

Supporting Information

**Pyrolyzed Cobalt Porphyrin-Based Conjugated Mesoporous
Polymers as Bifunctional Catalysts for Hydrogen Production and
Oxygen Evolution in Water**

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Experimental details

Materials. All chemicals such as pinacol ($C_6H_{14}O_2$, 98%), 4-formylphenylboronic acid ($C_7H_7BO_3$, 97%), pyrrole (C_4H_5N , 99%), 1,4-benzenediboronic acid ($C_6H_8B_2O_4$, 96%), 4,4'-dibromobiphenyl ($C_{12}H_8Br_2$, 98%), boron trifluoride diethyl etherate ($BF_3 \cdot C_4H_{10}O$, 98%), propionic acid ($C_3H_6O_2$, 99.5%), cobalt acetate tetrahydrate ($Co(OAc)_2 \cdot 4H_2O$, 99.5%), *p*-chloranil ($C_6Cl_4O_2$, 97%), tetrakis(triphenylphosphine)palladium(0) ($C_{72}H_{60}P_4Pd$, 99%), potassium carbonate (K_2CO_3 , 99%), 5 wt% Nafion solution, and potassium hydroxide (KOH, 85%) were purchased from Sigma Aldrich or Alfa Aesar, which were used without further purification. All organic solvents (benzene, THF, $CHCl_3$, MeOH, Et_3N , nitrobenzene, DMF, AcOH, and 1,4-dioxane) were obtained from China Medicine Shanghai Chemical Reagent Co. and used as received unless otherwise stated. All the aqueous electrolyte solutions involved in this report were freshly prepared using Millipore water ($\sim 18.0 \text{ M}\Omega \cdot \text{cm}$ resistivity at room temperature).

Synthesis

5,10,15,20-tetrakis(4'-bromophenyl)porphyrin (TBrPP), 5,10,15,20-tetrakis(4'-boronicacid-phenyl)porphyrin (TBPP) and cobalt (II) 5,10,15,20-tetrakis(4'-bromophenyl)porphyrin (CoTBrPP) were synthesized following a reported procedure from reference.^{S1-S3}

Cobalt (II) 5,10,15,20-tetrakis(4'-boronicacid-phenyl)porphyrin (CoTBPP). To a suspension of TBPP (200 mg, 0.18 mmol) in 20 mL of DMF was added with

Co(OAc)₂·4H₂O (460 mg, 1.85 mmol). After refluxed at 160 °C for 3 h under Ar atmosphere, the precipitate was washed thoroughly by centrifugation with deionized water (20 mL×3) and MeOH (20 mL×6) until the supernatant was colorless. The residue was dried in vacuum oven to give CoTBPP as a red powder (190 mg, 90%). MALDI-TOF MS *m/z* = 1175.1936 (M⁺), Calcd. for C₆₈H₇₂B₄CoN₄O₈⁺: 1175.5054 (Figure S1a). UV-vis (CH₂Cl₂) λ_{max} (nm) 412, 527 (Figure S1b).

CoP-2ph-CMP. To a suspension of CoTBrPP (42 mg, 43 μmol) and CoTBPP (51 mg, 43 μmol) in 8 mL of 1, 4-dioxane under Ar atmosphere was added with an aqueous solution (2.0 mL) of K₂CO₃ (60 mg, 430 μmol) and tetrakis(triphenylphosphine)palladium(0) (2.5 mg, 2.2 μmol). The mixture was further purged with Ar for another 0.5 h and stirred at 100 °C for 72 h. Upon cooling, the solid was collected by filtration and the precipitate was washed thoroughly with water, methanol, THF, CHCl₃, and acetone, then rigorously extracted by Soxhlet for 24 h with THF, CHCl₃, methanol, and acetone, respectively. Finally, the obtained residual was dried at room temperature in vacuum oven to give CoP-2ph-CMP (42 mg, 73%) as a dark red solid.

CoP-3ph-CMP. To a suspension of CoTBrPP (180 mg, 182 μmol) and 1,4-benzenediboronic acid (61 mg, 367 μmol) in 20 mL of 1, 4-dioxane under Ar atmosphere was added with an aqueous solution (5.0 mL) of K₂CO₃ (252 mg, 1820 μmol) and tetrakis(triphenylphosphine)palladium(0) (10.5 mg, 9 μmol). The mixture was further purged with Ar for another 0.5 h and stirred at 100 °C for 72 h. Upon cooling, the solid was collected by filtration and the precipitate was washed thoroughly

with water, methanol, THF, CHCl_3 , and acetone, then rigorously extracted by Soxhlet for 24 h with THF, CHCl_3 , methanol, and acetone, respectively. Finally, the obtained residual was dried at room temperature in vacuum oven to give CoP-3ph-CMP (121 mg, 81%) as a dark red solid.

