

Supporting Information

Cu(I)Cu(II)BTC, a microporous mixed-valence MOF via reduction of HKUST-1

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Experimental Details:

Chemicals and Reagents

1,3,5-Benzenetricarboxylic acid (BTC, 95%), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, absolute ethanol, methanol, and all the solvents were purchased from Sigma-Aldrich and used as received.

Preparation of HKUST-1 ($\text{Cu}_3(\text{BTC})_2$)

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (146 mg, 0.6 mmol) and BTC (280 mg, 1.3 mmol) were mixed together in a 1 : 1 ethanol– H_2O solution (4 cm^3), in a small glass vial which was fitted into a Teflon liner within a bomb (Parr Teflon Lined Acid Digestion Vessels, general purpose bomb with safety blow protection, purchased from Scientific & Medical Products Ltd). The resulting cloudy blue solution was heated in a sealed autoclave at 120 °C, under autogenous pressure, for 16 h. Once cooled, the turquoise materials were washed with fresh ethanol and left to dry in fume cupboard under ambient conditions to yield blue powders.

Hydrothermal reduction of HKUST-1

Preformed HKUST-1 (20 mg), water (2 cm^3) and hydroquinone (200 mg) were mixed together in a small glass vessel. Once the hydroquinone was completely dissolved, the mixture was heated in a sealed autoclave at 150 °C under autogenous pressure for 16 h. After the autoclave had cooled to room temperature, the resulting material was collected and washed with fresh methanol. The crystals were dried at room temperature for 24 h in a fume cupboard, resulting in dark green particles. The yields of the Cu(I,II)-MOF were ~ 50%. A time study on the reaction at 0.5, 1, 3, 5, 10, 16 hours was carried out by stopping the reaction at the designated time. After the autoclave was cool, 250 μl of the liquid solution was taken out and centrifuged at 3000 rpm for 1 minute to remove any suspended solids. The yield of the dry solid at reaction time 5 hours was close to 100%. The sample solution was diluted with distilled water to 5 mL for inductively coupled plasma (ICP) analysis.

Characterization

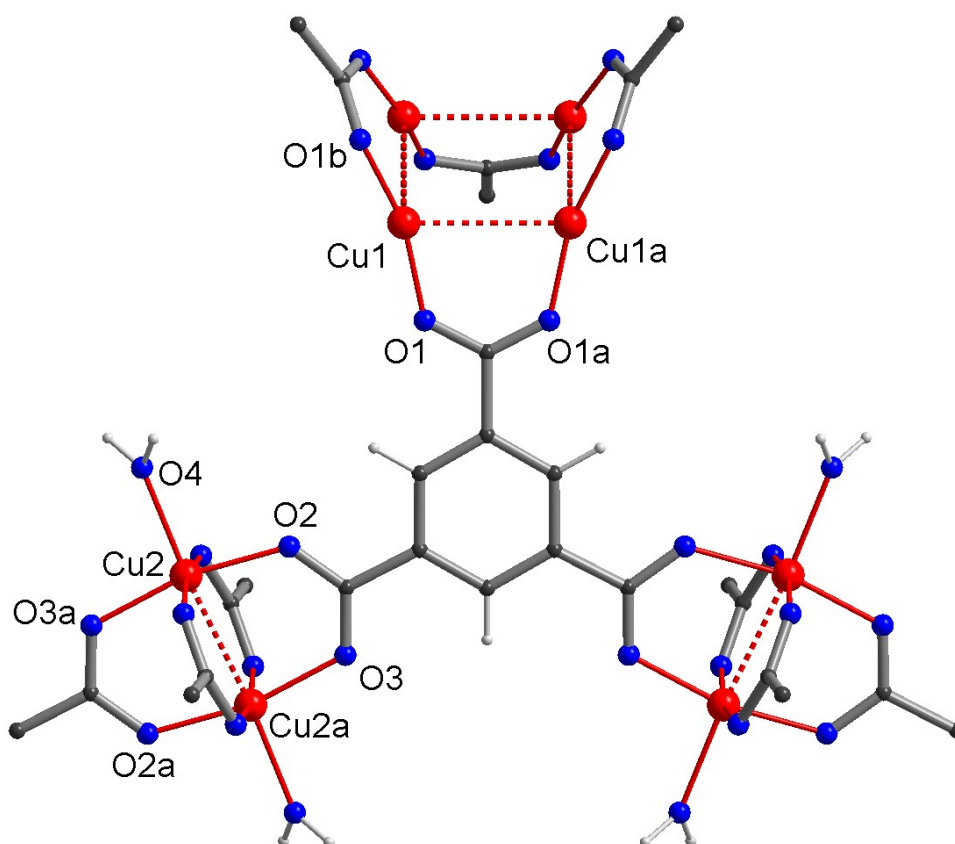
The morphologies were observed using a Hitachi S-4800 scanning electron microscope (SEM). The samples were coated with gold using a sputter-coater (EMITECH K550X) for 2 min at 25 mA before imaging. The Brunauer–Emmett–Teller (BET) surface area and pore size by N_2 sorption at 77 K were measured using a Micromeritics ASAP 2420 adsorption analyzer. The micropore size distributions were calculated by the non-local density functional theory (NLDFIT) method using the model of cylindrical pores in pillared clay (regularization values 0.2). Samples were degassed for 10 h at 120 °C before N_2 sorption analysis. Powder X-ray diffraction (PXRD) data were collected using a Panalytical X'Pert Pro Multi-Purpose Diffractometer in high-throughput transmission geometry. The Cu anode was operated at 40 kV and 40 mA. Samples were pressed into the well of an aluminium plate. The PXRD patterns were collected over the range of 2θ 5° – 30°. Thermal stability of the powder was investigated by thermal gravimetric analysis (TGA, Model Q5000IR TGA, TA Instruments).

