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Electronic Supplementary Information

A Metal-Metalloporphyrin Framework based on an Octatopic Porphyrin Ligand for Chemical Fixation of CO_2 with Aziridines

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Experimental Section

The porphyrin ligand tetrakis-3,5-bis[(4-carboxy)phenyl]phenyl porphine (H_{10}tbcppp) was synthesized according to a previously reported procedure.[1] The synthesis of aziridines was based on the literature.[2]

1. Synthesis of MMPF-10

A mixture of tetrakis-3,5-bis[(4-carboxy)phenyl]phenyl porphine (H_{10}TBCPPP) (2.0 mg), $Cu(NO_3)_2 \cdot 2.5H_2O$ (5.0 mg) and N,N-Dimethylacetamide (DMAC) (0.8 mL) with 2 drops of HBF_4 (50% aqueous) was sealed in a vial and then heated at 65 °C or 5 days. Dark red block-shaped crystals were obtained as the final product (yield: 83 % based on H_{10}tbcppp).

2. Characterization

X-ray diffraction (XRD) was conducted on a Bruker D8 Advance X-ray diffractometer in a scanning range of 5~30°.

The N_2 adsorption isotherm data at 77 K was collected on the Micrometrics ASAP 2020. Before the measurement, the freshly prepared sample was exchanged with methanol for 3 days. Then the sample was activated under super critical CO_2, followed by degassing under vacuum at 80 °C for 6 h. The CO_2 adsorption isotherms were measured at 273K and 298K using an ice-water and water bath, respectively.

3. Catalysis experiments

In a typical procedure, the catalytic reaction was conducted in a Schlenk tube in which the aziridine (1 mmol) was added with CO_2 purged at 1 bar under a solvent-free environment at room temperature catalyzed by MMPF-10 (0.00625 mmol, 0.625 mol% calculated based on copper paddlewheel units) and tetrabutylammonium bromide (TBAB, 16 mg) as co-catalyst for 3 days. For the high pressure reaction, the substrate and catalysts are charged into the autoclave, followed by purging 2 MPa CO_2 into the autoclave and then put it in a 100 °C oil bath for 10 h. The products were monitored by ^1H NMR (Varian UnityInova400 spectrometer.) using 1,4-phthaladehyde as an internal standard. For the recyclability experiment, MMPF-10 was recovered and washed with DMF and methanol three times before being reused in the next reaction.

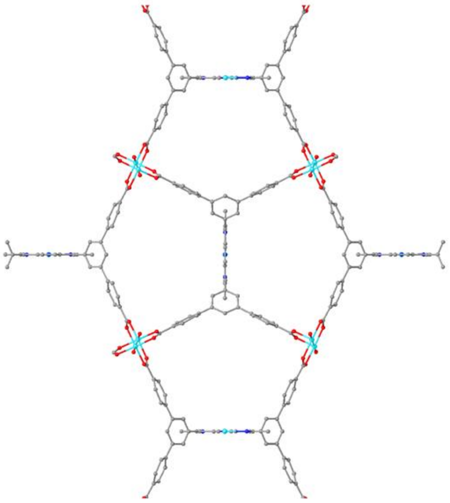


Fig. S1. The unit cell of MMPF-10 viewed along the *a*-axis.

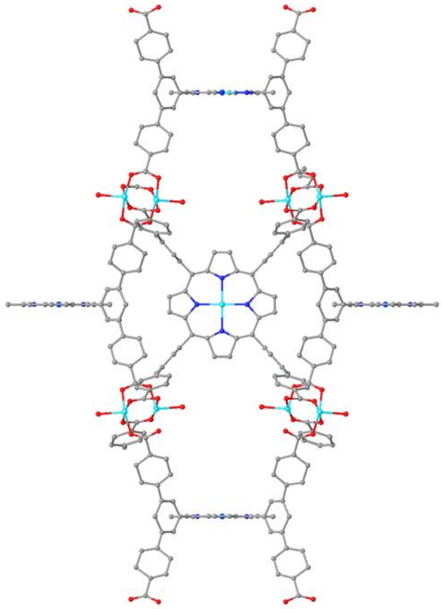


Fig. S2. The unit cell of MMPF-10 viewed along the *b*-axis.

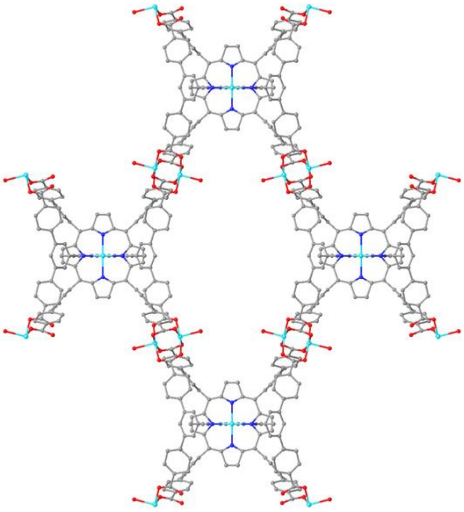


Fig. S3. The unit cell of MMPF-10 viewed along the *c*-axis.

