Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Comparison of Two Water Oxidation Electrocatalysts by Copper or Zinc Supermolecule Complexes based on Porphyrin Ligand

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Ligand Synthesis

0.565 g (8.46 mmol) of 4-formylbenzonitrile were added to 500 mL of dry CH_2Cl_2 under N_2 and continue to stirred 20 min to remove the air contained in the solution. 0.3 ml of pyrrole was added to the above mixture, after stirring for 30 min, 52.5 μL of BF_3•OEt_2 (0.85 nmol) was added via syringe, and the reaction mixture was protected from light with tin foil. After stirring at room temperature for 2 h, 0.78 g (0.37 mmol) of p-chloranil was added in the solid form and the solution was refluxed for 4 h. After the reaction mixture was cooled to room temperature, the residue was subjected to column chromatography on silica gel eluted with $CHCl_3$ to give 5, 10, 15, 20-Tetrakis(4-cyanophenyl) porphyrin (CNTCPP), yield 20%. H1NMR: 1H NMR (CDCl3) δ 8.84 (s, 8H), 8.35 (d, 8H), 8.12 (d, 8H).

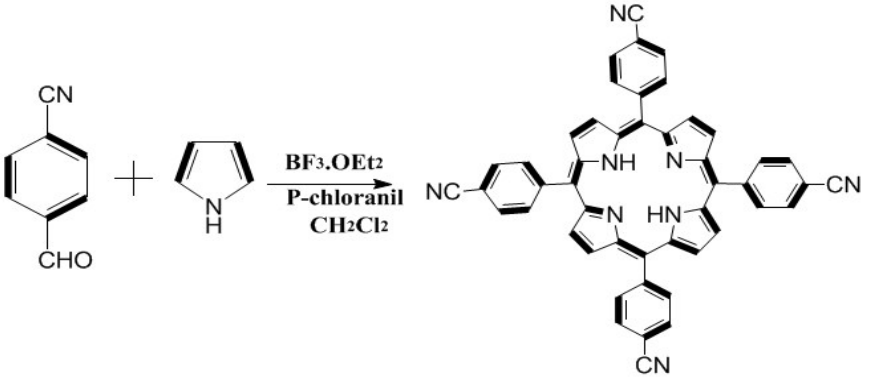

Fig. S1 Synthesis of CNTCPP ligand.

Synthesis of Cu-CNTCPP

A mixture of CNTCPP (20.0 mg, 0.028 mmol) and $CuCl_2·2H_2O$ (20.0 mg, 0.12 mmol) in a solvent of DMF (15.0 mL) was heated in a sealed Teflon stainless steel autoclave to 80 ℃ for 3 days. Deep violet crystals of **Cu-CNTCPP** were filtered, washed with EtOH, and dried at room temperature. Yield: 30%, based on CNTCPP. Anal. Calcd. for Cu-CNTCPP (%): C, 70.31; H, 4.15; N, 15.18. Found (%): C, 70.02; H, 4.65; N, 18.09.

Synthesis of Zn-CNTCPP

A mixture of CNTCPP (20.0 mg, 0.028 mmol) and $ZnCl_2$ (20.0 mg, 0.15 mmol) in a mixed solvent of DMF/EtOH (V:V=2:1, 1.0 mL) was heated in a sealed glas tube to

120 ℃ for 3000 min. Deep brownish crystals of **Zn-CNTCPP** were filtered, washed with EtOH and dried at room temperature. Yield: 25%, based on CNTCPP. Anal. Calcd. for Zn-CNTCPP (%): C, 74.09; H, 3.11; N, 14.40. Found (%): C, 74.52; H, 3.65; N, 14.02.

Table S1. Crystal data for complex of **Cu-CNTCPP.**

Empirical formula	$C_{54}H_{38}CuN_{10}O_2$
Formula weight	922.48
Temperature/K	294.07(10)
Crystal system	monoclinic
Space group	P 2/n
a/Å	15.3680(2)
b/Å	17.1635(2)
c/Å	33.5945(6)
α/°	90.00
β/°	93.8490(10)
γ/°	90.00
Volume/Å^3	8841.2(2)
Z	8
ρ_{calc}g/cm^3	1.386
μ/mm^{-1}	1.148
F(000)	3816
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	2.892 to 70.437
Index ranges	$-18 \leqslant h \leqslant 11$, $-15 \leqslant k \leqslant 20$, $-40 \leqslant l \leqslant 40$
Reflections collected	37932
Independent reflections	16592 [R_{int} = 0.0391]
Data/restraints/parameters	16592/0/1232
Goodness-of-fit on F^2	1.054
Final R indexes [$I>=2\sigma(I)$]	R_1 = 0.1020, wR_2 = 0.3093
Final R indexes [all data]	R_1 = 0.1271, wR_2 = 0.3318

