Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Cobalt Porphyrin Intercalation into Zirconium Phosphate Layers for Electrochemical Water Oxidation

Isabel Barraza Alvarez,[a‡] Yanyu Wu,[a‡] Joel Sanchez,[b] Yulu Ge,[a] Mario V. Ramos-Garcés,[c] Tong Chu,[a,d] Thomas F. Jaramillo,[b] Jorge L. Colón,[c] and Dino Villagrán[a]*

[a]Department of Chemistry and Biochemistry, The University of Texas at El Paso, El Paso, TX 79968, USA

[b]Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA

[c]Department of Chemistry, University of Puerto Rico at Río Piedras, 17 Ave. Universidad STE 1701, San Juan, PR 00925-2537, USA

[d]Department of Chemistry, Beijing Normal University, Beijing 100875, China

Table of contents

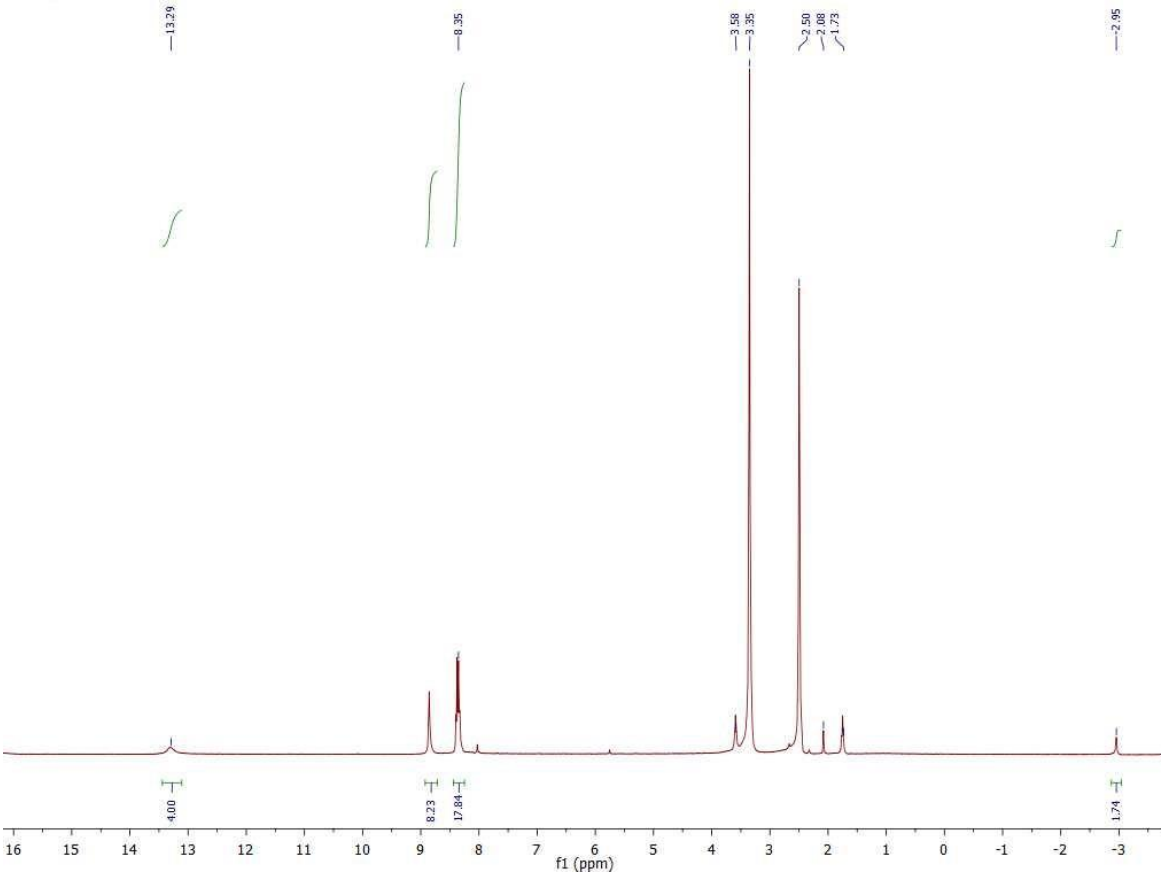


Figure S1. ^{1}H NMR spectrum of H_2TcPP in d^6-DMSO with residual peak for water (3.35 ppm).

