Supporting Information

A [(M₂)₆L₈] metal–organic polyhedron with high CO₂ uptake and chemical fixation of CO₂ under ambient conditions

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I. Materials and general methods

All chemicals for synthesis were commercially available reagents of analytical grade and were used without further purification. Crystallographic data of Cu-MOP were collected at 200 K with a SuperNova diffractometer equipped with Cu-Kα radiation (λ = 0.71073 Å) and graphite monochromator using the ω-scan mode. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using SHELXT-2018/2 (L).[1] The contribution of heavily disordered solvent molecules was treated as diffuse using the SQUEEZE routine of PLATON[2] and refined further using the data generated. The contents of guest molecules are not represented in the unit cell contents for the crystal data. Crystallographic data and experimental details for structural analyses are summarized in **Table S1**. In the crystal data of Cu-MOP, ca. 17 guest DMF molecules and 8 lattice water molecules were highly disordered, and attempts to locate and refine the peaks were unsuccessful. The diffused electron densities resulting from these residual molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated. The guest DMF and water molecules are not represented in the unit cell contents for the crystal data of Cu-MOP. The CCDC reference numbers 2132106 for Cu-MOP, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge form The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./data—request/cif. The FT-IR spectra were recorded from KBr pellets in the 4000-400 cm^{-1} range on a Nicolet 5DX spectrometer. Thermogravimetric analyses (TGA) were taken on a Perkin-Elmer Pyris l (25-800 °C, 5 °C min^{-1}, flowing N_2 (g)). Powder X-ray diffraction was recorded with a Bruker AXS D8 advanced automated diffractometer with Cu-Kα radiation. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed using Perkin Elmer, USA Optima 8000. The products of catalysis reaction were monitored by a SP-2100A Gas chromatograph (GC) equipped with a KB (Kromat-Bond) Series capillary column and a flame ionization detector. Pyridine adsorption fourier-transform infrared (Py-IR) spectra were collected on a PE FT-IR Frontier spectrometer.

II. Experimental Section

1. Synthesis of Cu-MOP

A mixture of H_3TCPT (8.2 mg, 0.017 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (8 mg, 0.033 mmol) were

dissolved in 1.5 mL mixed solvents of DMF (1.0 mL), CH_3CN (0.5 mL) and a drop of HBF_4 in a screw-capped vial. The resulting mixture was kept in an oven at 75 °C for 48 h. After cooling the vial to room temperature, the as-synthesized sample was purified through repeated washings with DMF to yield blue block-shaped crystals. Yield: 73 % (based on the crystal dried in vacuum). Anal. calcd. for $C_{210}H_{150}O_{84}N_{30}Cu_{12}$: C 48.50, H 2.91, N 8.08. Found: C 49.23, H 3.42, N 8.10. IR (KBr, cm^{-1}): 3414(s), 3074(m), 2933(m), 2620(w), 1648 (s),1571(s), 1490(m), 1386(s), 1210(s), 1125(s) , 905(m), 772(s), 692(m), 600(w).

2. Gas adsorption measurements

Gas adsorption-desorption experiments were carried out on a 3H-2000PS1 analyzer (Beishide Instrument Co., China). Before the gas adsorption analysis, Cu-MOP was soaked in dichloromethane until guest solvent, DMF, was exchanged totally. Then Cu-MOP was collected and heated at 60 °C under dynamic vacuum conditions for 10 h. The N_2 adsorption isotherm was measured at 77 K using a liquid N_2 bath. The CO_2 adsorption isotherms were measured at 195 K using a dry ice-acetone bath. The N_2 and CO_2 adsorption isotherms were measured at 283 and 298 K using a water bath. The N_2 and CO_2 adsorption isotherms were measured at 273 K using an ice-water bath.

3. Breakthrough measurements

Breakthrough experiments of Cu-MOP for CO_2/N_2 mixtures of 15/85 and 50/50 were purged into a packed column with a total inlet flow rate of 2.0 mL/min at 273 and 298 K.

4. General procedure for the cycloaddition of CO_2 and epoxides

Before the typical experiment, the catalysts were activated at 343 K for 12 h under vacuum to remove the residual solvent molecules in the cage of MOP. The reaction at room temperature and atmospheric pressure was performed in a 25 mL Schlenk tube using an epoxide (10 mmol) with CO_2 purged at 1 bar and 298 K under solvent free conditions. The catalyst loading was 0.01 mmol of Cu-MOP with the co-catalyst tetrabutylammonium bromide (TBAB, 0.46 mmol). After the mixture stirring for 48 h, the catalysts were separated by filtration and then the samples of the reaction mixture were analyzed by GC to determine the conversions. The catalyst system was quite versatile as a variety of epoxides could be converted to the corresponding cyclic carbonates in appropriate yields.