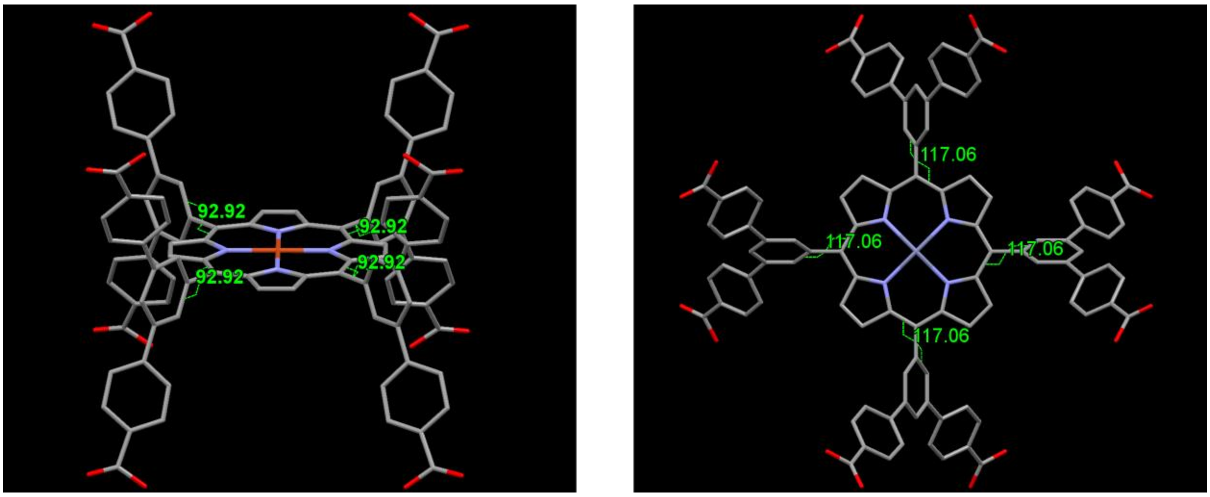


Fig. S4. The torsion angles between the porphyrin ring and its meso-substituent phenyl rings in MMPF-10 (left) and UNLFPF-1[1] (right).

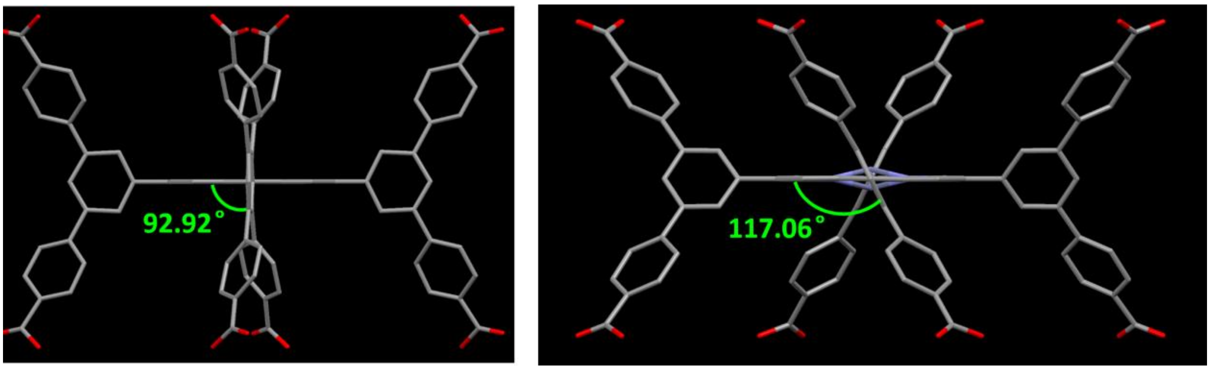


Fig. S5. The torsion angles between the porphyrin ring and its meso-substituent phenyl rings in MMPF-10 (left) and UNLFPF-1[1] (right) viewed parallel from the porphyrin plane.

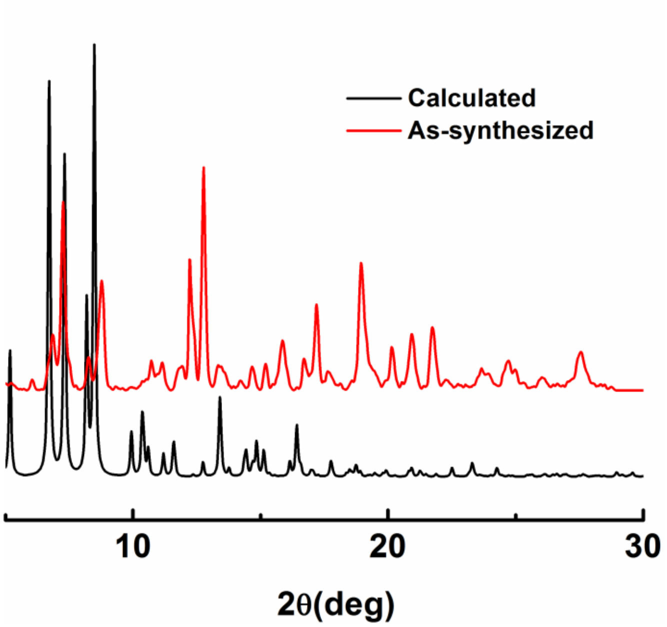


Fig. S6. Powder X-ray diffraction patterns of MMPF-10.