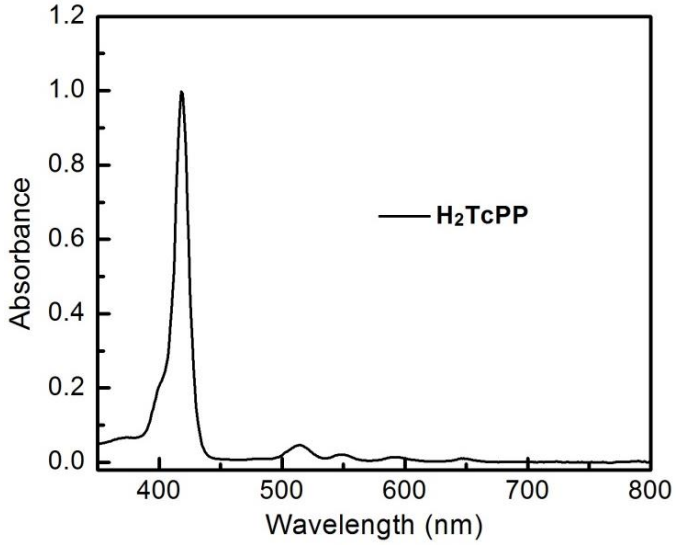
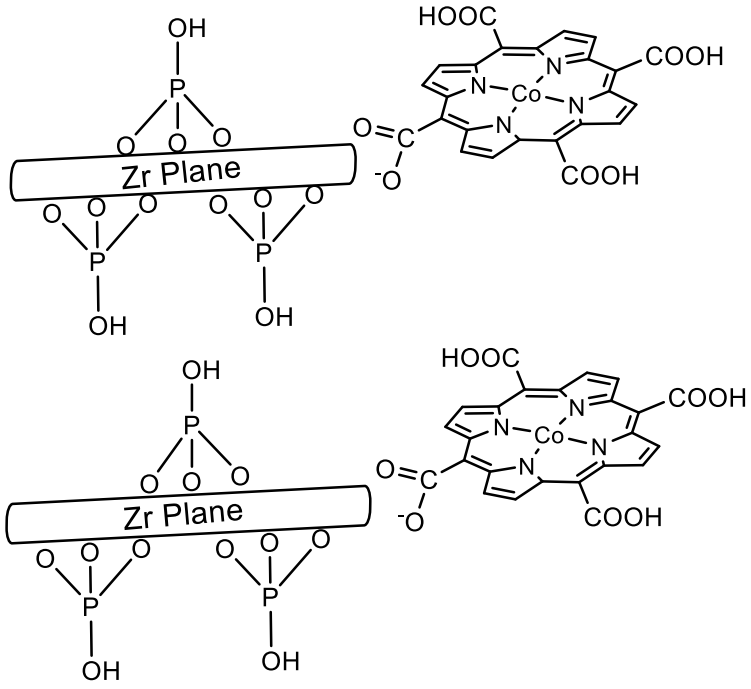


Figure S2. UV-Vis spectrum of H_2TcPP in EtOH.



Scheme S1. Proposed scheme of CoTcPP molecule intercalated by ZrP.

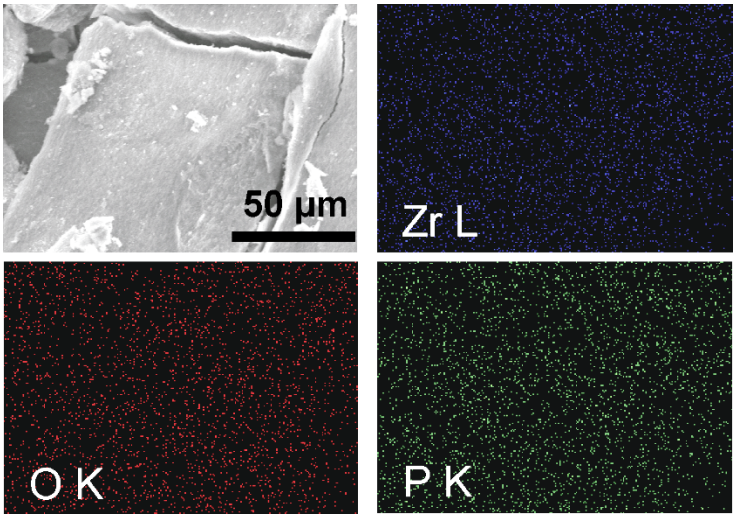


Figure S3. SEM image and the according elemental mapping graphs of pristine α-ZrP.

