Supplementary Information

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Experimental Section

1. Materials and chemicals

The ligand 4,4,4,4-(Porphine-5,10,15,20-tetrayl) tetrakis (benzoic acid) (H_2TCPP), 4,4'-Bipyridine (BPY), copper (II) chloride dihydrate, ascorbic acid (AA), dopamine (DA), uric acid (UA), glucose (Glu), $ZnSO_4$, NaCl, KCl, Na_2HPO_4 and Na_2HPO_4 were purchased from Wuhan Shen Shi Chemical Co. Ltd. The phosphate buffer solution (PBS) were prepared by mixing the stock solution of from 0.1 M Na_2HPO4 and 0.1 M Na_2HPO_4. All the chemicals are analytical grade and used without further purification.

2. Characterization

The mophology characterizations of the CuTCPP and CuTCPP-BPY were carried out on field-emission scanning electron microscope (FESEM, SU-8010). The functional groups of the sample were studied using Fourier transform infrared spectrometer (FTIR, Bruker INVENIO-R). Transmission electron microscopy (TEM) images, SAED patterns and mapping patterns were obtained by a high-resolution transmission electron microscopy with 200 kV (Tecnai G2 20). The optical property of CuTCPP and CuTCPP-BPY was measured by UV-vis absorption spectroscopy (SHIMADZU UV-2600). X-ray diffraction (XRD) analysis was carried out on Empyrean X-ray diffractometer using Cu Ka radiation (λ=1.5406 Å, scanning range: 10°-80°, scanning speed: 10° min^{-1}). Atomic force microscope (AFM, Shimadzu SPM 9700) was used to measure the thickness of CuTCPP and CuTCPP-BPY. An ultraviolet visible spectrophotometer (Shimadzu UV-2600) was employed to study the metalation of porphyrin rings by Cu^{2+}. All electrochemical test were performed by CHI760E electrochemical workstation.

3. Synthesis of CuTCPP and CuTCPP-BPY MOFs

First, 5.1mg of $CuCl_2 \cdot 2H_2O$ (0.03 mmol) were dissolved in 6 mL of the mixture of ethanol and DMF (V:V = 1:3) in a 15 mL breaker. Then, 7.9 mg of H_2TCPP (0.01 mmol) was added to the obtained solution with stirring. After the solution was stirred for 5 min, the breaker was sonicated for 20 min to form a

homogeneous solution. The mixture was heated to 80 °C and reacted for 5 h. The CuTCPP products were obtained by centrifugation and washing with DMF three times. The synthetic conditions for CuTCPP-BPY was similar to those of CuTCPP except for adding 5.76 mg BPY (0.02 mmol) to the breaker after dissolving $CuCl_2 \cdot 2H_2O$.

4. Preparation of the modified electrode

The as-prepared CuTCPP/CuTCPP-BPY MOF was dispersed in DMF (2 mg/mL) and sonicated in a bath for 10 min. Then Nafion (0.1 wt%) was added in the prepared CuTCPP/CuTCPP (SDS) MOF solution (V: V = 1:500) to form the CuTCPP/CuTCPP (SDS) MOF ink. The Nafion was used for preventing the CuTCPP/CuTCPP-BPY MOF from peeling off from the electrode surface. The modified electrode was made by dropping appropriate prepared ink on a cleaned GCE and dried for following measurement. 10 μL of CuTCPP/CuTCPP (SDS) MOF ink was dropped onto the GC electrode surface. Subsequently, CuTCPP/GC was allowed to dry at 60 °C to enhance the cohesiveness of the Nafion attached to the electrode surface.

5. Calculations for electrochemically active surface area

The electrochemically active surface area is calculated according to the following formula:

$$I_c = v \times C_{dl}$$

$$ECSA = C_{dl} / C_s$$

Where v is the scan rate in the CV test, I_c is the calculated changing current density (also known as the charging current), C_{dl} is the double-layer Capacitance (C_{dl}) of the catalytic material surface, and C_s is the specific capacitance of the sample under the same conditions.

