Supporting Information

Cu-based Metal−Organic Framework with High Specificity and Efficient Peroxidase-Like Catalytic Activity for Colorimetric Biosensing

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1. Experimental Section/Methods

Synthesis of Y-TCPP-2

The Y-TCPP-2 microcrystals were synthesized with the classical solvothermal method[1].To a 20 mL glass vial containing $Y(NO_3)_3 \cdot 6H_2O$ (14.8 mg, 0.034 mmol), H_4TCPP (5.0 mg, 0.009 mmol) and 2-FBA (300 mg, 2.14 mmol) dissolved in DMF (3.0 mL) and acetic acid (1.0 mL). The vial was heated to 120 °C for 48 h. Color-less regular hexagonal prism-shaped crystals were obtained.

Synthesis of MOF-808FA and MOF-808

MOF-808FA and MOF-808 was synthesized on the basis of recently published articles with slight modifications[2]. Briefly, $ZrCl_4$ (233 mg, 1.0 mmol), 1,3,5-benzene-tricarboxylic acid (H_3BTC, 70.6 mg, 0.236 mmol), formic acid (5.6 mL, 98 mmol), and N,N′-dimethylformamide (DMF, 10 mL) were placed in a screw-capped vial and ultrasonically dissolved. The mixture was then placed in an oven at 135 °C for 24 h. After the mixture was cooled naturally to 30 °C in the oven, the white precipitate was filtered and then extracted with methanol overnight via a Soxhlet extractor. Subsequently, the obtained precipitate was dried in a drying oven at 80 °C overnight to obtain MOF-808FA. MOF-808FA (500 mg) was placed in a screw-capped vial. Then, 110 mL of DMF and 10 mL of concentrated HCl were subsequently added. The suspension was then incubated at 80 °C for 24 h. After it was naturally cooled to 30 °C, the solid was collected by suction filtration and then extracted with methanol by a Soxhlet extractor overnight. The resulting white precipitate was dried at 80 °C in a vacuum drying oven to obtain MOF-808.

Synthesis of HKUST-1

The HKUST-1 microcrystals were synthesized with the classical solvothermal method[3]. $Cu(NO_3)_2 \cdot 3H_2O$ (2.6 g, 10.7 mmol) was dissolved in 30 mL of H_2O. In a separate flask, H_3BTC (0.68 g, 3.2 mmol) was dissolved in 30 mL of EtOH. The $Cu(NO_3)_2 \cdot 3H_2O$ solution was slowly added to the H_3BTC solution with stirring at room temperature. The solution became turbid, with a precipitate forming. DMF (2 mL) was added to the mixed solution, then the combination was transferred to a 100 mL Teflon-lined autoclave and allowed to be reacted at 80 °C for 20 h. After allowing the autoclave and its contents to cool to room temperature, a crystalline solid was collected and washed with H_2O and EtOH.

Steady-state Kinetic assay of ZJU-132 with H_2O_2 Substrate .

The velocity of the reaction was measured at 37 ℃ using x μL (x = 18, 24, 60, 120, 180, 240, 300) 100 mM H_2O_2 solution, (300 - x) ethanol, 300 μl of 1.0 $mg \cdot mL^{-1}$ ZJU-132 suspension, 2.1 ml of pH 5.0 PBS, and 300 μl of 10 mM OPD and then reacted at 37 °C. During the period, the suspension was taken out at preset time and immediately filtered with a syringe filter. The product was validated by measuring the UV-Vis absorbance at 430 nm and the content of OPDox in the filtrate was assessed through the UV absorbance. The oxidation and peroxidation reaction rates were calculated using the Michaelis-Menten equation.

Measurement and analysis.