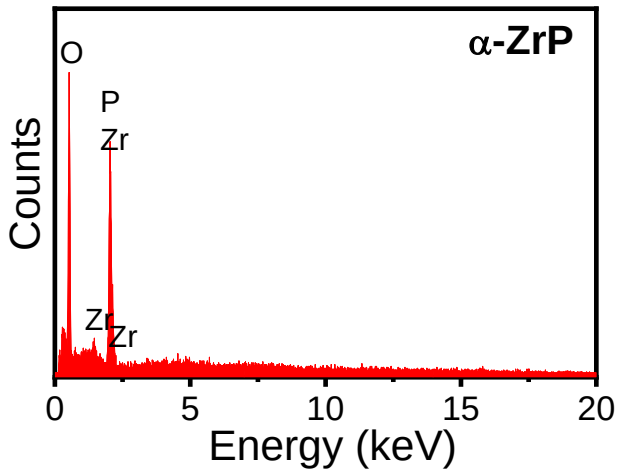


Figure S4. EDX spectrum of pristine α-ZrP.

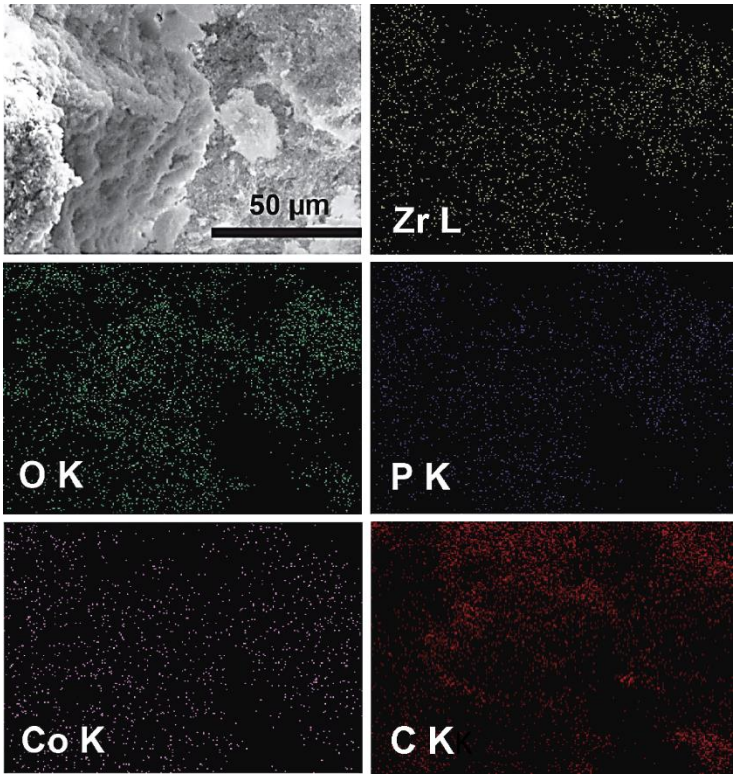


Figure S5. SEM image and the according elemental mapping graphs of CoTcPP/ZrP.

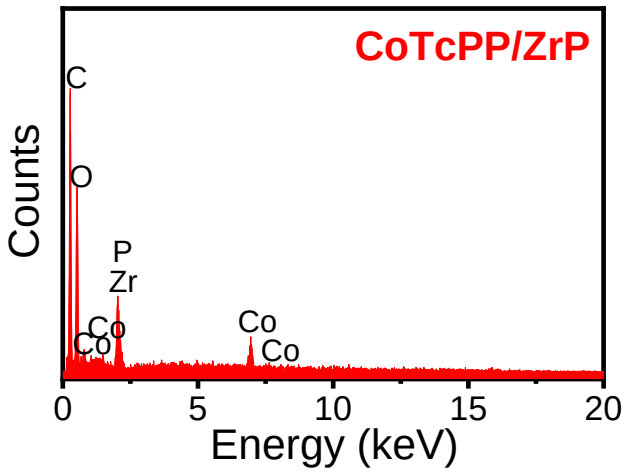


Figure S6. EDX spectrum of CoTcPP/ZrP.