The concentrations of Cu ions in the reaction solutions at different reaction times were determined using a Spectro Ciros Charged Coupled Device by ICP-Optical Emission Spectrometry-Side on Plasma.

XPS measurements were performed in a standard ultrahigh vacuum (UHV) chamber operating at a base pressure of less than 2×10^{-10} mbar with hydrogen as the main residual gas and consisting of a PSP Vacuum Technology electron energy analyser and a Mg K_{α} X-ray source ($h\nu=1253.6$ eV) operating at 144 W. The spectrometer was calibrated using the standard Ag $3d_{5/2}$ peak at 368.3 eV and charge correction was performed using the adventitious carbon peak at 284.8 eV.

Crystal data and structure refinement

Crystal data of **1** were collected on a Bruker D8 Venture diffractometer using Mo K_{α} radiation ($\lambda = 0.71073$ Å). The crystal structure was refined with SHELX by full-matrix least squares against F^2 using all data.^[S1] All non-hydrogen atoms were refined anisotropically. H-atoms were refined isotropically. H-atoms of channel bound water molecules could not be located in difference maps and were therefore omitted from refinement. $C_9H_5Cu_2O_7 \cdot 2H_2O$, $M_r = 388.24$, $T = 100$ K, Tetragonal space group $P4/nmm$, $a = 19.2100(5)$, $c = 6.9158(2)$ Å, $V = 2552.10(10)$ Å³, $Z = 8$, $\rho = 2.021$ g cm⁻³, $2\theta_{max} = 55^\circ$, 1626 unique reflections, $R_{int} = 0.048$, $R1 (I > 2\sigma(I)) = 0.040$, $wR2$ (all data) = 0.105.



The figure above shows selected bond lengths (Å) and angles (°) of crystal structure of 1:
Cu1-O1 1.832(3), Cu1-Cu1a 2.972(12), Cu2-O2 1.951(3), Cu2-O3a 1.956(3), Cu2 O4
2.150(3), Cu2-Cu2a 2.6189(11), O1-Cu1-O1b 161.80(18), O2-Cu2-O3a 167.77(11), O4 Cu2
Cu2a 172.64(11).