Figures, tables and captions

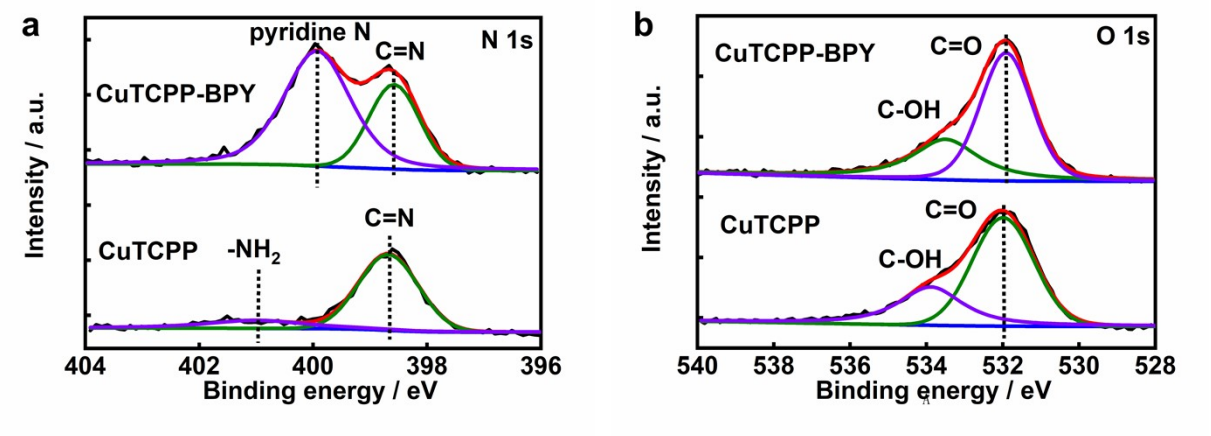

Figure S1. (a) N 1s and (b) O 1s XPS spectrume of CuTCPP and CuTCPP-BPY.

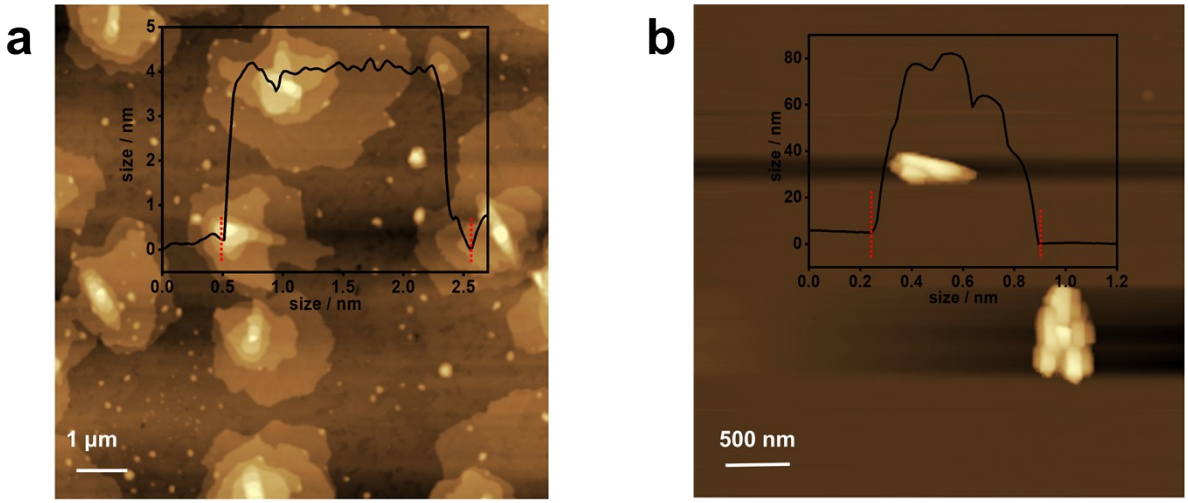

Figure S2. (a)AFM image of CuTCPP. (b) AFM image of CuTCPP-BPY.