Powder X-ray diffraction (PXRD) patterns in the range 2−50° were recorded on an

X'Pert Pro X-ray diffractometer with Cu Kα beam (λ = 1.542 Å) at room temperature. Elemental analyses (EA) of C, H, and N were carried out on an EA1112 microelemental analyzer.. The thermogravimetric curves from 30 to 800 °C in N_2 atmosphere were recorded on a Netszch TGA209F3 thermogravimeter with a heating rate of 5 °C· min^{-1}. The photoluminescent (PL) spectra at room temperature were recorded on a Hitachi F4600 fluorescence spectrometer. The Brunauer–Emmett–Teller (BET) specific surface areas and pore size distributions of all the materials were determined by CO_2 adsorption-desorption isotherms at 196 K on Micromeritics 3Flex gas adsorption analyzer. Before the test, the as-synthesized sample (50–100 mg) was first solvent-exchanged with anhydrous ethanol within three days. The solvent-exchanged sample was evacuated at room temperature for 12 h and further at 393 K for other 12 h. The CO_2 adsorption isotherms were measured at 196 K,

Single-Crystal X-ray Crystallography.

The crystallographic measurement and structure determination of **ZJU-132** was performed similarly to our previous literature[4]. The single-crystal X-ray diffraction (SCXRD) collection was taken on a Bruker APEX-II diffractometer, and the structure was determined by direct methods and refined with the SHELX-2014 program package. The hydroxy units of ligands were split into four equivalent parts during structural refinement. Crystallographic data collection and refinement results are summarized in Table S1. **CCDC 2544395** contains the supplementary crystallographic data of **ZJU-132**, which can be obtained from the authors or the Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data-request/cif.

General considerations of solution preparation

MOF suspensions in PBSx1 pH 7.4 (ZJU-132, MOF-808 (Zr), Y-TCPP-2 and HKUST-1 (Cu) were produced at a concentration of 1 mg/mL. The MOF suspensions were kept at room temperature and before use vortexed for 5 minutes. Aqueous solutions of 10 mM H_2O_2 and different concentrations were prepared by dilutions of purchased H_2O_2 (30%) in H_2O.

2- Characterization data

Table S1. Crystal data, collection and structure refinement result of **ZJU-132**.

compund	**ZJU-132**
CCDC	2544395
Empirical formula	$C_{128}H_{80}Cu_8N_8O_{40}$
Formula weight	1431.09
Temperature/K	241
Crystal system	orthorhombic
Space group	Imma
a/Å	22.202(6)
b/Å	29.395(6)
c/Å	10.878(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7099(3)
Z	8
ρ_{calc}g/cm^3	0.673
μ/mm^{-1}	0.970
F(000)	1456.0
Crystal size/mm^3	0.06 × 0.1 × 0.12
Radiation	CuKα (λ=1.54178 Å)
2Θ range for data collection/°	3.982 to 68.492
Index ranges	-26 ≤ h ≤ 26, -35 ≤ k ≤ 32, -13 ≤ l ≤ 13
Reflections collected	39348
Independent reflections	3425 [R_{int} = 0.0718, R_{sigma} = 0.0811]
Data/restraints/parameters	3425/126 /178
Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0762, wR_2 = 0.2235
Final R indexes [all data]	R_1 = 0.0890, wR_2 = 0.2556
Largest diff. peak/hole / e Å^{-3}	1.189/-0.902

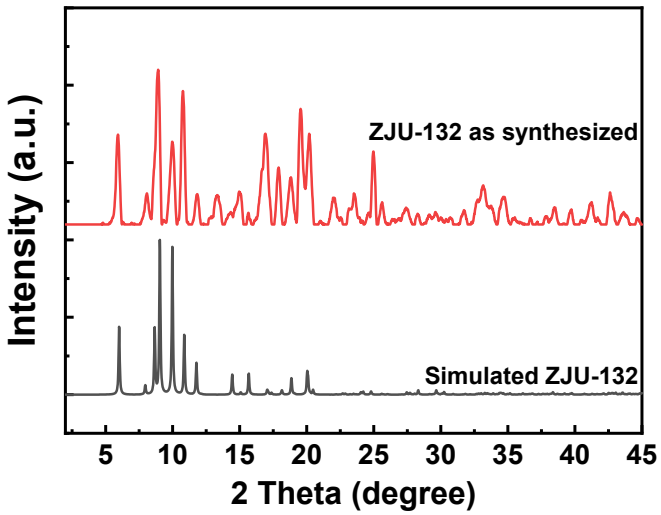

Figure S1. PXRD patterns of synthesized ZJU-132.

