Supplementary Information (SI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2025

Supporting information

Big pyridyl Schiff base π -conjugated skeleton based cobalt/iron metal complexes: a bimetallic electrocatalyst for oxygen evolution reaction

Yuwei Dong,^a Mingyu Wu,^a Yu Ren,^a Zhou Yu*^a and Zhen Zhao*^{ab}

^a Institute of Catalysis for Energy and Environment, College of Chemistry & Chemical Engineering, Shenyang Normal University, Shenyang, Liaoning 110034, People's Republic of China
^b State Key Laboratory of Heavy Oil Processing, College of Science, China University of Petroleum, Beijing 102249, People's Republic of China

* Corresponding author. E-mail address: yuzhou198807@163.com and zhenzhao@cup.edu.cn

Experimental section

Instruments and measurements

Elemental analyses of C, H and N were conducted using a Vario EL elemental analyzer. ¹H and ¹³C NMR spectra of PM-TPDA were obtained using a Bruker Avance– 400 MHz spectrometer in CDCl₃ at 298 K. FT–IR spectra were recorded using a TENSOR II (Bruker) spectrophotometer using a KBr pellet in the range of 4000–400 cm⁻¹. UV–vis spectra were recorded by using a Shimadzu UH5300 (Japan) spectrophotometer in the range of 200–800 nm at room temperature. Fluorescence spectra were obtained using a Hitachi F-7100 FL spectrophotometer equipped with a 150 W xenon lamp as the excitation and emission source at room temperature, and the slit width of the acetonitrile solution fluorescence spectra was 5.0 nm both the excitation and emission, and that for the solid-state fluorescence spectra was 5.0 nm for excitation and 1.0 nm for emission. The sample concentration for UV–vis and fluorescence spectra testing was 2×10^{-5} mol L⁻¹ in CH₃CN.

Synthesis of CoPM-TPDA. PM-TPDA (416.15 mg, 0.502 mmol, 1 eq.) was dissolved in CH₃CN (15 mL). Then a solution of Co(NO₃)₂·6H₂O (582.91 mg, 2.002 mmol, 4 eq.) in CH₃CN (15 mL) was added. The resulting mixture was heated under reflux for 24 hours at 90 °C. After cooling down, the mixture was washed with water (3×15 mL) and filtered and evaporated. Finally, the obtained product was dried under vacuum at 60 °C for 24 hours to gain dark purple CoPM-TPDA in a yield of 89%. FT-IR: 3279(w), 3042(w), 1671(w), 1594(w), 1495(m), 1444(w), 1387(w), 1282(s), 1158(m), 1107(m), 1018(m), 947(w), 917(w), 827(m), 767(m), 689(w), 555(w), 512(w), 416(w) cm⁻¹.

Synthesis of Co₃FePM-TPDA. PM-TPDA (415.91 mg, 0.501 mmol, 1 eq.) was dissolved in CH₃CN (15 mL). Then a solution of Co(NO₃)₂·6H₂O (473.22 mg, 1.502 mmol, 3 eq.) and Fe(NO₃)₃·9H₂O (202.95 mg, 0.502 mmol, 1 eq.) in CH₃CN (15 mL) was added. The resulting mixture was heated under reflux for 24 hours at 90 °C. After cooling down, the mixture was washed with water (3 × 15 mL) and filtered and evaporated. Finally, the obtained product was dried under vacuum at 60 °C for 24 hours

to gain dark purple Co₃FePM-TPDA in a yield of 85%. FT-IR: 3292(w), 3086(w), 1669(w), 1571(m), 1497(m), 1448(w), 1320(s), 1285(s), 1158(w), 1103(m), 1037(w), 947(w), 823(m), 766(m), 687(m), 489(m), 418(w) cm⁻¹.

Synthesis of CoFe₃PM-TPDA. PM-TPDA (419.06 mg, 0.506 mmol, 1 eq.) was dissolved in CH₃CN (15 mL). Then a solution of Co(NO₃)₂·6H₂O (146.81 mg, 0.504 mmol, 1 eq.) and Fe(NO₃)₃·9H₂O (608.95 mg, 1.507 mmol, 3 eq.) in CH₃CN (15 mL) was added. The resulting mixture was heated under reflux for 24 hours at 90 °C. After cooling down, the mixture was washed with water (3×15 mL) and filtered and evaporated. Finally, the obtained product was dried under vacuum at 60 °C for 24 hours to gain dark purple CoFe₃PM-TPDA in a yield of 93%. FT-IR: 3253(w), 3083(w), 1671(w), 1571(m), 1526(m), 1499(m), 1324(s), 1282(s), 1160(w), 1101(m), 1023(w), 827(w), 763(w), 689(w), 489(w), 419(w) cm⁻¹.