Table S1. Comparison of ZrP and metalloporphyrin-derived OER electrocatalysts.

Catalyst	Overpotential at the corresponding current density (V)	Current density (mV/cm^2)	Tafel slope (mV/dec)	Reference
CoTcPP/ZrP	0.467	10	76.4	This work
CoTcPP/ZrP	0.380 (1.61 V vs. RHE)	onset	/	This work
Co(II):α-ZrP $_{adsorbed}$	0.491	10	79.0	1
Co(II):α-ZrP $_{exfoliated}$	0.450	10	53.4	1
Co/$ZrP_{\alpha,hexagonal}$	0.451	3	79	2
CuCMP	0.450	10	62	3
CoPc350@FTO	0.580	10	108	4
CoP-2ph-CMP-800	0.37	10	86	5
CoP-4ph-CMP-800	0.43	10	Not reported	5
CoPc1	0.620 (1.85 V vs. RHE)	onset	Not reported	6
CoPc2	0.57 (1.80 V vs. RHE)	onset	Not reported	6
CoPc3	0.480 (1.71 V vs. RHE	onset	120	6

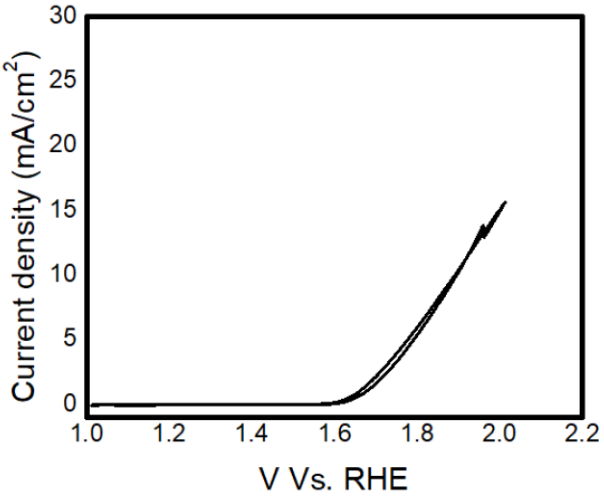


Figure S7. Cyclic voltammogram of glassy carbon working electrode modified by physical combination of CoTcPP, ZrP and carbon black in 0.1 M KOH electrolyte.

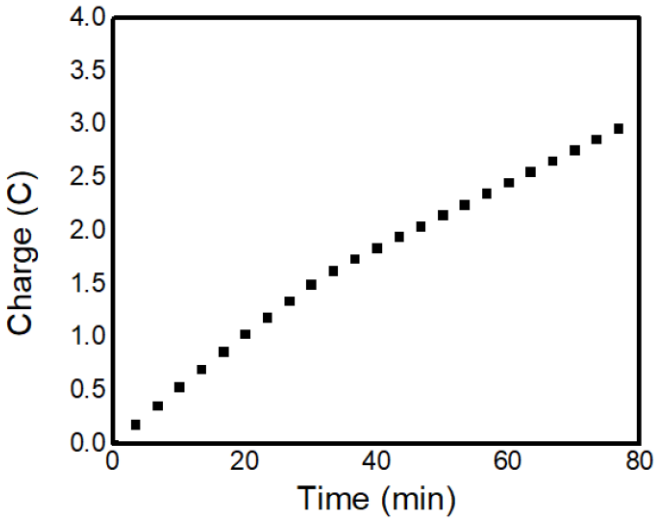


Figure S8. Bulk electrolysis measurement of CoTcPP/ZrP in 0.1 M KOH electrolyte solution at a controlled potential of 1.9 V Vs. RHE.