Table S2. Crystal data for complex of **Zn-CNTCPP.**

Empirical formula	$C_{48}H_{24}N_8Zn$
Formula weight	778.12
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.7858(3)
b/Å	9.3797(2)
c/Å	21.3172(5)
α/°	90.00
β/°	100.777(3)
γ/°	90.00
Volume/Å^3	1922.15(9)
Z	2
ρ_{calc}g/cm^3	1.344
μ/mm^{-1}	0.685
F(000)	796.0
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.06 to 52.74
Index ranges	$-12 \leq h \leq 12$, $-11 \leq k \leq 11$, $-26 \leq l \leq 26$
Independent reflections	3927 [$R_{int} = 0.0227$, $R_{sigma} = 0.0301$]
Data/restraints/parameters	3927/0/259
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	$R_1 = 0.0446$, $wR_2 = 0.1323$
Final R indexes [all data]	$R_1 = 0.0543$, $wR_2 = 0.1403$

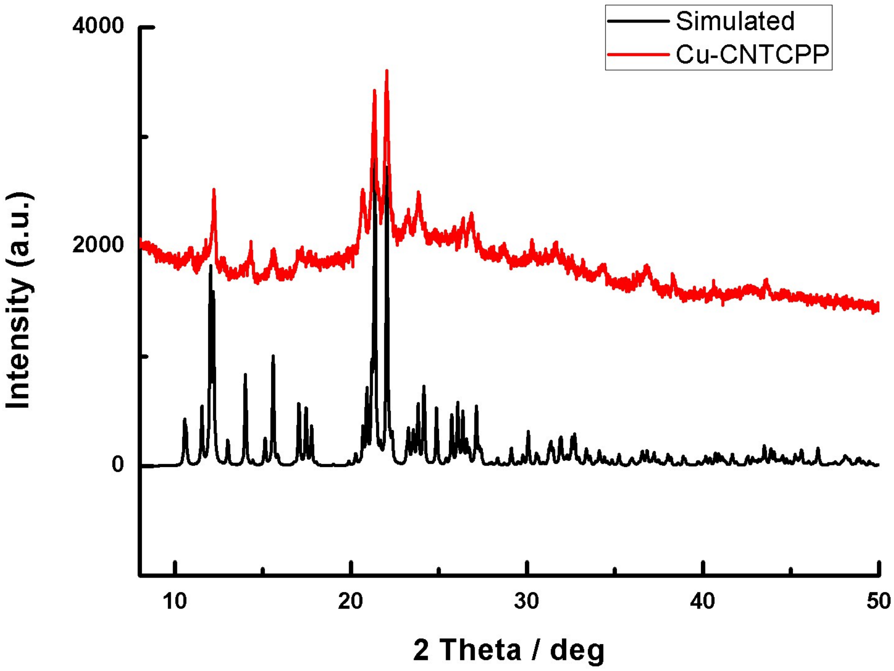

Fig. S2 XRD of **Cu-CNTCPP**.

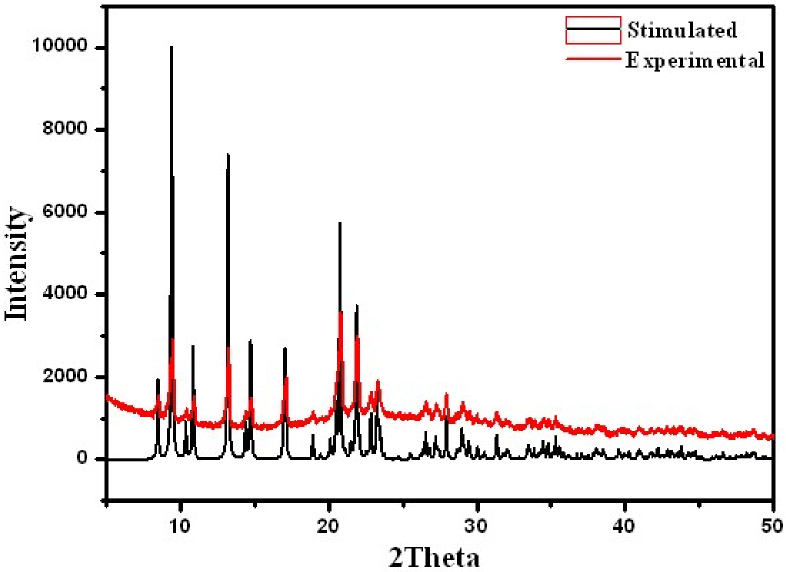

Fig. S3 XRD of **Zn-CNTCPP**.

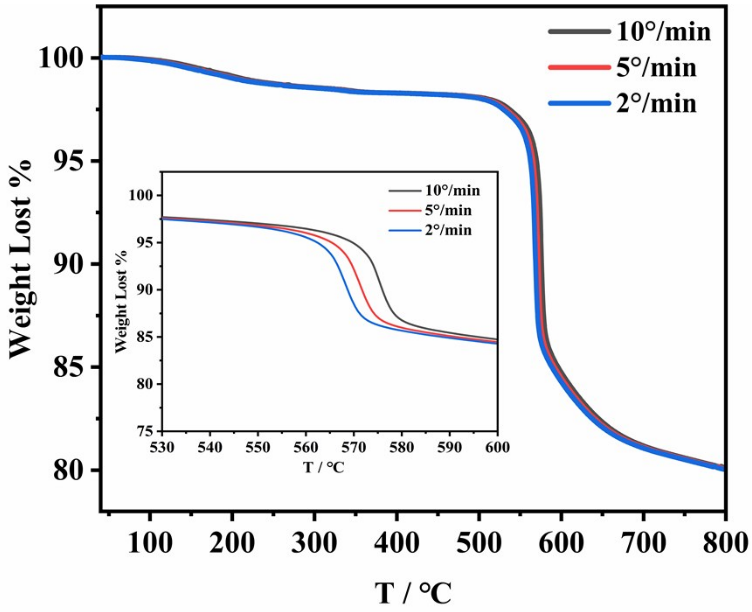

Fig. S4 TGA curve of **Cu-CNTCPP**.