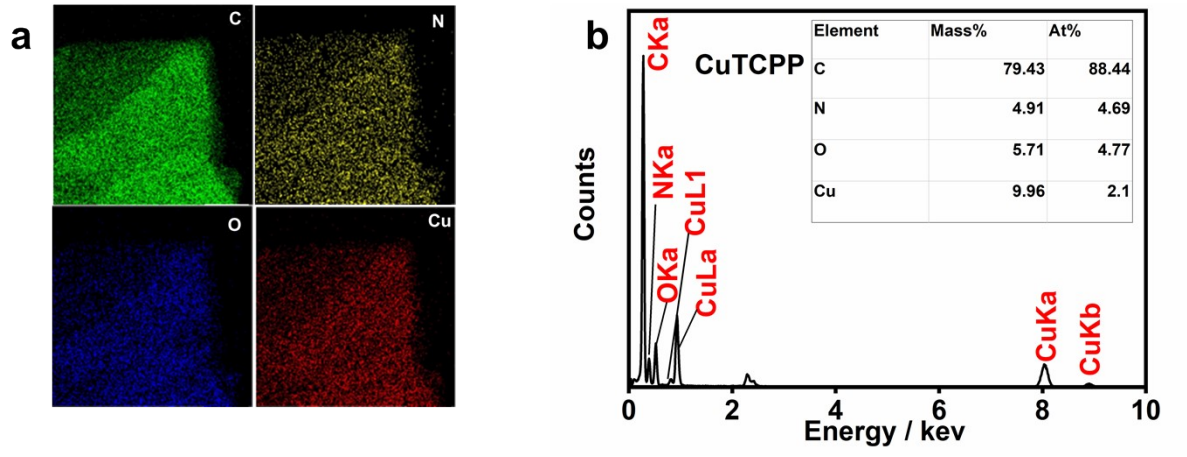

Figure S3. (a) TEM mapping image of different elements in CuTCPP. (b) Energy dispersive X-ray spectrogram of CuTCPP.

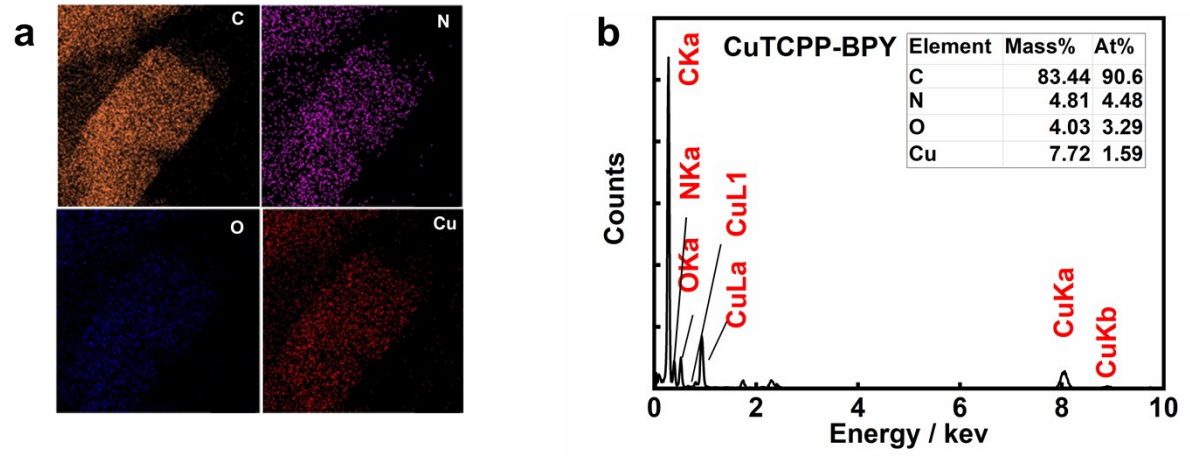

Figure S4. (a) TEM mapping image of different elements in CuTCPP-BPY. (b) Energy dispersive X-ray spectrogram of CuTCPP-BPY.