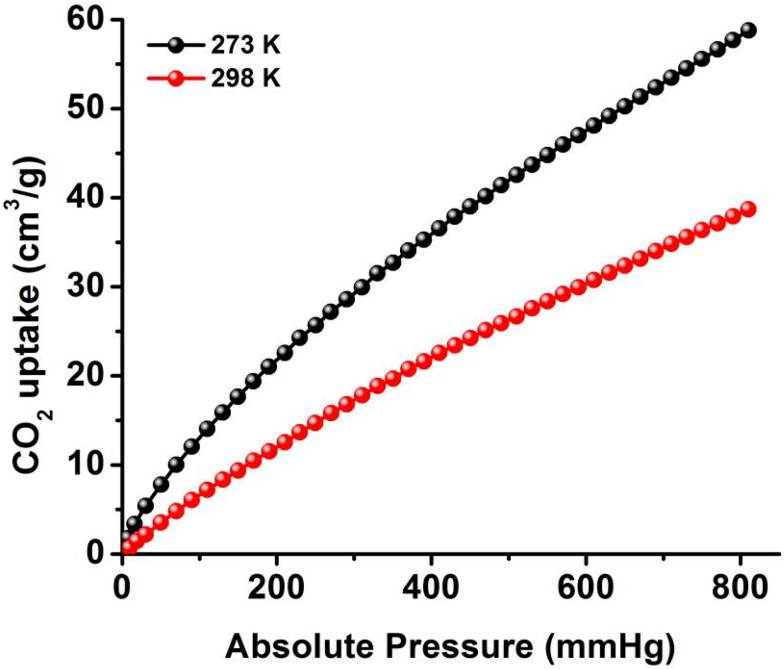


Fig. S7. CO_2 adsorption isotherms of MMPF-10 at 273 K and 298 K.

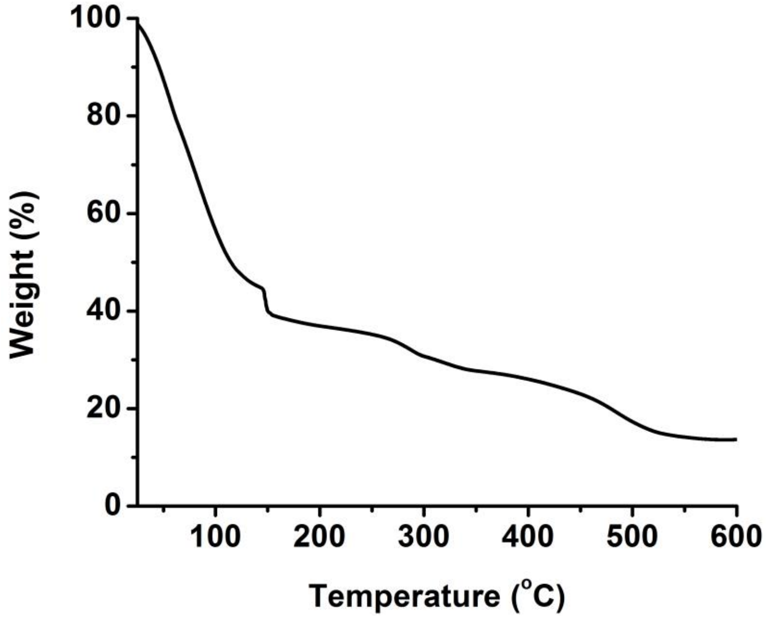


Fig. S8. Thermogravimetric analysis plot of MMPF-10.

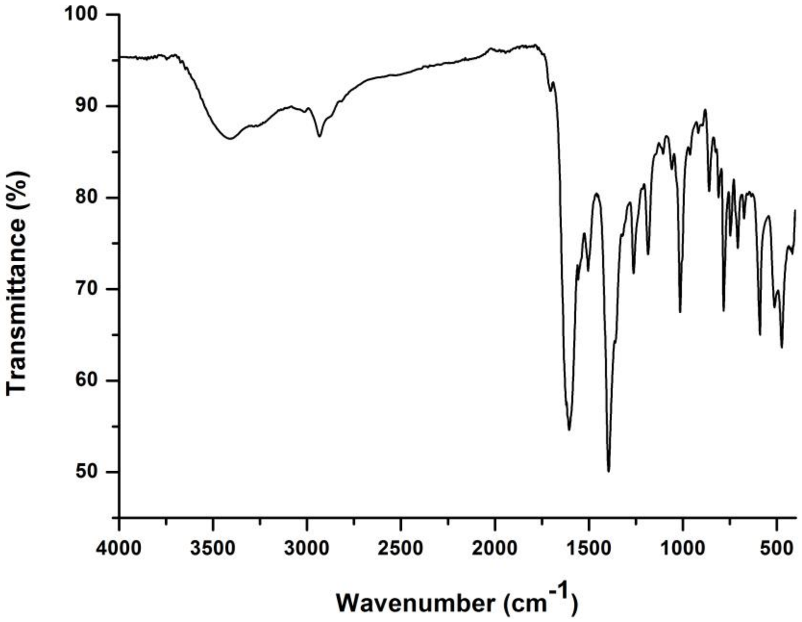


Fig. S9. FTIR spectra of MMPF-10.