CoP-4ph-CMP. To a suspension of 4,4'-dibromobiphenyl (74 mg, 237 μmol) and CoTBPP (140 mg, 119 μmol) in 16 mL of 1,4-dioxane under Ar atmosphere was added with an aqueous solution (4.0 mL) of K_2CO_3 (164 mg, 1190 μmol) and tetrakis(triphenylphosphine)palladium(0) (7 mg, 6 μmol). The mixture was further purged with Ar for another 0.5 h and stirred at 100 °C for 72 h. Upon cooling, the solid was collected by filtration and the precipitate was washed thoroughly with water, methanol, THF, CHCl_3 , and acetone, then rigorously extracted by Soxhlet for 24 h with THF, CHCl_3 , methanol, and acetone, respectively. Finally, the obtained residual was dried at room temperature in vacuum oven to give CoP-4ph-CMP (95 mg, 82%) as a dark red solid.

Pyrolysis procedure for Co-2ph-CMP. The pyrolysis procedure of CoP-2ph-CMP was carried out under N_2 atmosphere in tube furnace. The samples were first heated from the room temperature to 800 °C at a heating rate of 3 °C/min, and then pyrolyzed at this temperature for 2 h. Finally, it is allowed to cool down to give CoP-2ph-800-CMP as a black powder. The N_2 flow was kept at 100 sccm during the whole process. In addition, CoP-3ph-800-CMP and CoP-4ph-800-CMP were also prepared following similar pyrolysis procedure.

Characterizations. High-resolution MALDI-TOF mass spectrometry (HRMS) data were collected on a Bruker Daltonics Inc. LTQ Orbitrap XL hybrid Fourier Transform High-resolution Mass Spectrometer. UV-vis spectra were obtained for samples in standard glass cuvettes with a UNIC-3802 spectrophotometer. Scanning electron microscopy (SEM) pictures and transmission electron microscopy (TEM) images were taken using a SIRION200 Schottky field emission scanning electron microscope and a JEM-2011 electron microscope, respectively. Fourier transformed-Infrared spectroscopy (FT-IR) spectra were performed on a Thermo Fisher Scientific instrument (Nicolet iS10). Powder X-ray diffraction (PXRD) patterns were collected on D/max-TTR III X-ray diffractometer with a scan rate of 5°/min. The nitrogen sorption measurements were carried out on Quantachrome instrument (ASIQM0000-5). The surface area and the pore size distribution was analyzed using Brunauer-Emmett-Teller (BET) method and Quenched Solid Density Functional Theory (QSDFT), respectively. X-ray photoelectron spectroscopy (XPS) data were obtained via a Thermo ESCALAB 250 X-ray photoelectron spectroscopy system equipped with a 150-watt Al K Alpha excitation source.

Electrochemistry. All the electrochemical measurements were performed on an electrochemical work station (CHI760E, purchased from Shanghai Chen Hua Instrument Co., Ltd.) in a standard three-electrode system in 1 M KOH solution. The modified glassy carbon electrode (GCE, 3 mm, 0.071 cm²) was used as the working electrode, while an Ag/AgCl electrode (3 M KCl, corrected before each test) served as the reference electrode and a platinum wire served as the counter electrode. All the

potentials in this report were versus the reversible hydrogen electrode (RHE) unless otherwise noted, according to the equation:

$$E = E_{appl} + E_{Ag/AgCl} + 0.059\text{pH}$$

Where E_{appl} represents the applied potential versus Ag/AgCl, and $E_{Ag/AgCl}$ is the potential of the reference electrode (Ag/AgCl electrode). The catalyst ink was prepared according to the following proportions: 2 mg of catalyst powders, 900 μL of ethanol and 100 μL of 5 wt% Nafion solution. Then the suspension was vigorously sonicated for 30 min. For fabricating the working electrode, 5 μL of the as-prepared homogeneous ink was carefully dropcast onto the polished mirror-like GCE (catalyst loading: $\sim 0.14 \text{ mg/cm}^2$) and it was allowed to dry in air at room temperature.