Figure S2. Optical images of the as-synthesized ZJU-132. Scale bar: 50 um.

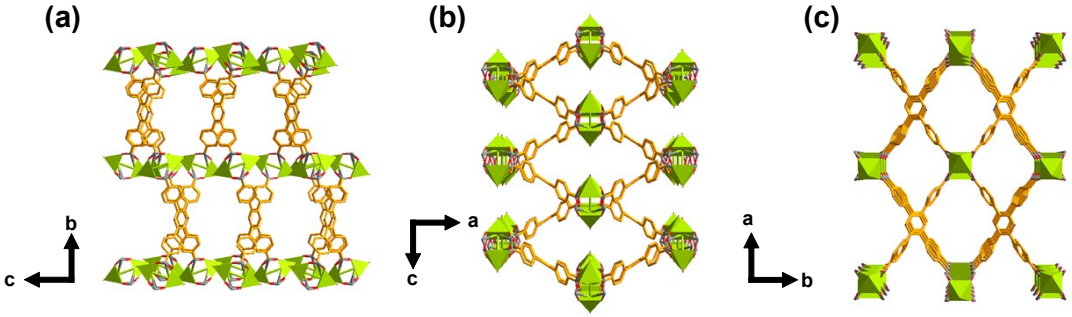

Figure S3. (a-c) The structure of ZJU-132 seen from the *a*-axis (a), *b*-axis (b) and *c*-axis (c).