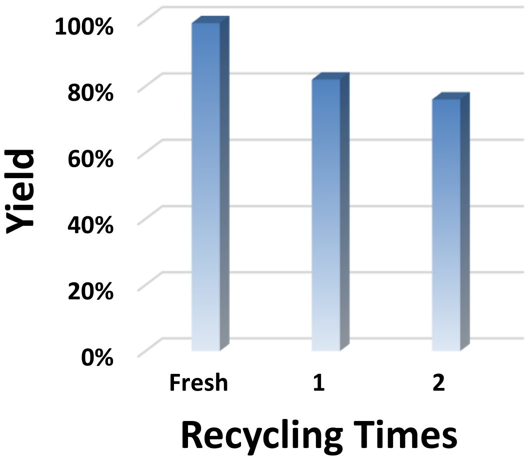
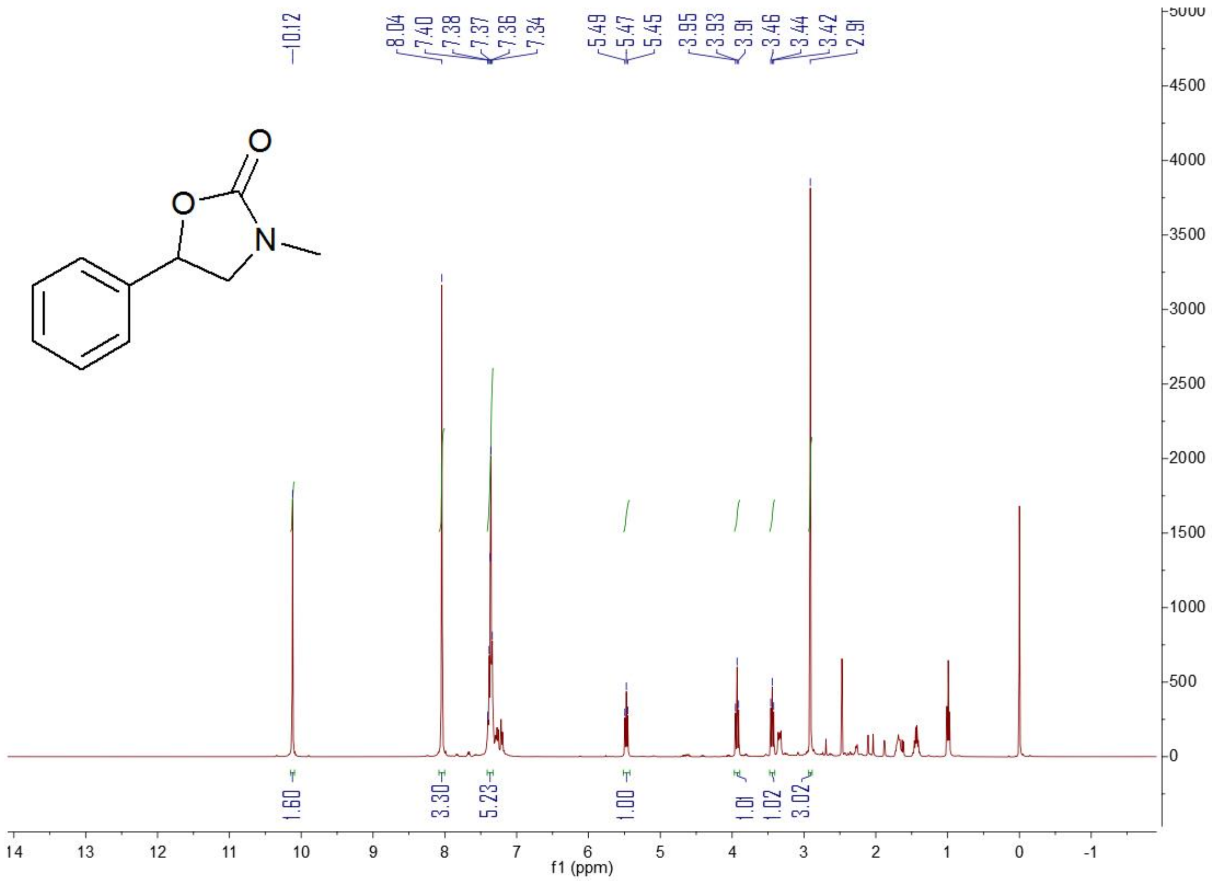
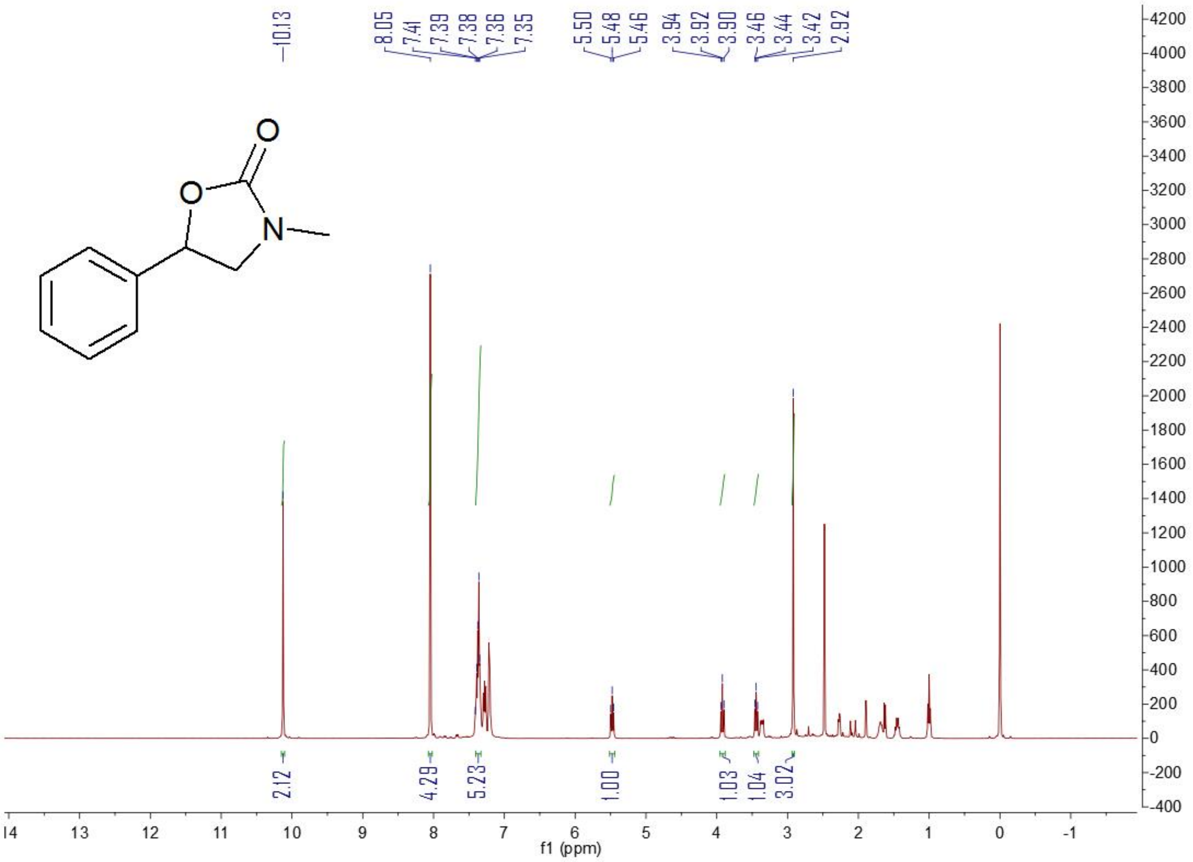