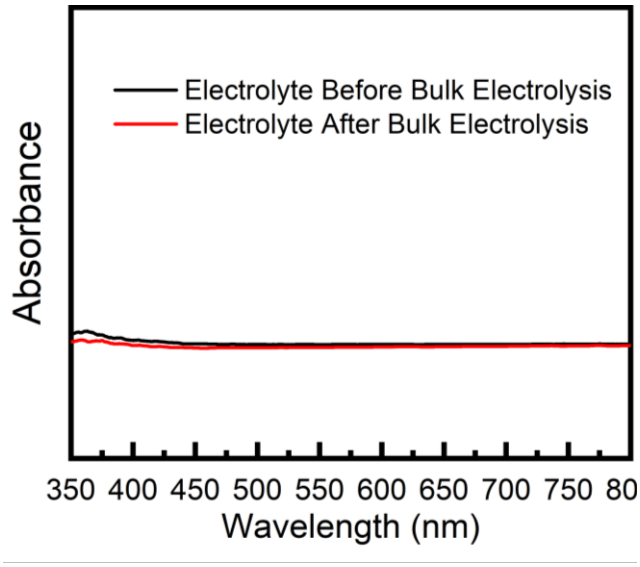


Figure S9. Overlaid UV-Vis spectra of 0.1 M KOH electrolyte before and after long-term electrolysis using CoTcPP/ZrP modified working electrode.

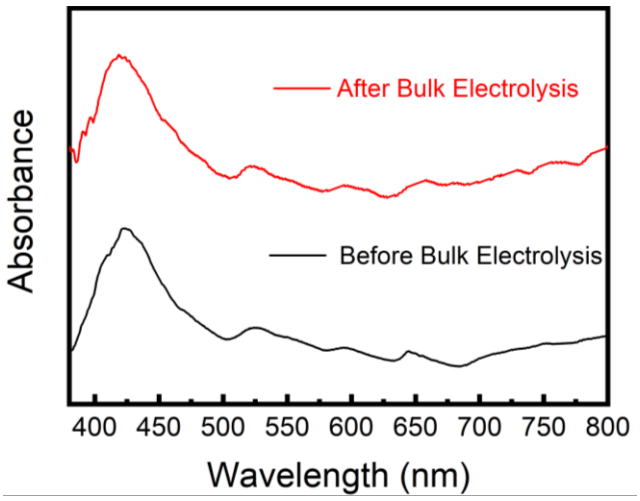


Figure S10. Overlaid UV-Vis spectra of CoTcPP/ZrP combined with carbon black in EtOH suspension before and after long-term electrolysis performed in 0.1 M KOH solution.

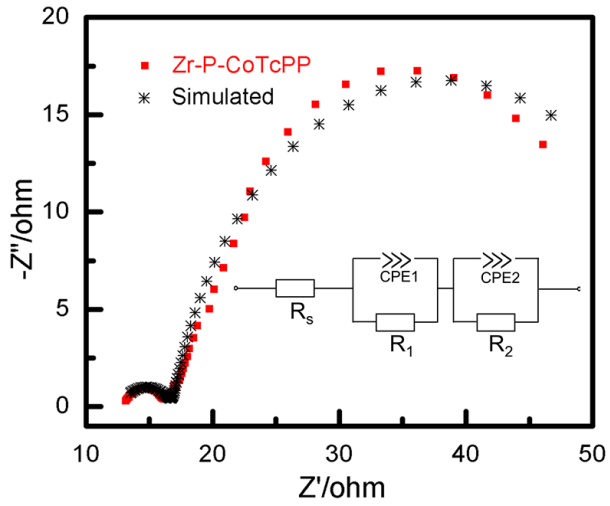


Figure S11. Electrochemical impedance spectroscopy and electrical equivalent circuit (EEC) used to simulate the impedance spectra of oxygen evolution reaction on the CoTcPP/ZrP electrode in 0.1 M KOH aqueous solution with simulation fit.

Table S2. Electrical equivalent circuit (EEC) parameters for CoTcPP/ZrP simulated from the impedance spectra.