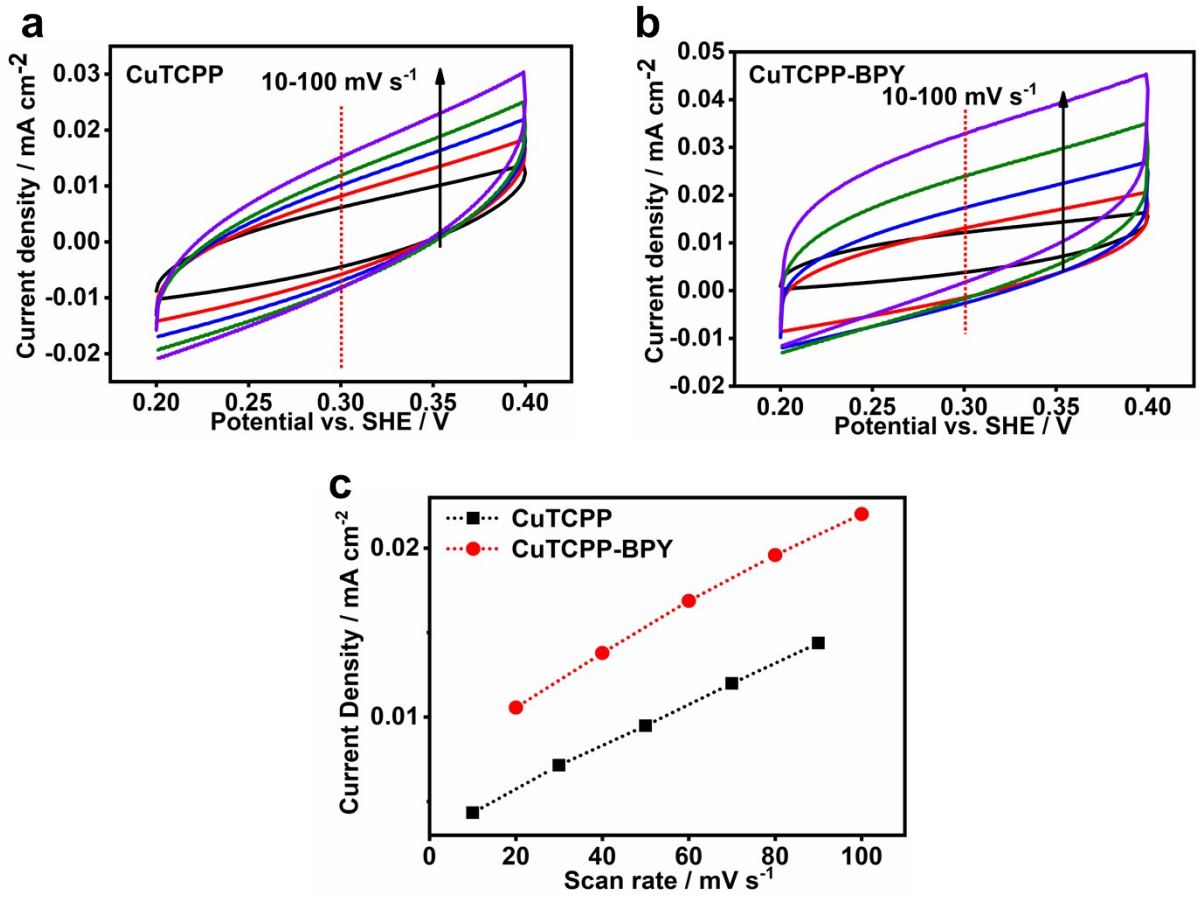

Figure S5. (a) CuTCPP and (b) CuTCPP-BPY CV curve of different scan rate in 0.01 M PBS solution. (c) Electrochemically active surface area of CuTCPP and CuTCPP-BPY

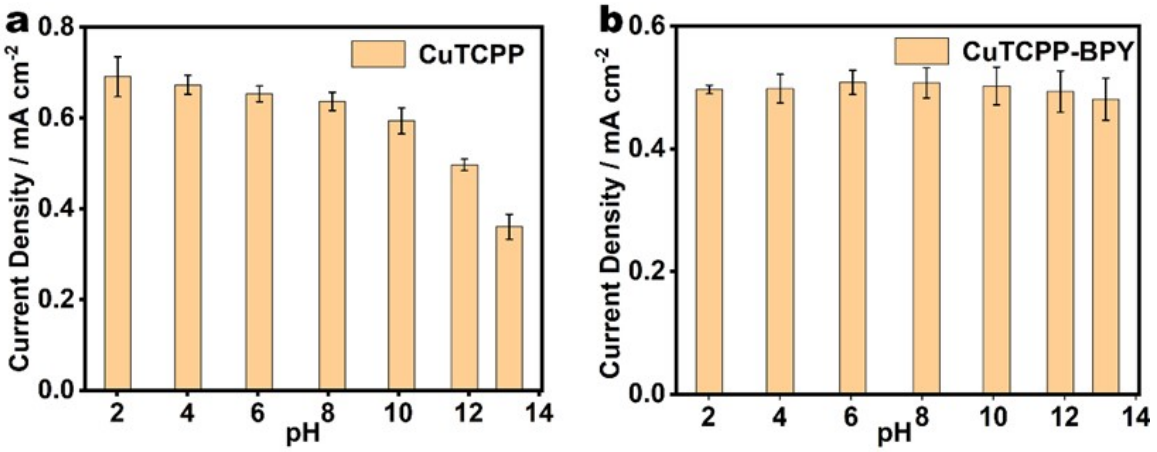

Figure S6. (a) CuTCPP and (b) CuTCPP-BPY error analysis of three groups parallel experiments of acid and alkali resistance