Fig. S10. Recyclability of MMPF-10 catalyst.

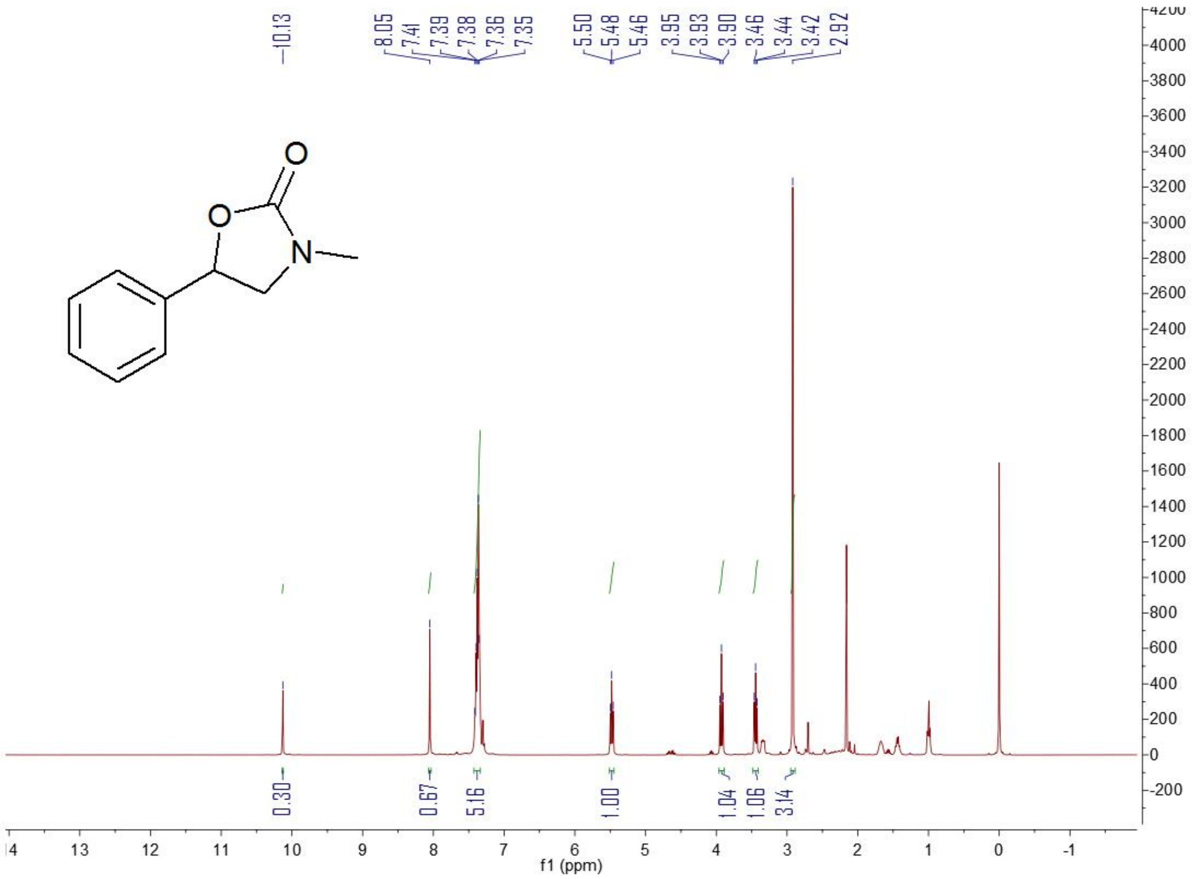
^{1}H NMR data of oxazolidinones after reactions (400 MHz, $CDCl_3$, 1,4-phthaladehyde as internal standard (δ 10.12 (2H), δ 8.04 (4H))