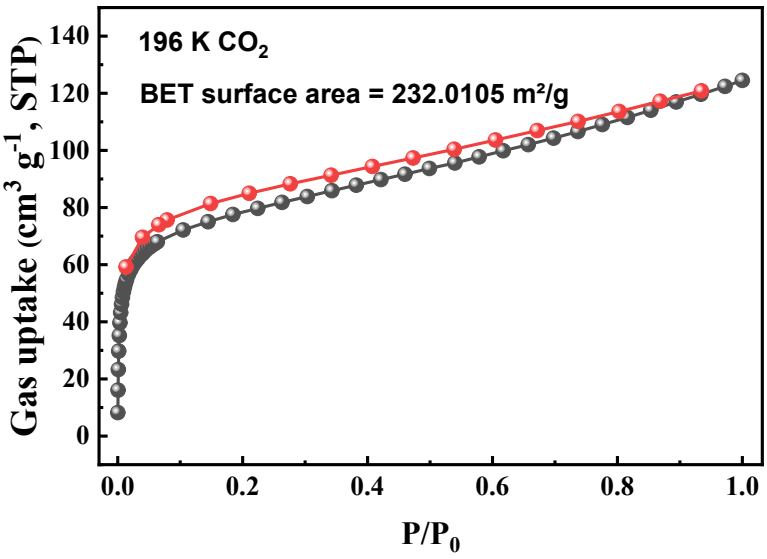

Figure S4. CO_2 sorption isotherms of ZJU-132 at 196 K

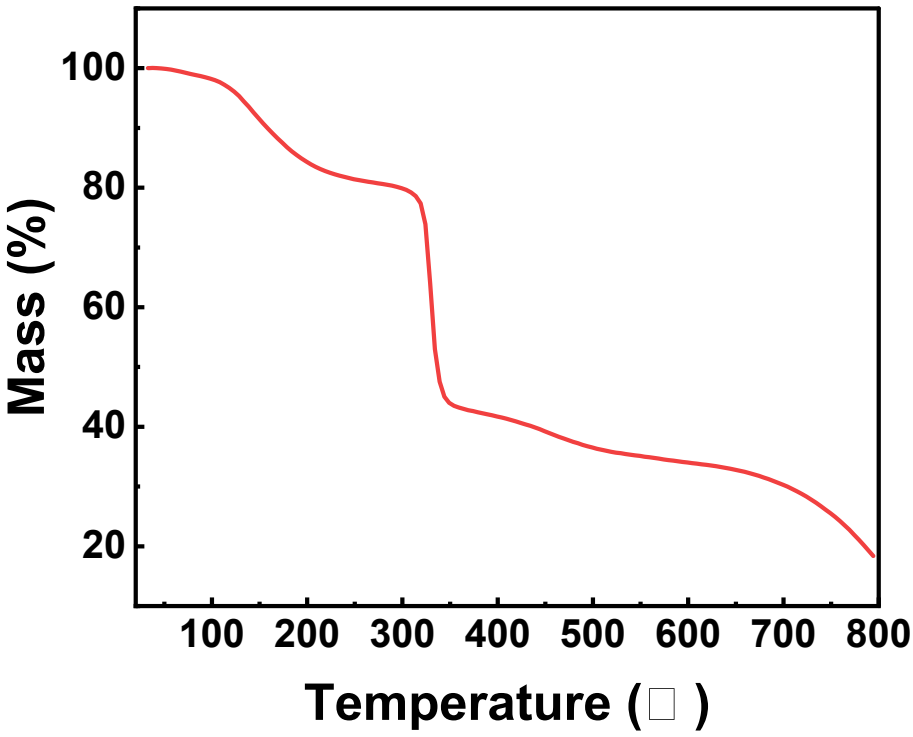

Figure S5. TGA curves for ZJU-132 under nitrogen.

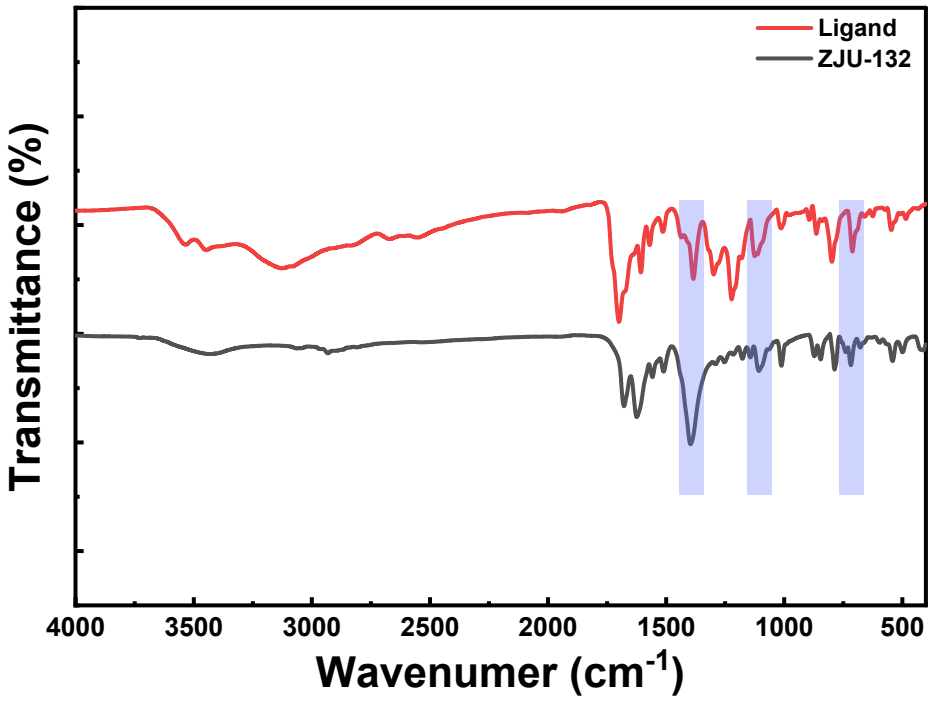

Figure S6. FTIR spectrums for ZJU-132 and Ligand.