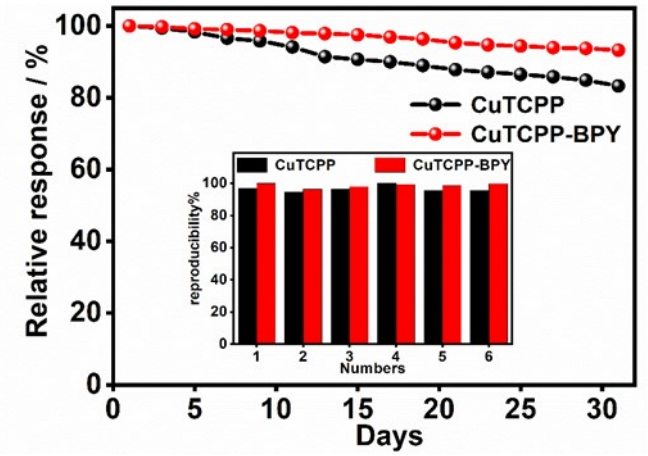

Figure S7. long-term Stability of CuTCPP and CuTCPP MOFs cruves. Inset is the reproducibility picture.

Table S1 The corresponding impedance values for different MOFs calculated by fitting.

Samples	$R_S(\Omega)$	CPE-T(Ω cm^{-2} s^n)	CPE-P	$R_{ct}(\Omega)$	W-R(Ω)	W-T((Ω cm^{-2} s^n)	W-P
CuTCPP	2	0.00052	0.8	17	1586	0.07	0.73
CuTCPP-BPY	2	0.00036	0.08	19	1726	0.09	0.59

Table S2 Impedance fitting data of CuTCPP.

Freq	Z' (a)	Z'' (b)	Mag	Phase
681600	7.5829	-6.2333	9.816	-39.421
382800	10.596	-7.0844	12.746	-33.767
215800	13.744	-7.1182	15.478	-27.381
121100	16.466	-6.6278	17.75	-21.925
68120	18.586	-6.186	19.588	-18.409
38330	20.337	-6.2076	21.263	-16.974
21530	22.034	-6.9137	23.093	-17.42
12110	23.955	-8.4535	25.403	-19.437
6812	26.377	-11.02	28.587	-22.674
3833	29.608	-14.908	33.15	-26.725
2153	34.055	-20.591	39.796	-31.159
1211	40.224	-28.706	49.417	-35.514
683.6	48.791	-40.137	63.178	-39.442
380.9	61.112	-56.693	83.359	-42.852
214.8	78.109	-79.612	111.53	-45.546
122.1	101.6	-111.34	150.72	-47.618
68.13	135.74	-157.47	207.9	-49.237
38.31	183.29	-222.07	287.94	-50.464
21.54	250.93	-308.35	397.55	-50.862

Table S3 Impedance fitting data of CuTCPP-BPY.

Freq	Z' (a)	Z'' (b)	Mag	Phase
681600	6.7557	-5.5542	8.7458	-39.425
382800	9.5146	-6.4605	11.501	-34.177
215800	12.585	-6.4943	14.162	-27.295
121100	15.286	-5.7254	16.323	-20.534
68120	17.214	-4.6973	17.844	-15.263
38330	18.487	-3.8983	18.893	-11.908
21530	19.381	-3.569	19.707	-10.434
12110	20.138	-3.8142	20.496	-10.725
6812	20.953	-4.7322	21.481	-12.726
3833	22.001	-6.5018	22.941	-16.464
2153	23.487	-9.4547	25.319	-21.927
1211	25.677	-14.106	29.297	-28.782
683.6	28.944	-21.241	35.901	-36.273
380.9	34.016	-32.455	47.015	-43.654
214.8	41.582	-49.27	64.472	-49.837
122.1	52.879	-74.437	91.307	-54.61
68.13	70.634	-114.05	134.15	-58.229
38.31	97.784	-173.99	199.59	-60.664
21.54	137.79	-271.65	304.6	-63.104