The used catalyst was collected by filtration, washed abundantly with DMF, and dried under at room temperature before reuse.

5. Leaching tests

Leaching tests were performed to verify the heterogeneous nature of the catalysts. The mixture of catalyst (0.01 mmol), PO (10.0 mmol), TBAB (0.46 mmol) and 0.1 MPa CO_2 was stirred at 25 °C. After 24 h, the catalysts were isolated from the mixture via filtration, then the remaining filtrate reacted with CO_2 (0.1 MPa) continually at 25 °C.
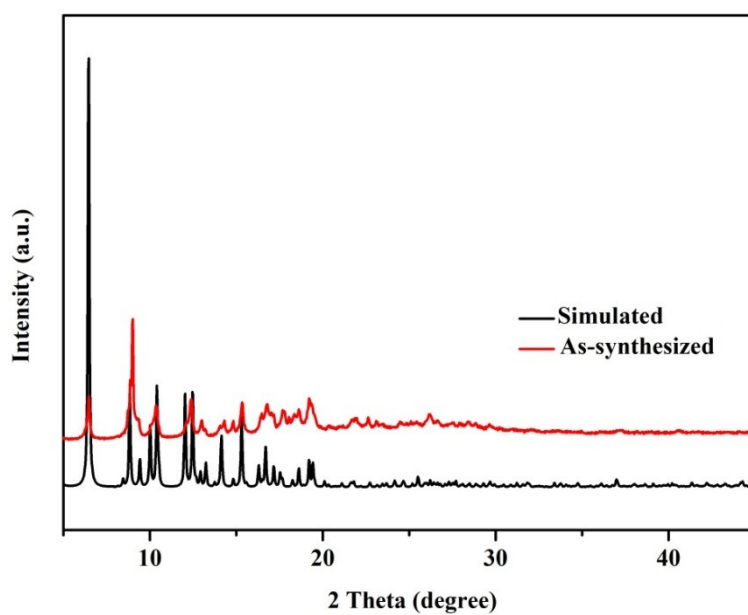
Fig. S1. The simulated and experimental PXRD patterns of Cu-MOP.
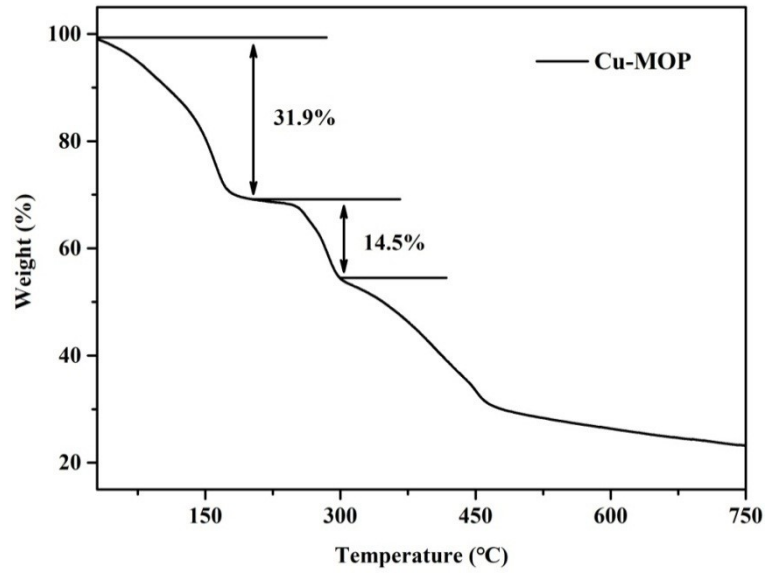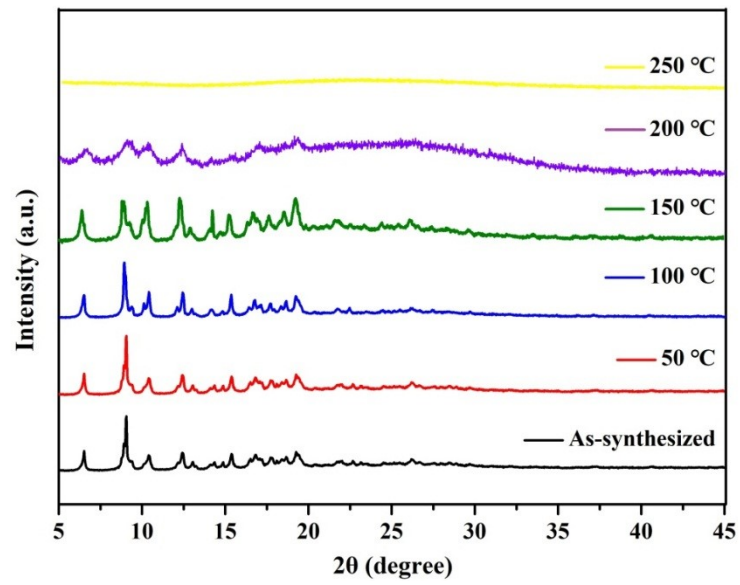
Fig. S2. The TG curve of Cu-MOP.