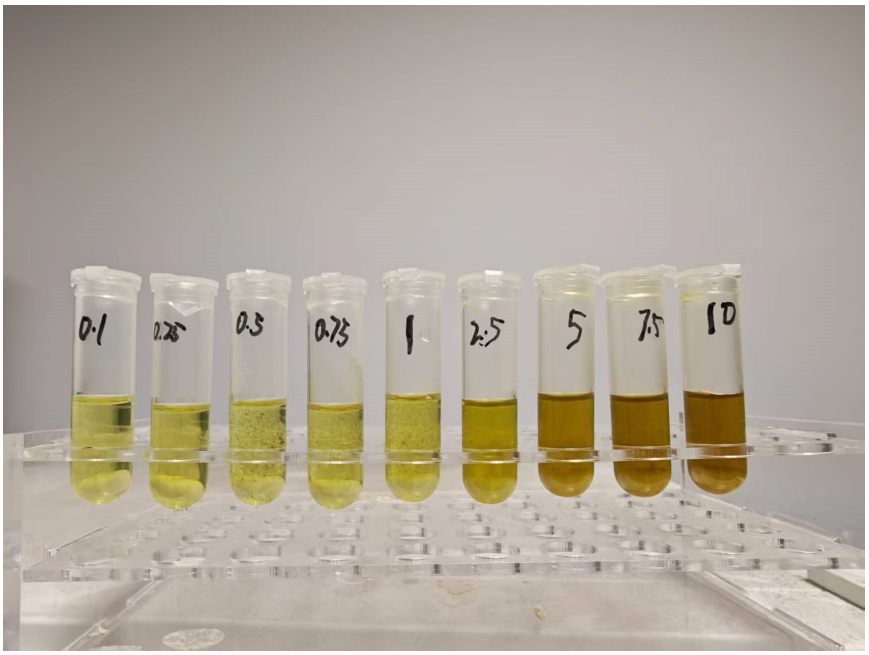

Figure S7. optical photographs of the OPD oxidation reaction system catalyzed by ZJU-132 under a series of H_2O_2 concentrations (0.1 mM-10 mM).

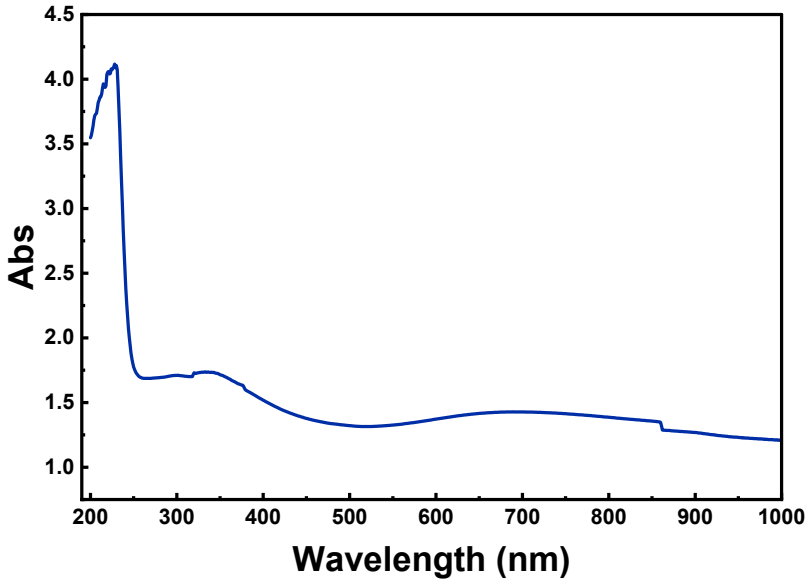

Figure S8. The solid-state UV-vis absorption spectrum of the ZJU-132 powder sample.

