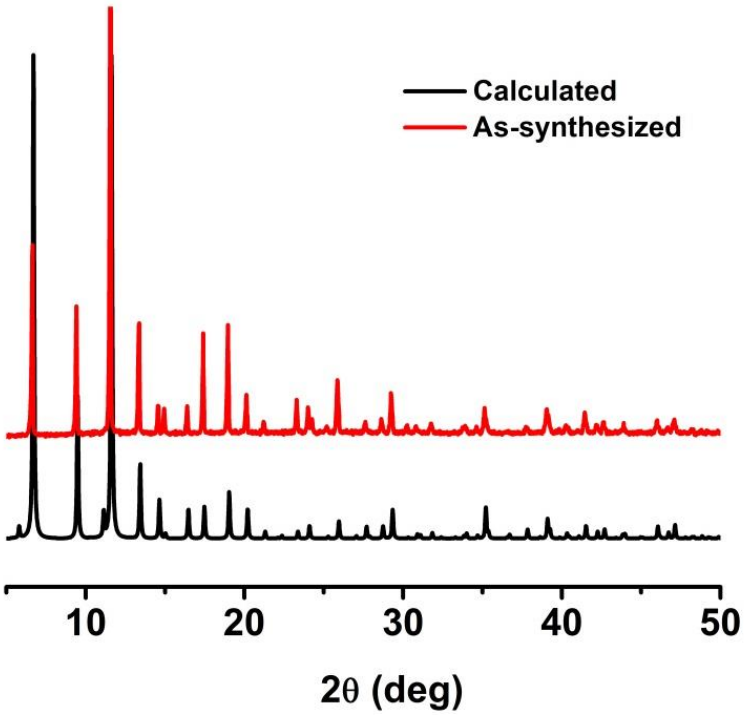

Fig. S1. Powder X-ray diffraction patterns of HKUST-1.

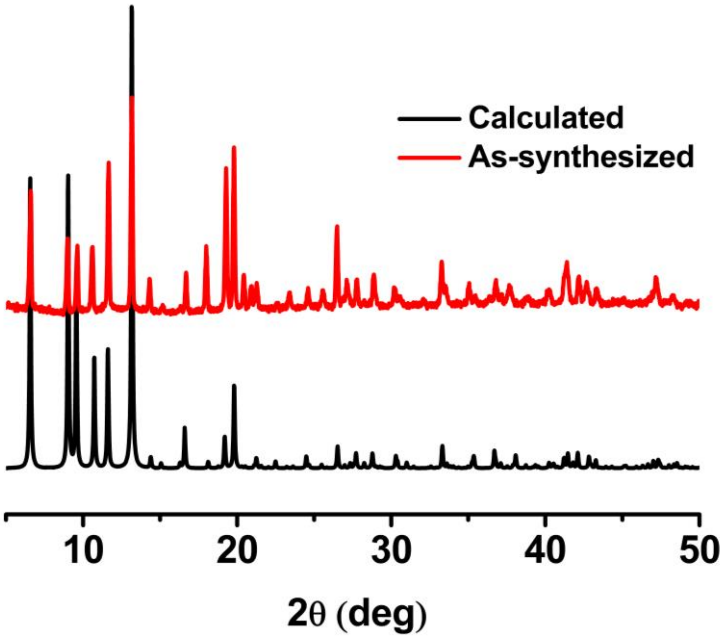

Fig. S2. Powder X-ray diffraction patterns of MOF-505.

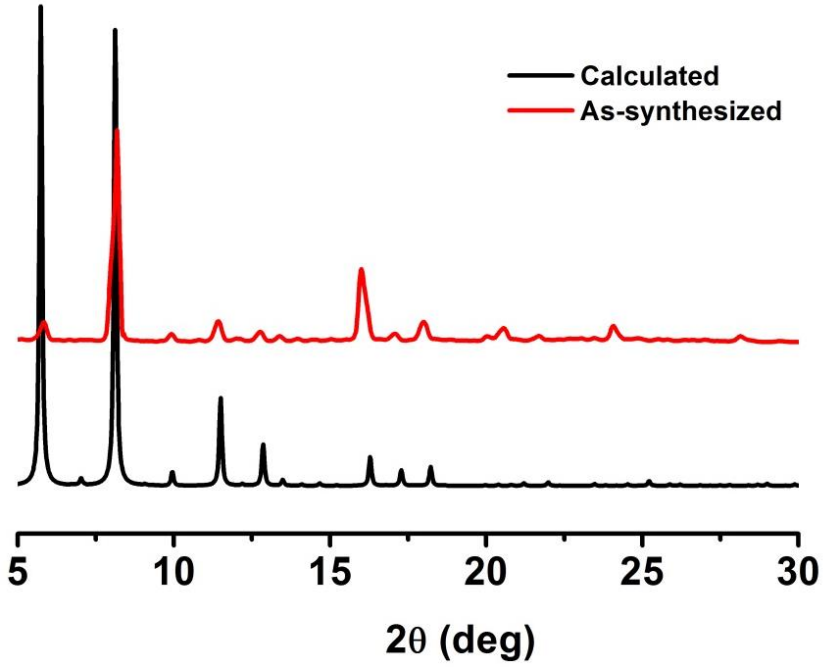

Fig. S3. Powder X-ray diffraction patterns of MMCF-2.