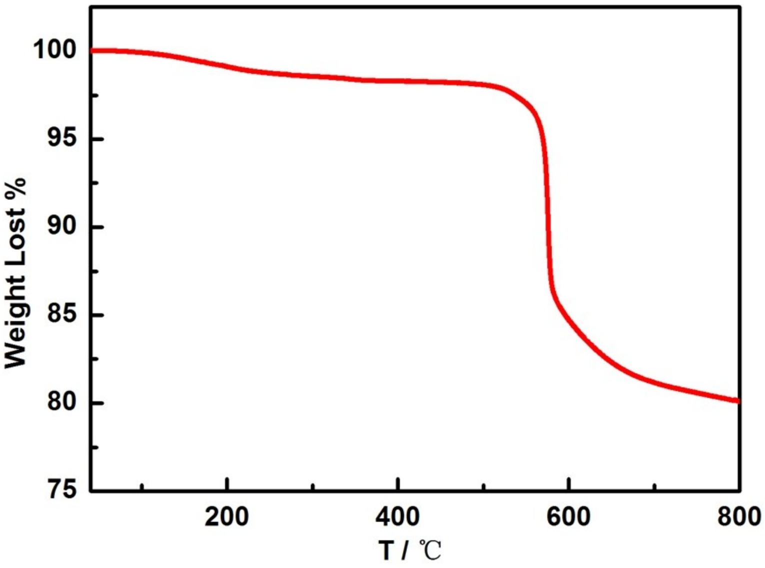

Fig. S5 TGA curve of **Zn-CNTCPP**.

Method for electrochemical measurements: The glassy carbon electrode (GCE) as work electrode with the diameter of 4.0 mm (Gamry Reference 600 Instruments, USA) was polished with alumina slurry and cleaned with ethanol and DI water. A conventional three-electrode system was used with SCE (saturated KCl) as the reference electrode and Pt foil as counter electrode. The potential values are corrected to the reverse hydrogen electrode (RHE) according the equation E(RHE)=E

(SCE)+0.245+0.0591pH V. Typically, 5.0 mg of sample and 20.0 μL Nafion solution (5 wt%) were dispersed in mixed solution containing deionized water and ethanol with volume ratio of 1:1 by sonicating for 1 h to form a homogeneous ink. Then 5.0 μL of the dispersion was loaded onto a glassy carbon electrode. The cathodic current density was calculated by the geometric area of GCE which is 0.1256 cm^2. Prior to each electrochemical measurement, the electrolyte solution was purified with O_2 for 30 min to saturate the electrolyte and the O_2 flow was maintained over the solution during the test. Linear sweep voltammogram curves were examined in 1.0 M KOH (pH=14). The scan rate is 20 mV·s^{-1} and the scan region ranges from 0 to 0.8 V vs SCE, AC impedance spectra for different electro-catalysts at overpotential of 0.65 V vs SCE from 10^5 to 10^{-2} Hz with an AC voltage of 5 mV.

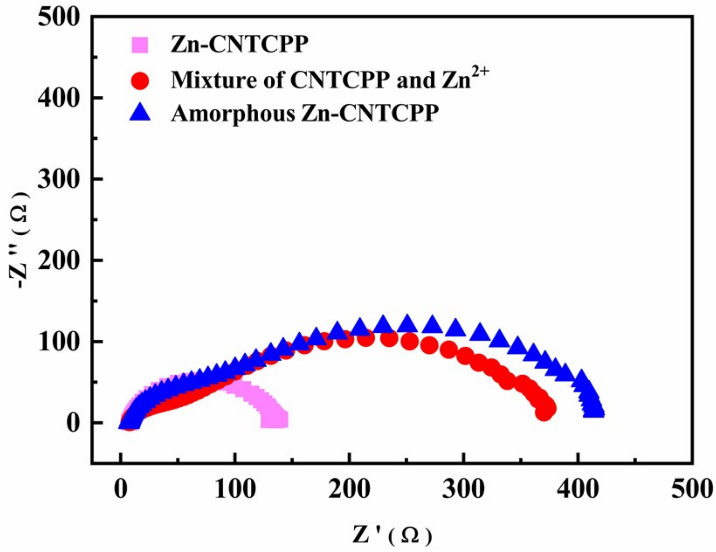

Fig. S6 Nyquist plots examined at 0.5 V (vs SCE) for **Zn-CNTCPP**.