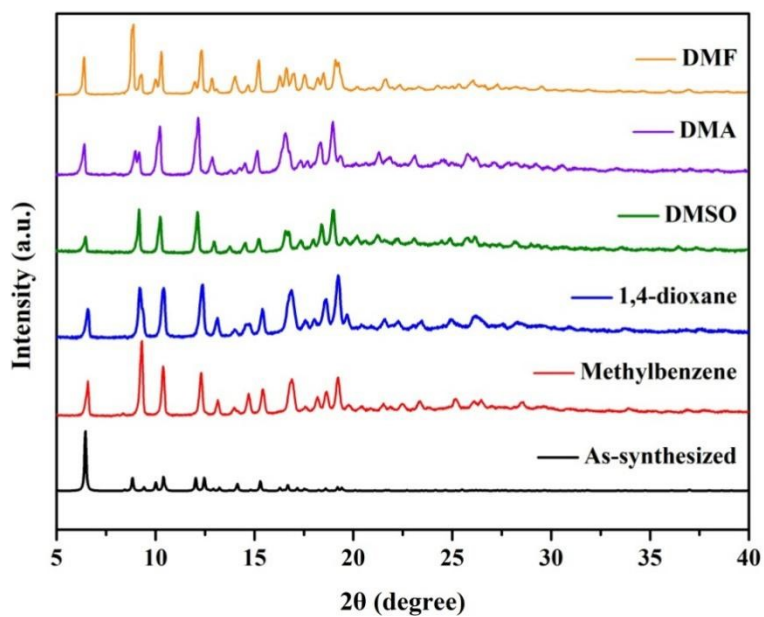**Fig. S3.** Thermal stability tests for Cu-MOP monitored by PXRD analysis at ambient conditions.

Fig. S4. PXRD patterns of Cu-MOP and the samples treated in various organic solvents for 24 h.
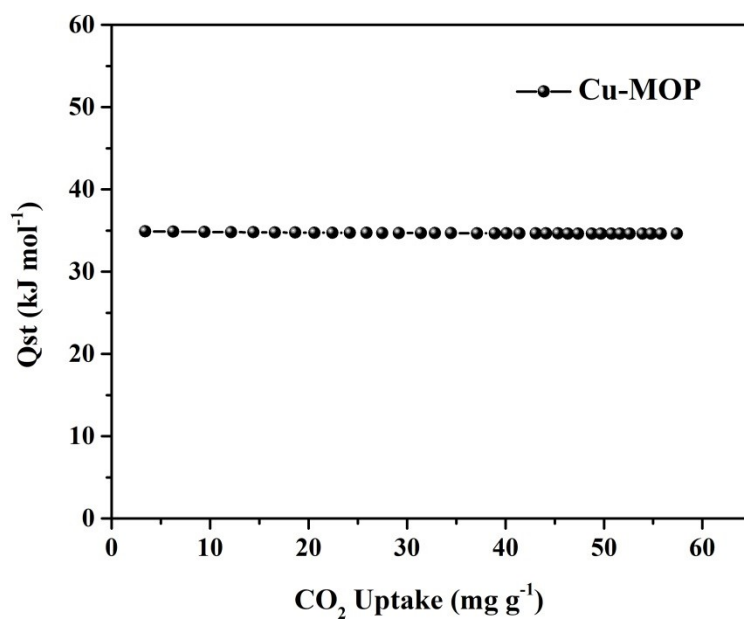