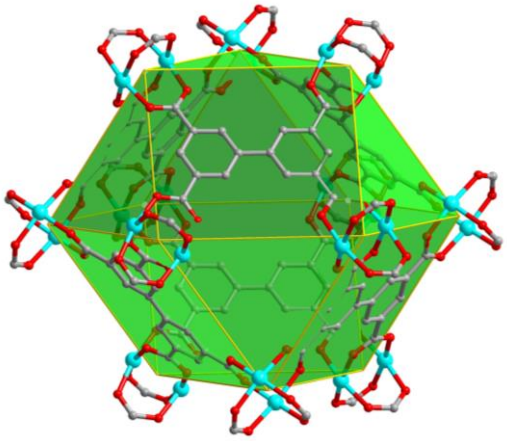

Fig. S4. The cuboctahedral cage in MOF-505.

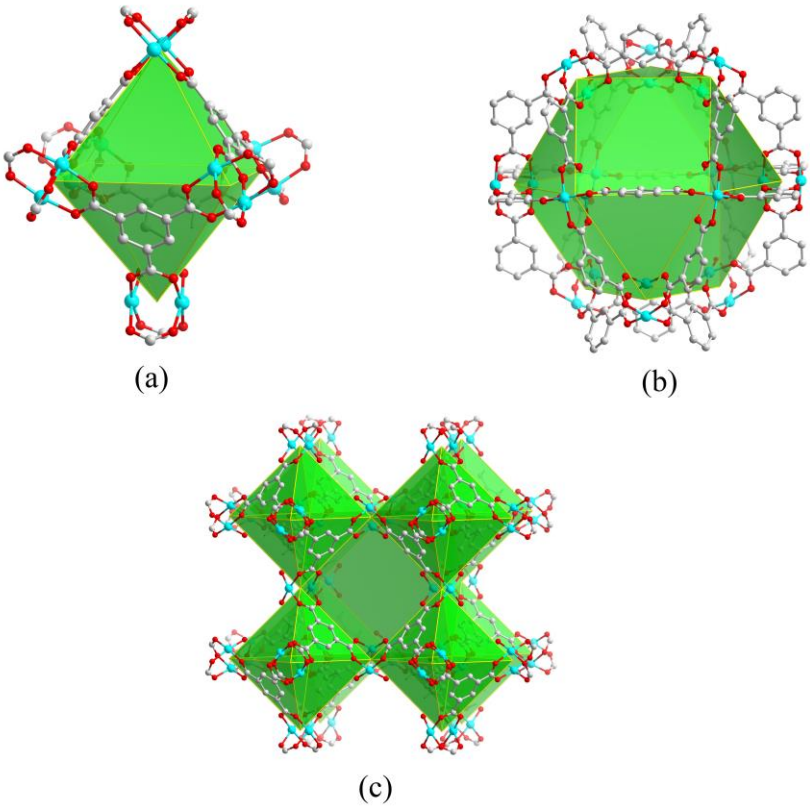

Fig. S5. Pictures of HKUST-1 (a) octahedral cage; (b) cuboctahedral cage; (c) close packing of polyhedral cages.

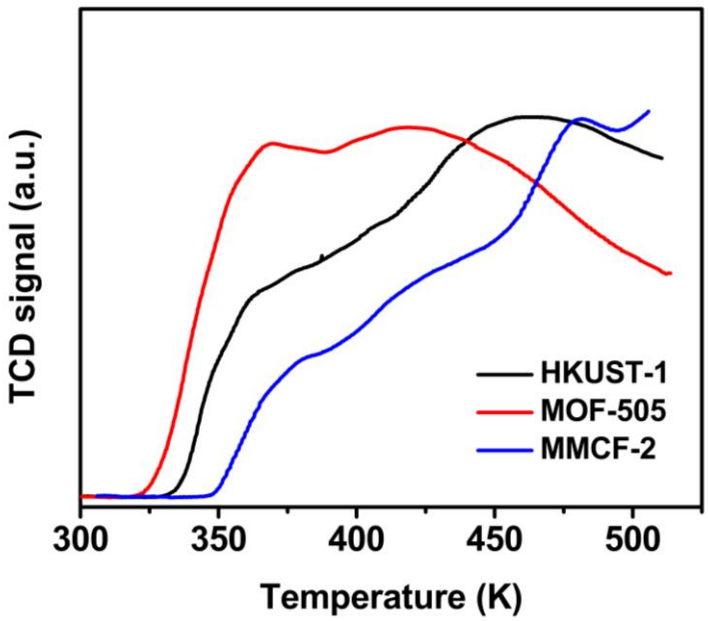

Fig. S6. NH_3-TPD profiles of HKUST-1, MOF-505 and MMCF-2 catalysts.

References.

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2. Chen, B.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. *Angew. Chem. Int. Ed.*, **2005**, *44*, 4745.
3. Gao, W.-Y.; Chen, Y.; Niu, Y.; Williams, K.; Cash, L.; Perez, P. J.; Wojtas, L.; Cai, J.; Chen, Y.-S.; Ma, S. *Angew. Chem. Int. Ed*., **2014**, *53*, 2615-2619.