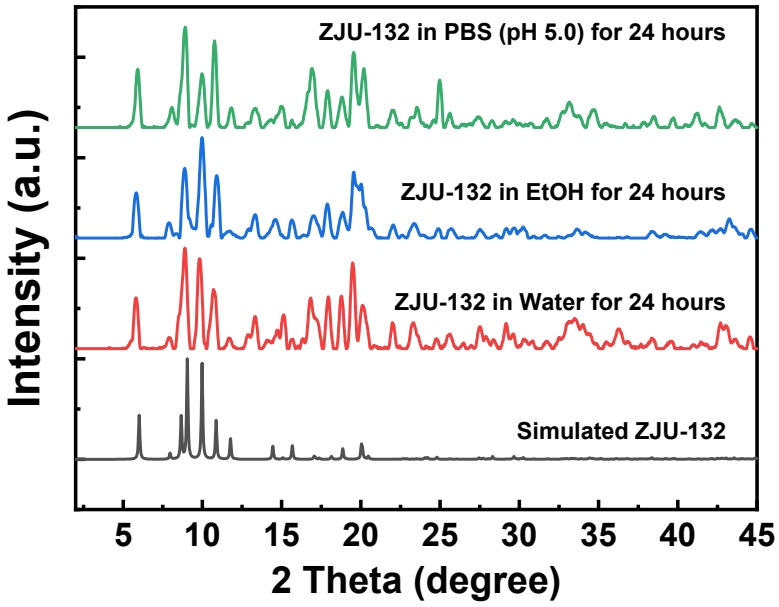

Figure S9. The stability of ZJU-132 under different environments.

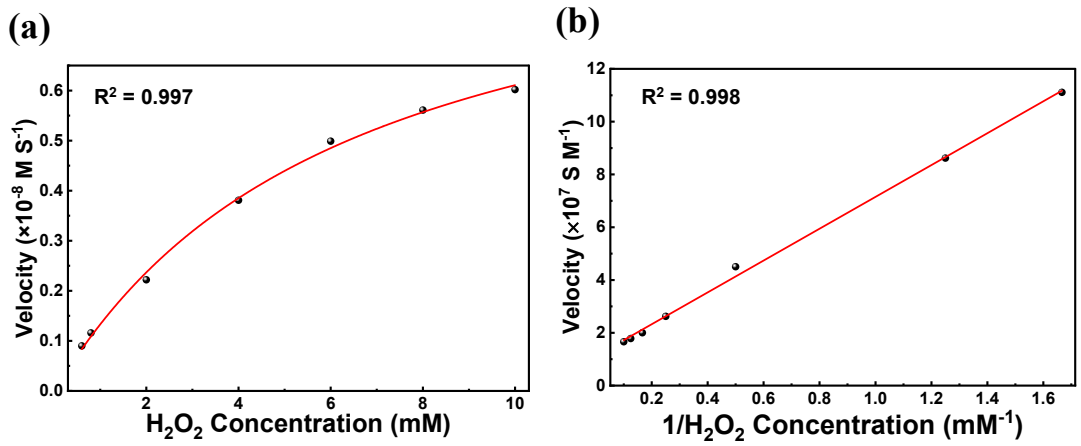

Figure S10. Results of nonlinear fitting of Michaelis-Menten curves for H_2O_2 by ZJU-132.

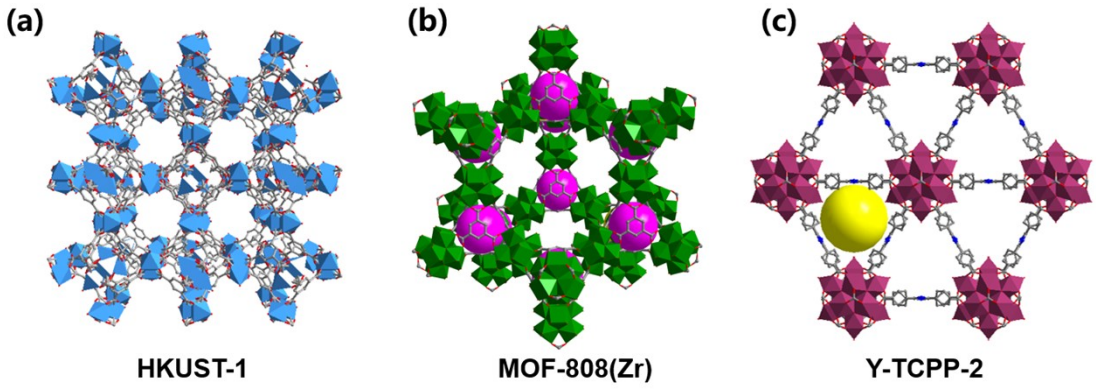

Figure S11. Crystal structure of (a) HKUST-1(Cu), (b) MOF-808(Zr), (c) Y-TCPP-2.

