Supporting Information

Ligand-oriented assembly of a porous metal-organic framework by $[Cu^{I}_4I_4]$ clusters and paddle-wheel $[Cu^{II}_2(COO)_4(H_2O)_2]$ subunits

Guoming Wang,[*a] Zhenzhen Xue,[a] Jie Pan,[a] Li Wei,[a] Songde Han,[a] Jinjie Qian[b] and Zonghua Wang[a]

[a] *College of Chemistry and Chemical Engineering, Collaborative Innovation Center for Marine Biomass Fiber Materials and Textiles, Qingdao University, Shandong 266071, P. R. China.*

[b] *College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, P. R. China.*

E-mail: *gmwang_pub@163.com*; Tel: +86-532-85957339

1.1. Materials and Instruments.

All chemicals purchased commercially were used as received without further purification. Powder X-ray diffraction (PXRD) measurements were recorded on a Philips X'Pert-MPD diffractometer with Cu-Kα_1 radiation (λ = 1.54076 Å). Element analyses for C, H, and N were performed with a Vario MICRO CHONS Element Analyzer. Thermogravimetric analyses were performed on a NETZSCH STA 449C instrument from room temperature to 800 °C under nitrogen flow. X-ray Photoelectron Spectroscopy (XPS) measurements were carried out using a Thermo Fisher ESCALAB 250Xi system. Single component low pressure gas adsorption measurements were performed using an ASAP (Accelerated Surface Area and Porosimetry) 2020 instrument.

1.2. Synthesis of $[(Cu^{I}_4I_4)Cu^{II}_4(pdc)_4(H_2O)_4]\cdot 4DMF$

CuI (38 mg, 0.2 mmol) and H_2pdc (17 mg, 0.1 mmol, H_2pdc = 3,5-pyridinedicarboxylic acid) were added to a screw cap vials, then 5 mL DMF was added to the mixture with a drop of HI (45 wt%). The content was heated at 80 °C for 1 day, giving green X-ray-quality crystals with the yield of 66% based on the ligand. Elemental analysis calcd (%) for $C_{40}H_{48}Cu_8I_4N_8O_{24}$: C 23.52, H 2.35, N 5.49; found: C 23.09, H 2.28, N 5.10. The SQUEEZE routine of the PLATON software suit was used to remove the highly disordered solvent molecules.

1.3. X-ray Crystallographic Study

Data collection was performed on a Rigaku XtaLAB mini CCD diffractometer equipped with graphitemonochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. The structure was resolved by direct methods and refined by full-matrix least-squares fitting on F^2 by *SHELX*-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically. The SQUEEZE process was used to remove the highly disordered solvent molecules. Crystallographic data and structure determination summaries are listed in Table S1. The CCDC number: 1498722.

Table S1 Crystal data and refinement details for the complex

Complex	$[(Cu^{I}_4I_4)Cu^{II}_4(pdc)_4(H_2O)_4]\cdot 4DMF$
Empirical formula	$C_{40}H_{48}Cu_8I_4N_8O_{24}$
Formula weight	2040.83
Crystal system	Tetragonal
Space group	*P4/nmm*
a (Å)	19.3577 (13)
b (Å)	19.3577 (13)
c (Å)	11.0242 (15)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	4131.0 (7)
Z	2
Dc (g/cm^3)	1.406
μ (mm^{-1})	3.555
θ range (°)	3.33–27.57
h, k, l, ranges	–25 to 25, –25 to 25, –14 to 14
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0700, 0.2075
GOF on F^2	1.012

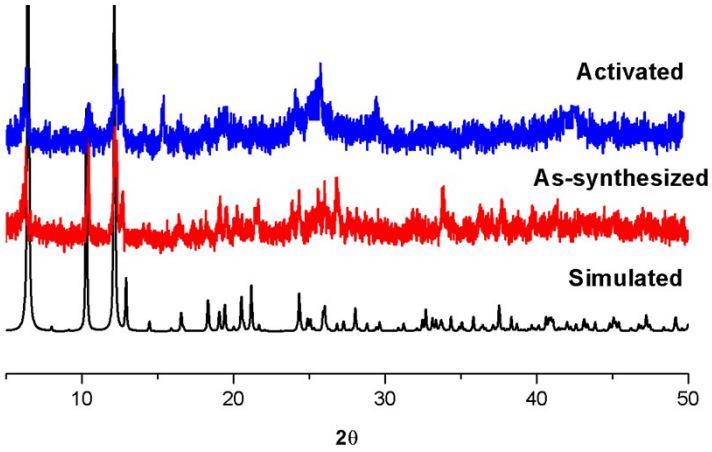

Figure S1 PXRD patterns of simulated from the single-crystal data (black); as-synthesized (red); activated solid (blue).