Fig. S5. Isosteric enthalpies of adsorption (Qst) for the Cu-MOP were calculated by the virial equation based on the isotherms collected at 273, 283, and 298 K.
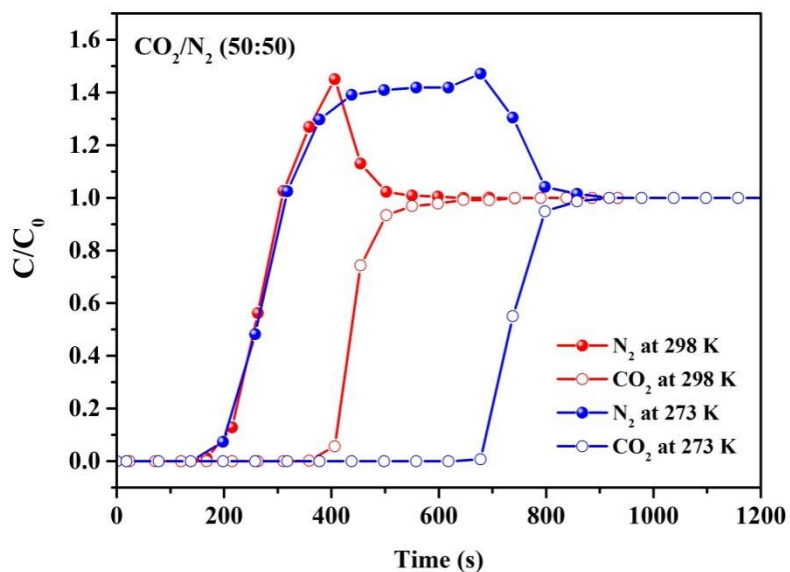
Fig. S6. Comparison of experimental breakthrough curves for a 50/50 CO_2/N_2 mixture at 273 K and 298 K in an adsorption column packed with Cu-MOP.
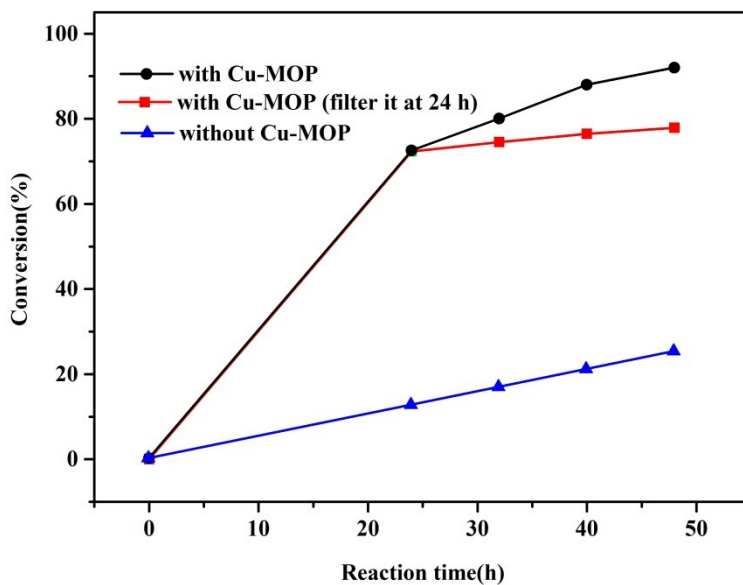