[S1] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

Table S1 Cu ion concentration in the reaction solution during the course of the HKUST-1 modification reaction as measured by ICP analysis

	Sampling at reaction time (hours)	Cu ion concentration (ppm)
Hydrothermal modification of HKUST-1 with water and hydroquinone	0.5	20
	1	72
	3	162
	5	185
	10	196
	16	203

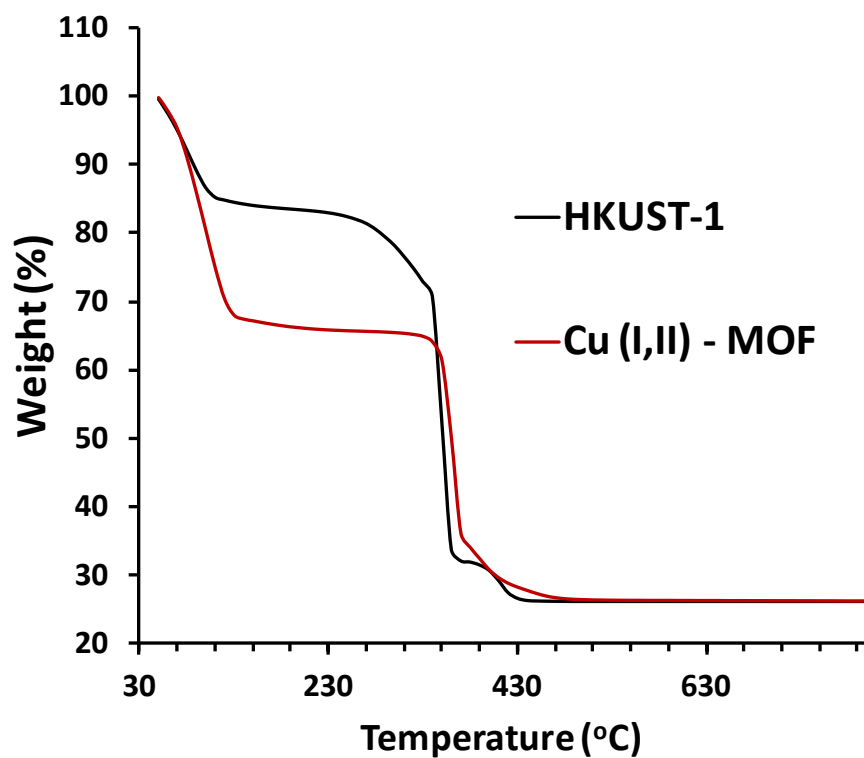


Fig. S1. TGA curves of the synthesized HKUST-1 and the Cu(I,II)-MOF (**1**).

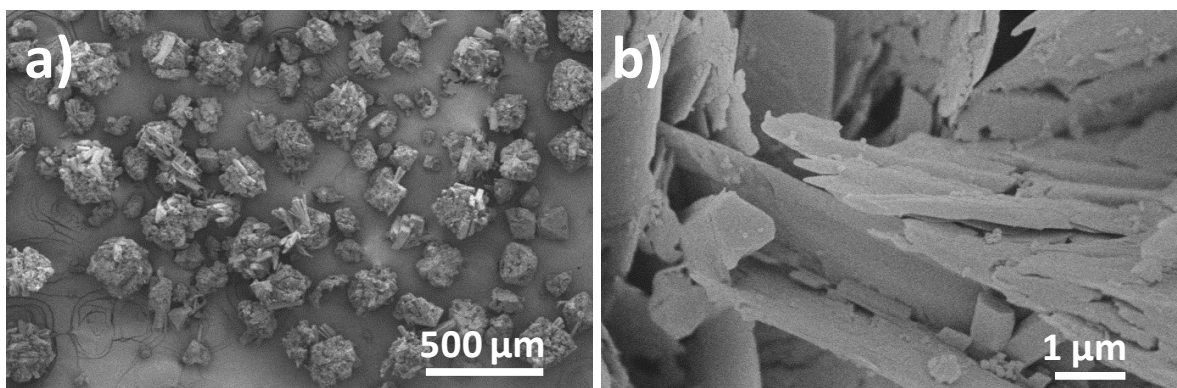


Fig. S2. SEM images show the morphology of the Cu(I,II)-MOF (**1**).