References

- (1) Liu, X. M.; Xu, Y. H.; Guo, Z. Q.; Nagai, A.; Jiang, D. L. *Chem. Commun.* **2013**, 49, 3233.
- (2) Toi, H.; Nagai, Y.; Aoyama, Y.; Kawabe, H.; Aizawa, K.; Ogoshi, H. *Chem. Lett.* **1993**, 1043.
- (3) Wan, S.; Gandara, F.; Asano, A.; Furukawa, H.; Saeki, A.; Dey, S. K.; Liao, L.; Ambrogio, M. W.; Botros, Y. Y.; Duan, X. F.; Seki, S.; Stoddart, J. F.; Yaghi, O. M. *Chem. Mater.* **2011**, 23, 4094.

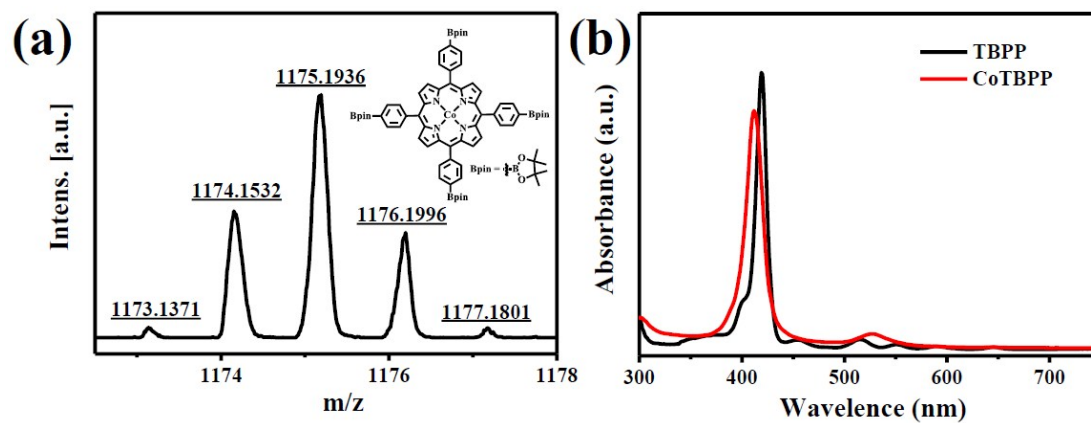


Figure S1. (a) HRMS data for CoTBPP. (b) UV-vis spectra for TBPP (black) and CoTBPP (red).