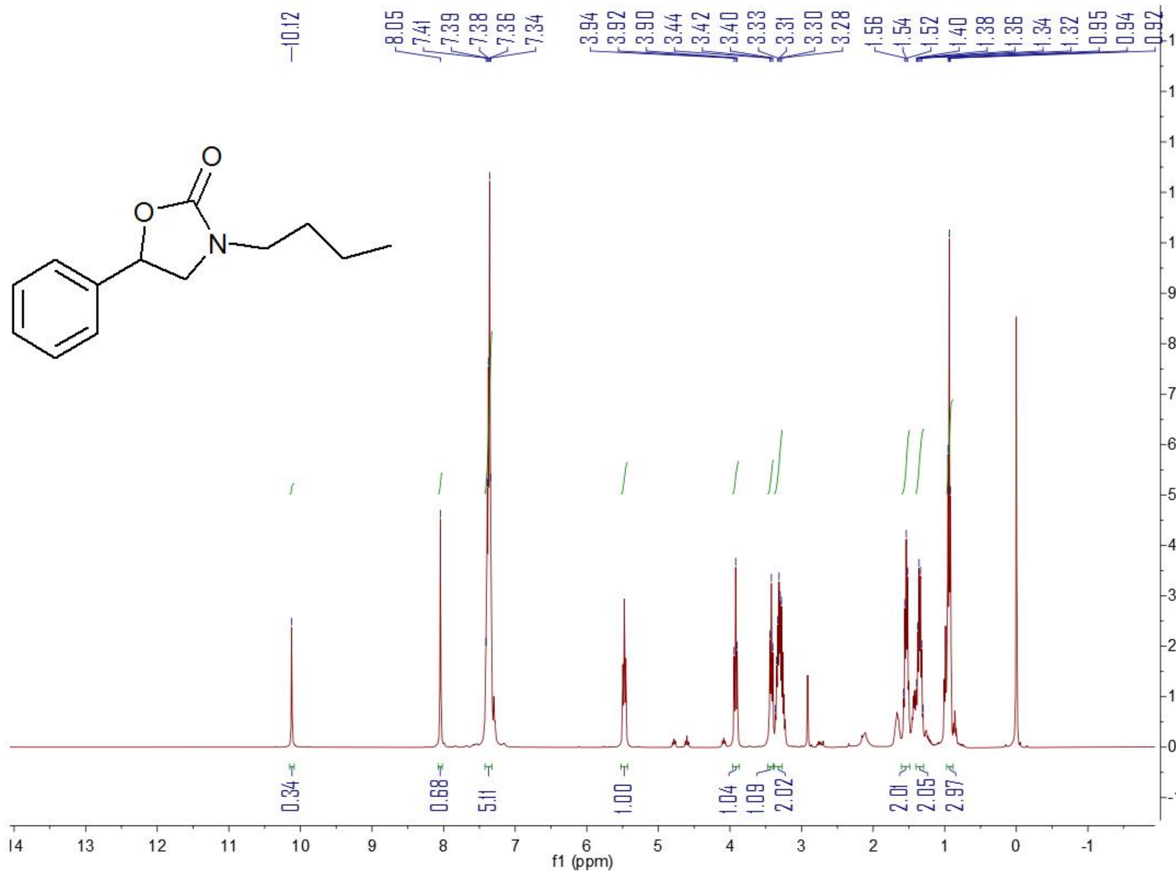
^{1}H NMR data of the resulting mixture containing 3-methyl-5-phenyloxazolidinone after reaction under 0.1 MPa CO_2