Fig. S7. Time-conversion plot for Catalyst leaching tests of the cycloaddition of CO_2 and PO catalyzed by Cu-MOP. The conversions are determined by GC.
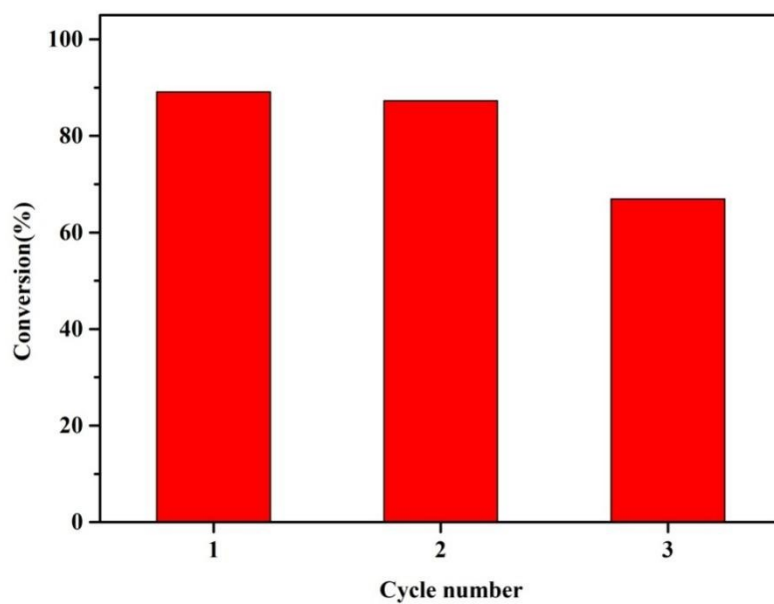
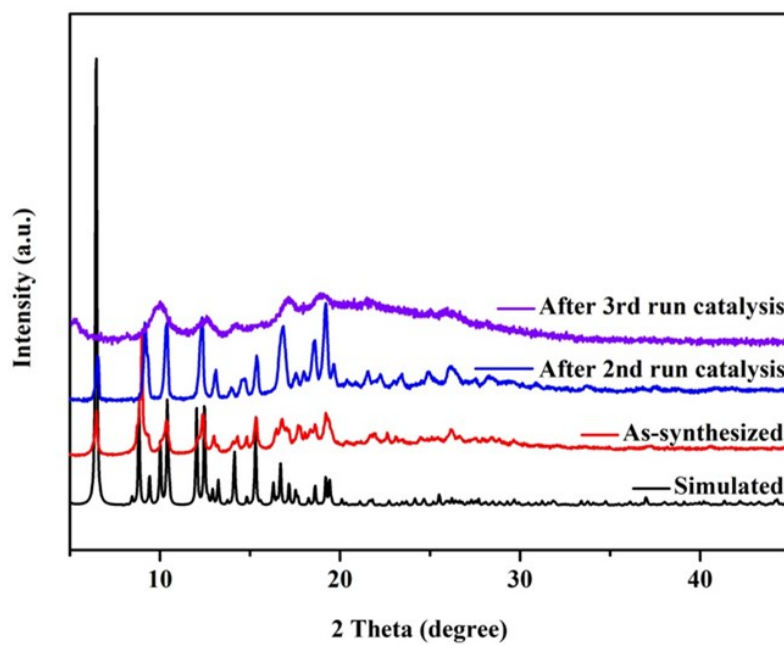**Fig. S8.** Recycle experiments of Cu-MOP for the cycloaddition of CO_2 and PO.

Fig. S9. PXRD patterns of Cu-MOP after 3 cycles of cycloaddition of CO_2 and PO.

Table S1 Crystal data and structure refinement for Cu-MOP

Compound	Cu-MOP
Empirical formula	C210H150Cu12N30O84
CCDC number	2132106
Formula weight	5200.07
Wavelength/ Å	0.71073
Crystal system	Trigonal
Space group	P-3c1
V/ Å^3	16274(10)
Unit cell imensions:	
a/ Å	21.671(6)
b/ Å	21.671(6)
c/ Å	40.013(13)
α/ o	90.000
β/ o	90.000
γ/ o	120.000
Z	2
Dc/mg m^{-3}	1.061
μ/ mm^{-1}	0.836
F(000)	5256
θ Range for data collection/^{o}	2.872-20.656
Reflections collected	10836
T/ K	200
Data/restraints/parameters	8265/75/1013
Final R indices[I> 2σ(I)]^a	R_1=0.0909, wR_2=0.1986
R indices(all data)	R_1=0.1107, wR_2=0.2159
Largest diff. peak and hole /e Å^{-3}	0.691,-0.563

^{a} $R_1 = \sum||F_o|-|F_C||/\sum|F_o|$; $wR_2 = \sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$

Table S2 Hydrogen-bond geometry data of Cu-MOP (Å, °).

D — H$\cdots A$	D — H	H$\cdots A$	$D\cdots A$	D — H$\cdots A$
C35 — H35C$\cdots$O5^i	0.98	2.55	3.496 (18)	162
C5 — H5$\cdots$N1^{ii}	0.95	2.57	3.402 (16)	146
C16 — H16$\cdots$O7^{iii}	0.95	2.53	3.396 (16)	153

Symmetry code: (i) 1+x-y, 1-y, 3/2-z; (ii) 1-x+y, 1-x, z; (iii) 1-y, x-y, z

Reference

[1] Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Crystallogr. C Cryst. Struct. Commun. 71, 3–8 (2015).

[2] Spek, A. L. PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. Acta Crystallogr. C Cryst. Struct. Commun. 71, 9–18 (2015).