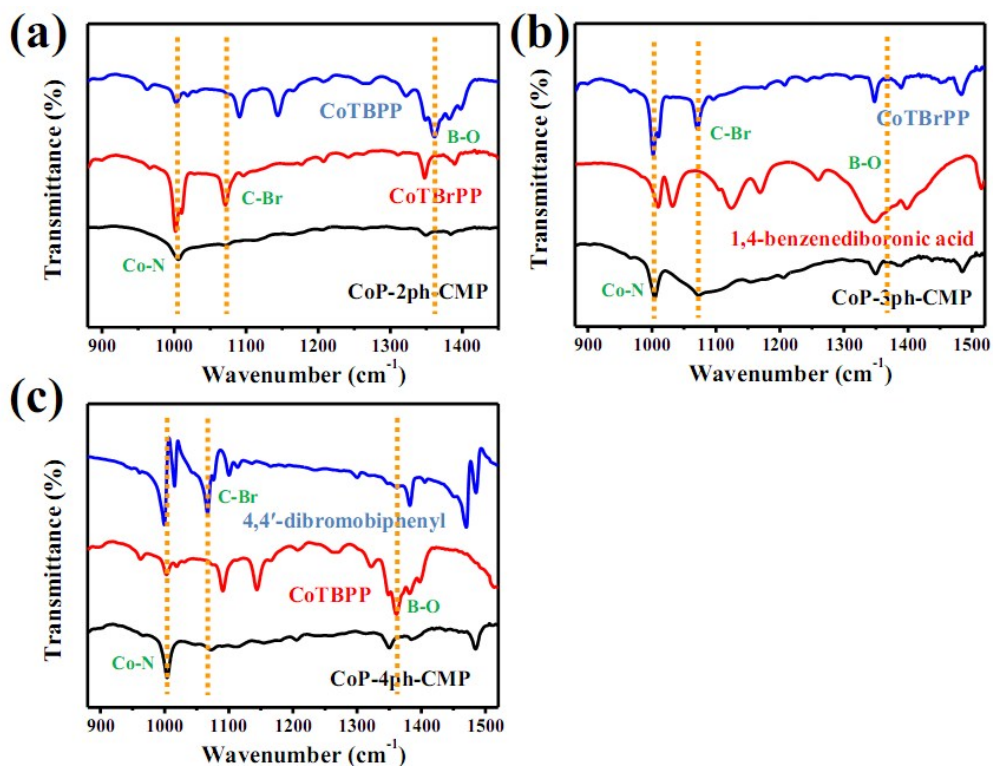


Figure S2. FT-IR spectra for (a) CoTBPP (blue), CoTBrPP (red), and CoP-2ph-CMP (black). (b) CoTBrPP (blue), 1,4-benzenediboronic acid (red), and CoP-3ph-CMP (black). (c) 4,4'-dibromobiphenyl (blue), CoTBPP (red), and CoP-4ph-CMP (black).

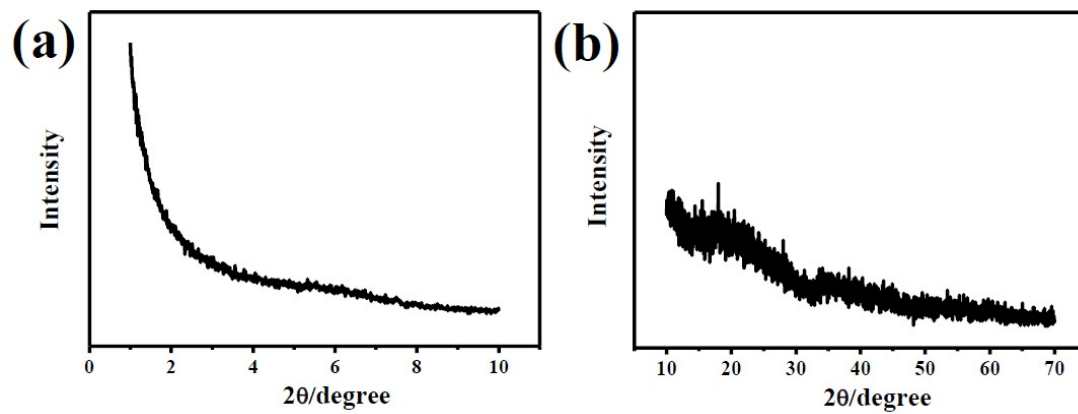


Figure S3. Powder XRD pattern of CoP-2ph-CMP: (a) $2\theta = 1^\circ$ to 10° ; (b) $2\theta = 10^\circ$ to 70° .

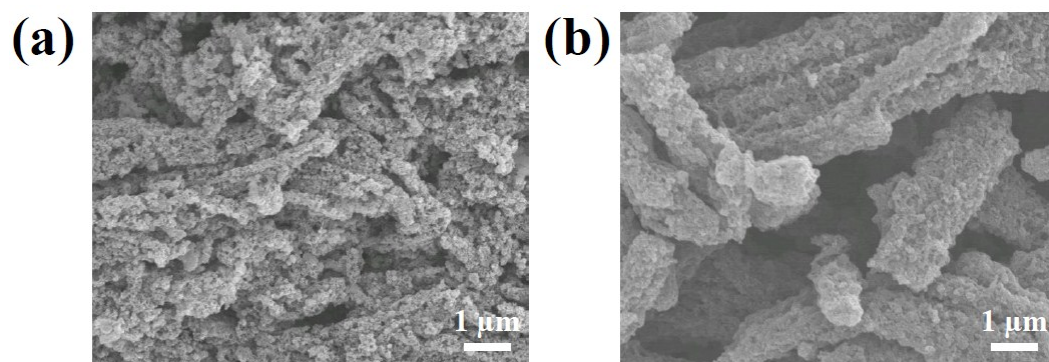


Figure S4. SEM images of (a) CoP-3ph-CMP-800 and (b) CoP-4ph-CMP-800.