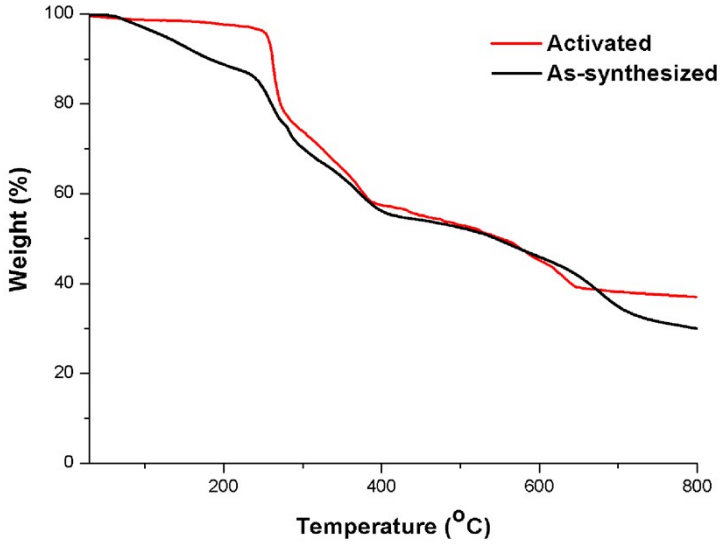

Figure S2 TGA curves for the as-synthesized and activated samples.

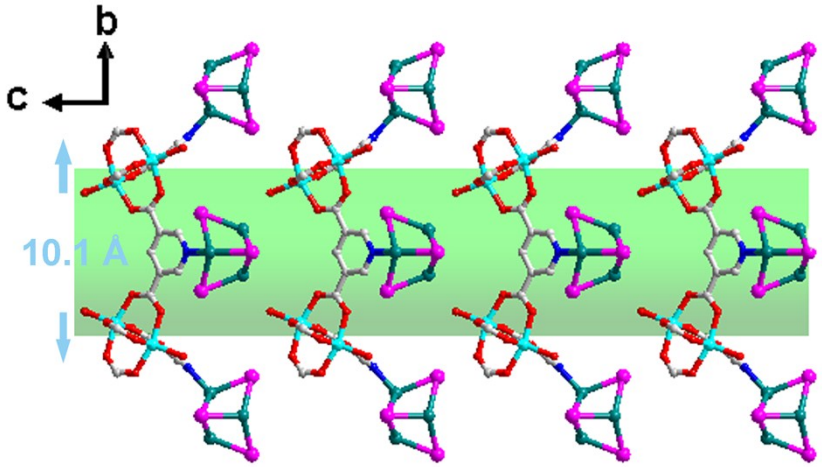

Figure S3 The 1D channel viewed along the a-aixs.

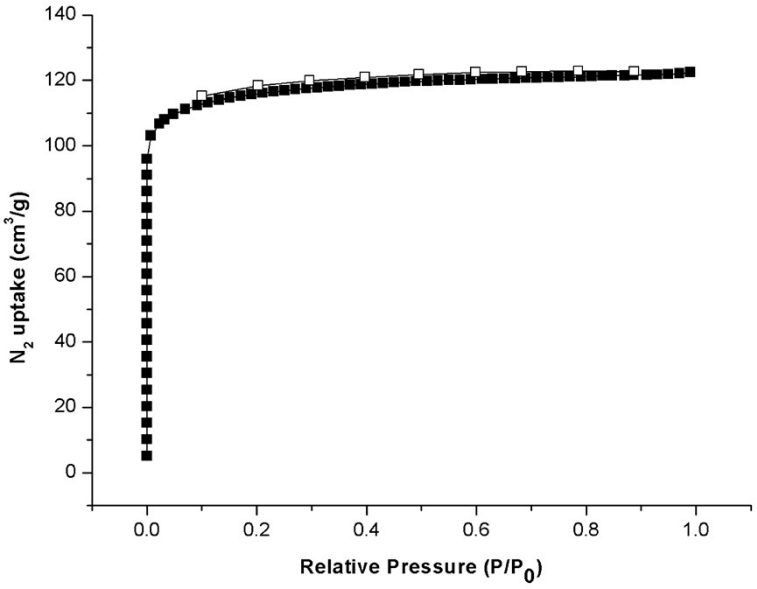

Figure S4 N_2 sorption isotherms at 77K (■, adsorption; □, desorption).