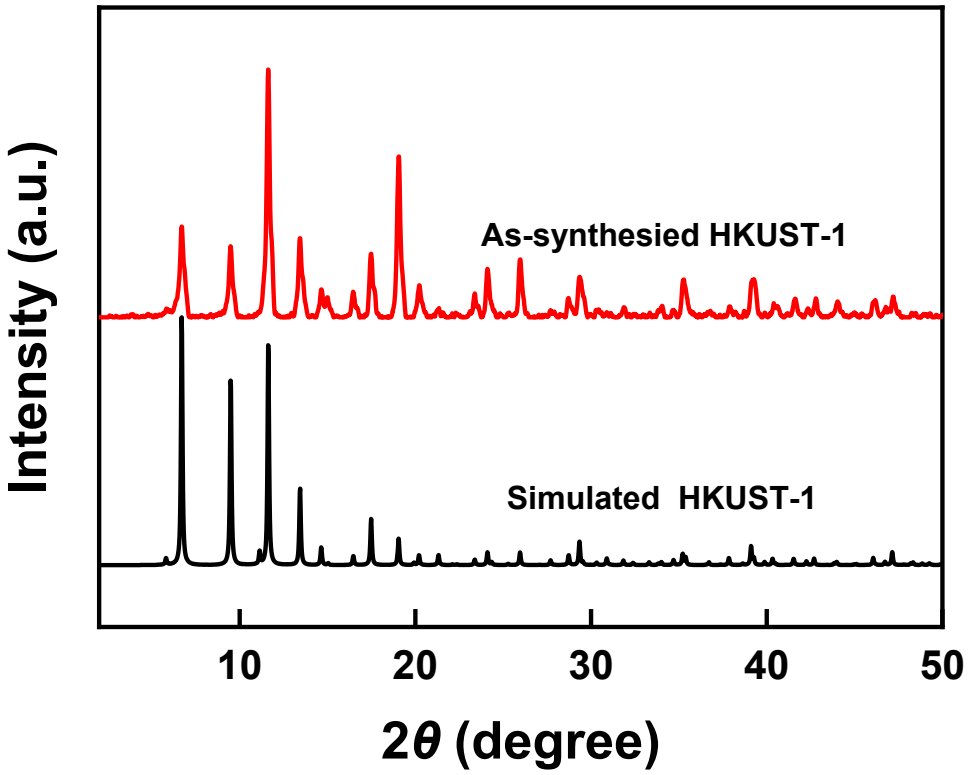

Figure S12. PXRD patterns of synthesized **HKUST-1**.