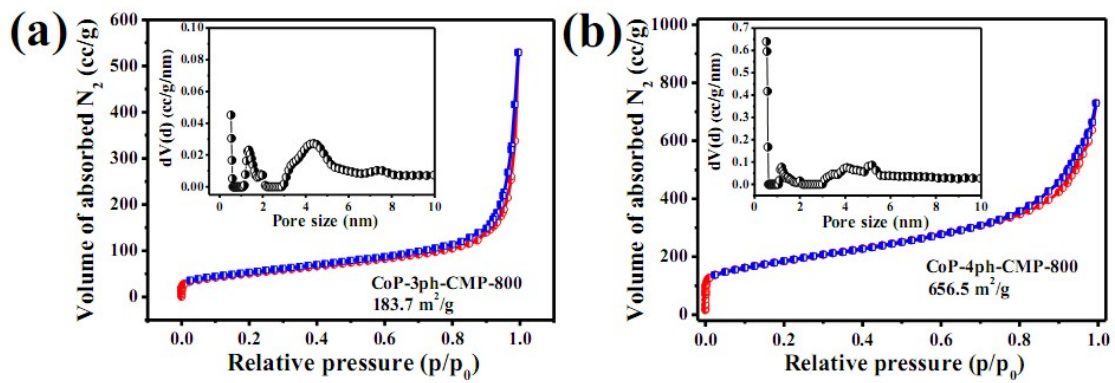


Figure S5. Nitrogen sorption isotherm plot and DFT pore size distribution (inset) of (a) CoP-3ph-CMP-800 and (b) CoP-4ph-CMP-800.

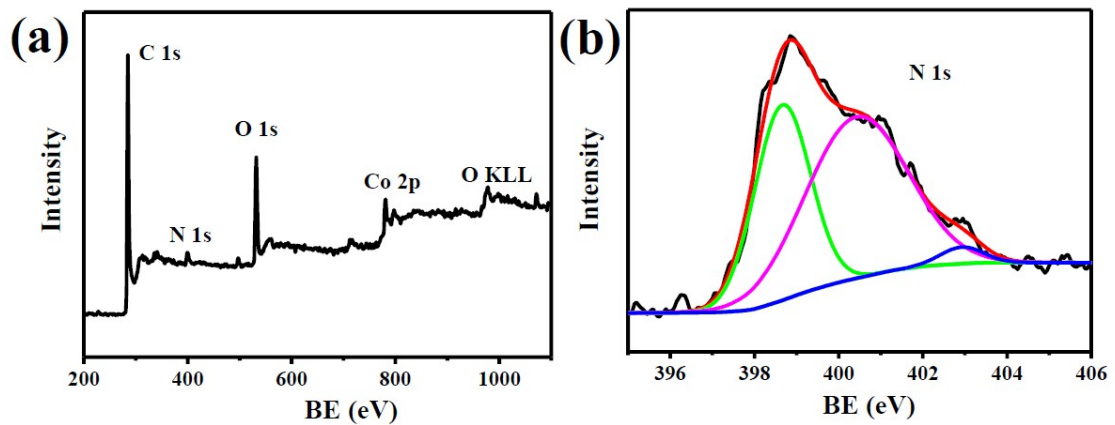


Figure S6. (a) XPS survey scan of CoP-2ph-CMP-800. (b) The high-resolution N 1s XPS spectrum of CoP-2ph-CMP-800.

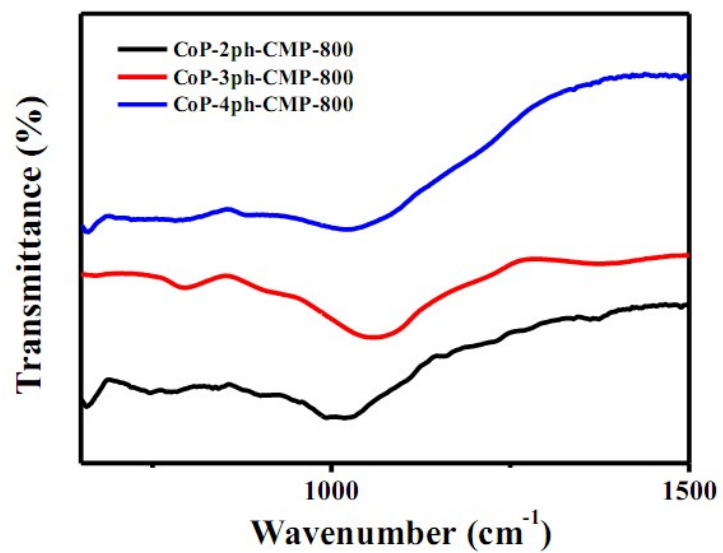


Figure S7. FT-IR spectrum for CoP-2ph-CMP-800 (black), CoP-3ph-CMP-800 (red), and CoP-4ph-CMP-800 (blue).

Table S1 ICP-AES analysis for cobalt content

	CoP-2ph-CMP-800	CoP-3ph-CMP-800	CoP-4ph-CMP-800
Sample mass (μg)	2180	2080	1980
Cobalt content (μg)	109	78	71
Cobalt content (wt%)	5.0	3.8	3.6