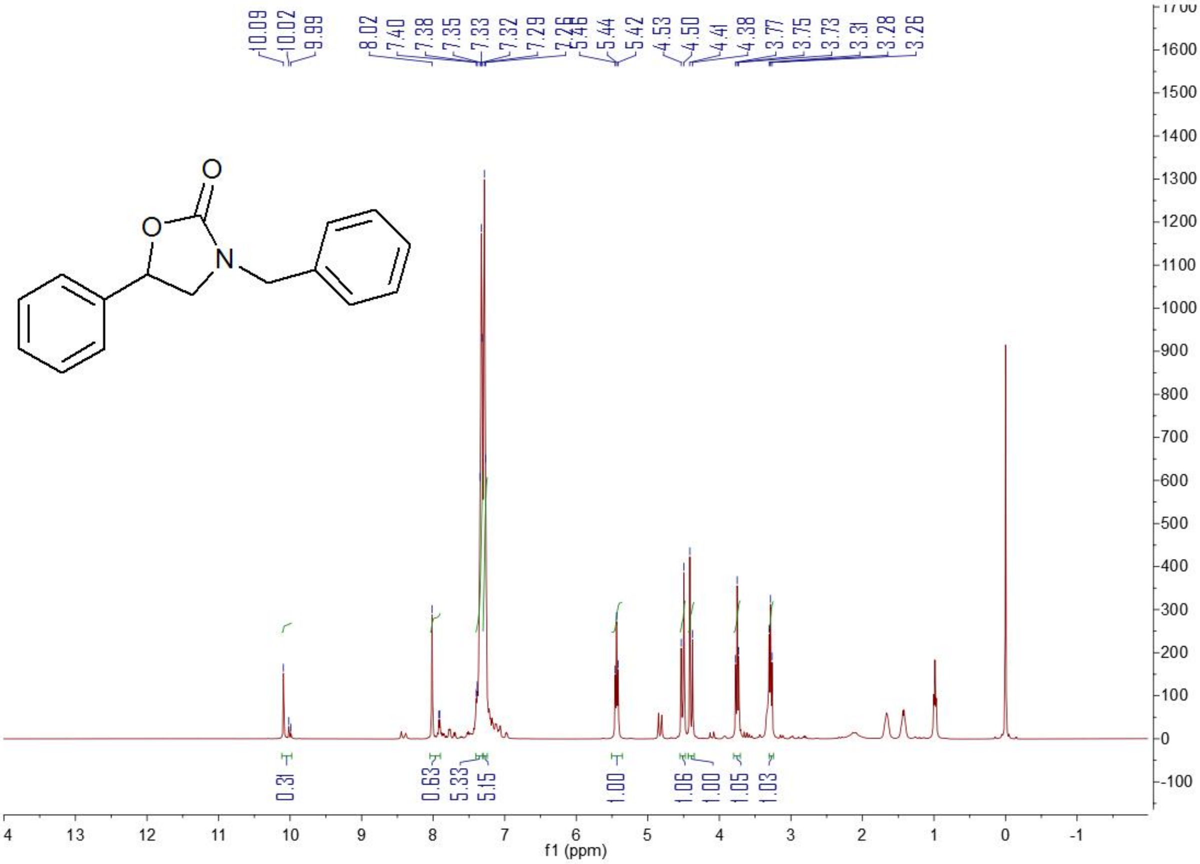
^{1}H NMR data of the resulting mixture containing 3-methyl-5-phenyloxazolidinone after reaction under 0.1 MPa CO_2 catalyzed by HKUST-1