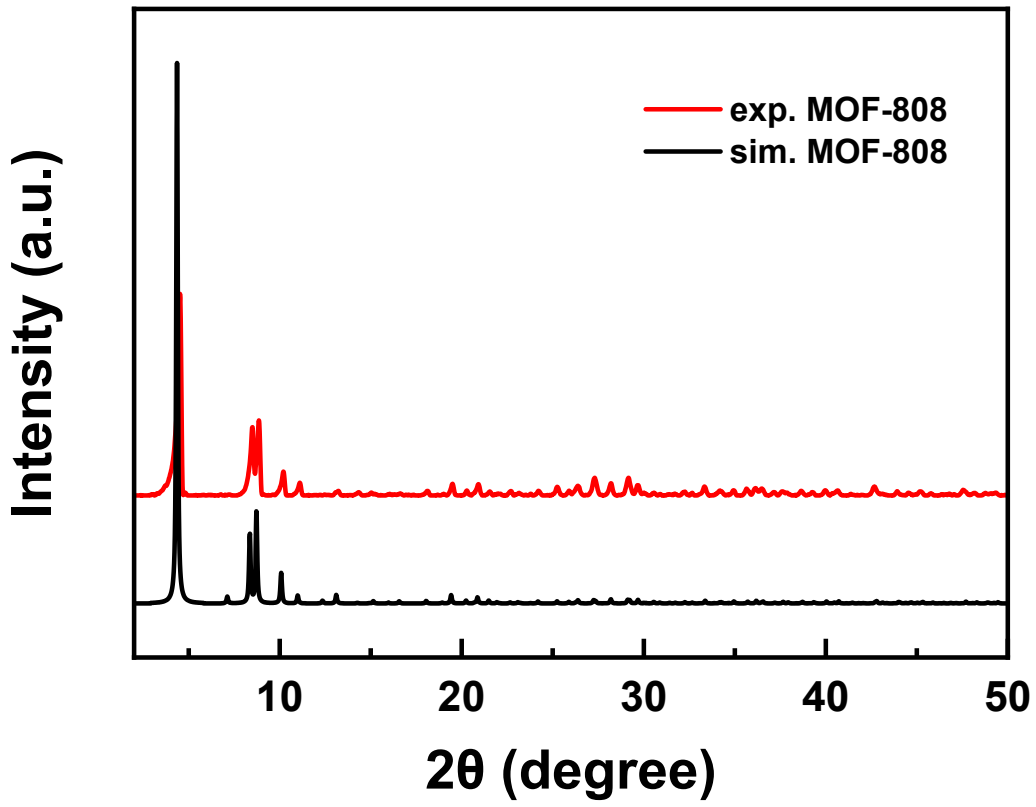

Figure S13. PXRD patterns of synthesized MOF-808(Zr).

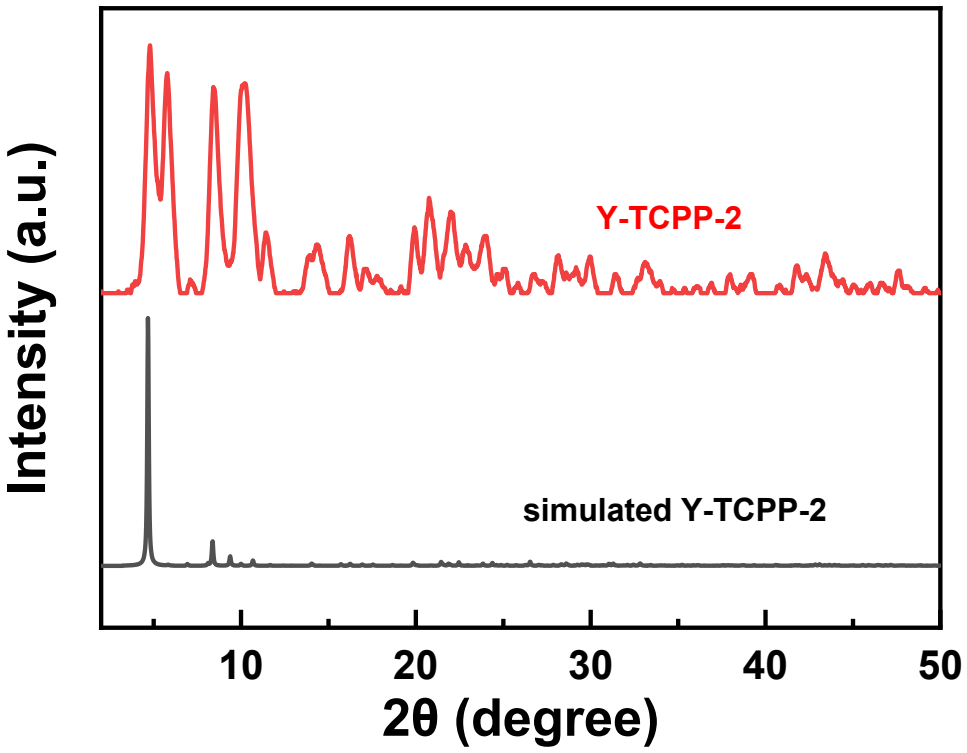

Figure S14. PXRD patterns of synthesized Y-TCPP-2.

References

1. H.-Q. Zheng, L. Zhang, M. Lu, X. Xiao, Y. Yang, Y. Cui and G. Qian, *Research*, 2022, **2022**.
2. H. Furukawa, F. Gándara, Y.-B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson and O. M. Yaghi, *J. Am. Chem. Soc.*, 2014, **136**, 4369-4381.
3. N. C. Jeong, B. Samanta, C. Y. Lee, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 51-54.
4. L. Zhang, H. Li, H. He, Y. Yang, Y. Cui and G. Qian, *Small*, 2021, **17**, 2006649.