Rs (ohm)	CPE ($F \cdot s^{a1-1}$)	R1 (ohm)	CPE2 ($F \cdot s^{a2-1}$)	R2 (ohm)	a1	a2
12.62	0.5304e-3	4.278	0.02053	42.31	0.5561	0.8532

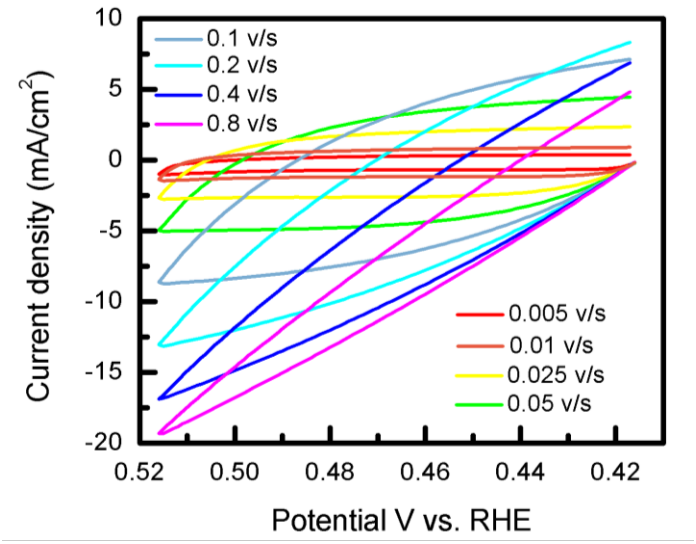


Figure S12. Cyclic voltammograms of as-prepared CoTcPP/ZrP at different scan rates in the 0.1 V potential window with no faradaic process in 0.1 M KOH solution.

References:

(1) Ramos-Garcés, M. V.; Sanchez, J.; Del Toro-Pedrosa, D. E.; Barraza-Alvarez, I.; Wu, Y.; Valle, E.; Villagrán, D.; Jaramillo, T. F.; Colón, J. L. Transition Metal-Modified Exfoliated Zirconium Phosphate as an Electrocatalyst for the Oxygen Evolution Reaction. *ACS Appl. Energy Mater*. **2019**, *2* (5), 3561–3567. https://doi.org/10.1021/acsaem.9b00299.

(2) Ramos-Garcés, M. V.; Sanchez, J.; La Luz-Rivera, K.; Toro-Pedrosa, D. E. D.; Jaramillo, T. F.; Colón, J. L. Morphology Control of Metal-Modified Zirconium Phosphate Support Structures for the Oxygen Evolution Reaction. *Dalton Trans.* **2020**, 49, 3892–3900. https://doi.org/10.1039/C9DT04135D.

(3) Cui, S.; Qian, M.; Liu, X.; Sun, Z.; Du, P. A Copper Porphyrin-Based Conjugated Mesoporous Polymer-Derived Bifunctional Electrocatalyst for Hydrogen and Oxygen Evolution. *ChemSusChem* **2016**, *9* (17), 2365–2373. https://doi.org/10.1002/cssc.201600452.

(4) Joya, K. S.; Ul Ain Babar, N.; Gilani, S. R.; Yasmeen, F.; Sarfaraz, M.; Ikram, S.; Colak, S. G.; Ocakoglu, K.; Ince, M. Heterogeneous Electrocatalysts for Efficient Water Oxidation Derived from Metal Phthalocyanine. *ChemistrySelect* **2018**, *3* (40), 11357–11366. https://doi.org/10.1002/slct.201802089.

(5) Jia, H.; Yao, Y.; Gao, Y.; Lu, D.; Du, P. Pyrolyzed Cobalt Porphyrin-Based Conjugated Mesoporous Polymers as Bifunctional Catalysts for Hydrogen Production and Oxygen Evolution in Water. *Chem. Commun.* **2016**, *52* (92), 13483–13486. https://doi.org/10.1039/C6CC06972J.

(6) Morlanés, N.; Joya, K. S.; Takanabe, K.; Rodionov, V. Perfluorinated Cobalt Phthalocyanine Effectively Catalyzes Water Electrooxidation. *Eur. J. Inorg. Chem.* **2015**, *2015* (1), 49–52. https://doi.org/10.1002/ejic.201403015.