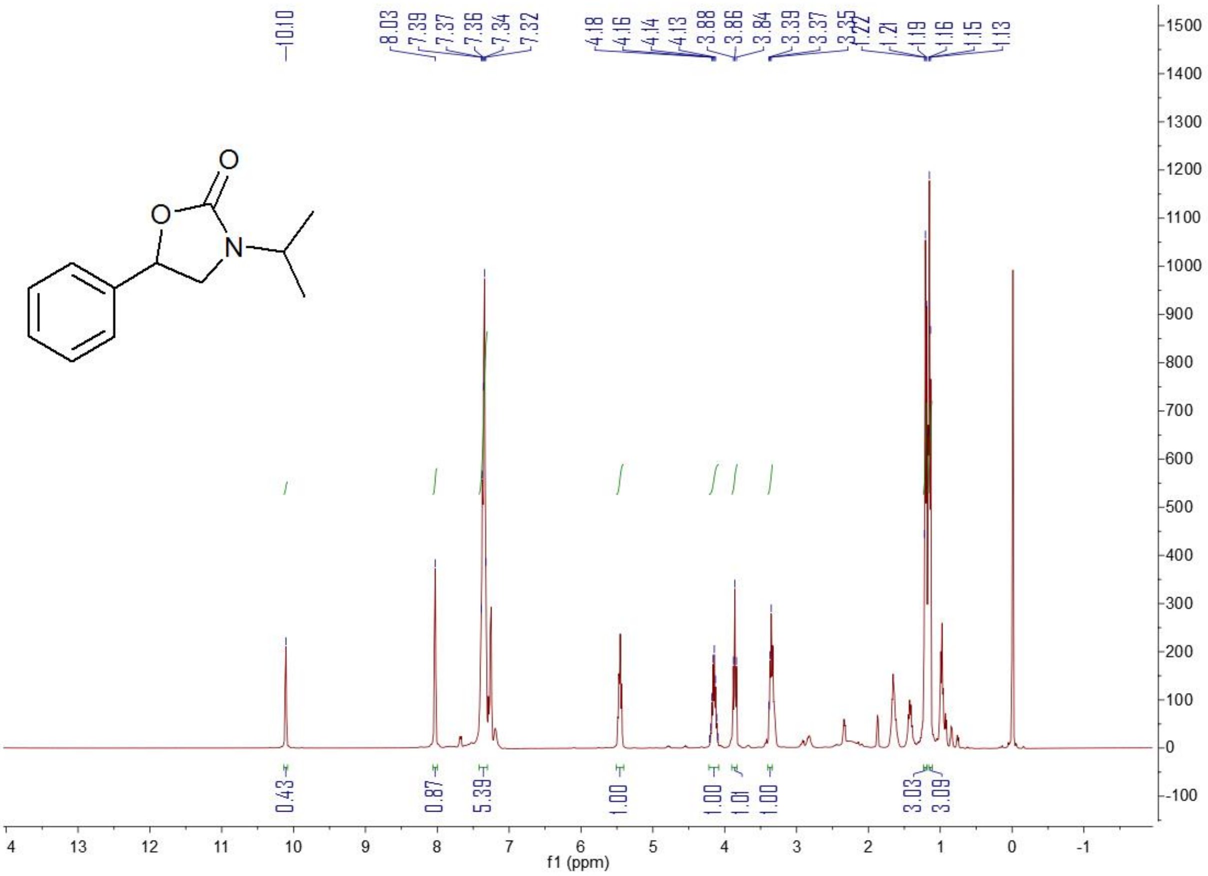
^{1}H NMR data of the resulting mixture containing 3-methyl-5-phenyl-2-oxazolidinone after reaction under 2 MPa CO_2



^{1}H NMR data of the resulting mixture containing 3-butyl-5-phenyl-2-oxazolidinone after reaction under 2 MPa CO$_2$



^{1}H NMR data of the resulting mixture containing 3-benzyl-5-phenyl-2-oxazolidinone after reaction under 2 MPa CO_2



^{1}H NMR data of the resulting mixture containing 3-isopropyl-5-phenyl-2-oxazolidinone after reaction under 2 MPa CO$_2$

Single-Crystal X-ray Diffraction for MMPF-10

The X-ray diffraction data were collected using synchrotron radiation ($\lambda = 0.49594$ Å) at the Advanced Photon Source Beamline 15-ID-B of ChemMatCARS in Argonne National Lab, Argonne, IL. Indexing was performed in Apex3 software.[3] Data integration and reduction were performed using SaintPlus.[4] Absorption correction was performed by multi-scan method implemented in SADABS.[5] Space group was determined using XPREP implemented in APEX2[3]. Structure was solved using SHELXT 6 and refined using SHELXL-2014[7~9] (full-matrix least-squares on F2) through OLEX2 interface program.[10] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically calculated positions and were included in the refinement process using riding model with isotropic thermal parameters. The diffraction spots were observed only up to ca. 1.2A resolution and all atoms were refined with geometry and ADP restraints. The model of crystal structure was refined in space group Immm (corresponding to highest symmetry of corresponding **fmj** topological network) as two-component pseudomerohedral twin with 4-fold rotation along [100] as twinning operator. After detwinning of the diffraction data the contribution of heavily disordered solvent molecules in structural voids was treated as diffuse using Squeeze procedure implemented in Platon program.[11,12] Crystal data and refinement conditions are shown in Table S1.

Table S1 Crystal data and structure refinement for MMPF-10.

Identification code	MMPF-10
Empirical formula	$C_{100}H_{52}Cu_5N_4O_{20}$
Formula weight	1947.15
Temperature/K	100.15
Crystal system	orthorhombic
Space group	Immm
a/Å	26.294(4)
b/Å	34.046(6)
c/Å	34.098(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	30525(9)
Z	4
ρ_{calc}g/cm^3	0.424
μ/mm^{-1}	0.137
F(000)	3940.0
Crystal size/mm^3	0.021 × 0.02 × 0.02
Radiation	synchrotron (λ = 0.49594)
2Θ range for data collection/°	2.462 to 22.884
Index ranges	$-19 \leq h \leq 20$, $-27 \leq k \leq 27$, $-27 \leq l \leq 20$
Reflections collected	43373
Independent reflections	4352 [R_{int} = 0.0826, R_{sigma} = 0.0491]
Data/restraints/parameters	4352/49/323
Goodness-of-fit on F^2	1.007
Final R indexes [I>=2σ (I)]	R_1 = 0.0685, wR_2 = 0.1999
Final R indexes [all data]	R_1 = 0.0922, wR_2 = 0.2191
Largest diff. peak/hole / e Å^{-3}	0.31/-0.41

References.

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