Synthesis of Co₂Fe₂PM-TPDA. PM-TPDA (419.42 mg, 0.506 mmol, 1 eq.) was dissolved in CH₃CN (15 mL). Then a solution of Co(NO₃)₂·6H₂O (295.36 mg, 1.015 mmol, 2 eq.) and Fe(NO₃)₃·9H₂O (410.56 mg, 1.016 mmol, 2 eq.) in CH₃CN (15 mL) was added. The resulting mixture was heated under reflux for 24 hours at 90 °C. After cooling down, the mixture was washed with water (3×15 mL) and filtered and evaporated. Finally, the obtained product was dried under vacuum at 60 °C for 24 hours to gain dark purple Co₂Fe₂PM-TPDA in a yield of 91%. FT-IR: 3270(w), 3086(w), 1671(w), 1571(m), 1528(m), 1495(m), 1322(s), 1285(s), 1158(w), 1100(m), 1034(w), 947(w), 827(w), 766(w), 687(w), 488(w), 416(w) cm⁻¹.

Synthesis of FePM-TPDA. PM-TPDA (419.95 mg, 0.507 mmol, 1 eq.) was dissolved in CH₃CN (15 mL). Then a solution of Fe(NO₃)₃·9H₂O (809.45 mg, 2.004 mmol, 4 eq.) in CH₃CN (15 mL) was added. The resulting mixture was heated under reflux for 24 hours at 90 °C. After cooling down, the mixture was washed with water (3×15 mL) and filtered and evaporated. Finally, the obtained product was dried under vacuum at 60 °C for 24 hours to gain dark purple FePM-TPDA in a yield of 83%. FT-IR: 3255(w), 3082(w), 1665(w), 1571(m), 1501(m), 1412(w), 1328(w), 1284(s), 1160(w), 1100(s), 1023(m), 947(w), 829(m), 760(m), 693(m), 646(m), 448(w) cm⁻¹.

Electrochemical Measurements

The electrochemical data of all catalysts were performed by CHI660E electrochemical workstation used typical three-electrode system in a 1 M KOH and simulated seawater (1.0 M KOH + 0.5 M NaCl). The glassy carbon (GC) electrode (3 mm diameter) was utilized as the working electrode. The Ag/AgCl electrode and Pt mesh were used as the reference electrode and counter electrode, respectively. 2 mg sample was dispersed in 500 µL Nafion (5 wt%) -water-isopropyl alcohol mixture solution with a volume ratio of 0.05:4:1 by sonicating. Then, 6 μ L of the dispersion was deposited onto a GC and dried in air overnight. Polarization curves were carried out at a scanning rate of 5 mV s⁻¹. In this work, all potentials were converted to reversible hydrogen electrode (RHE) potential. The long-term durability test was performed using chronoamperometry measurement. Electrochemical impedance spectroscopy (EIS) measurements were measured at potentiostatic mode with 5 mV amplitude in a frequency range from 100 kHz to 0.01 Hz. The electrochemical double layer capacitance (C_{dl}) was assessed by cyclic voltammetry (CV) at varied scan rates of 10, 20, 40, 60, 80 and 100 mV s⁻¹. The overall water splitting was performed in a twoelectrode system, the Co₃FePM-TPDA suspensions was then dropped on the treated nickel foam (NF).

Computational Details

In our work, all electrochemical DFT calculations were carried out by the Vienna ab initio simulation package (VASP).^{S1,S2} Spin-polarization calculations were performed. The electron exchange-correlation effect was described by the Perdew-Burke-Ernzerhof functional within the generalized gradient approximation (GGA-PBE).^{S3} The PAW pseudopotential was used to describe the interactions between core and valence electrons.^{S4} The plane-wave basis set with an energy cutoff of 400 eV was used in these calculations. For all the geometric optimization, the conjugate gradient algorithm was used in ionic optimization and the convergence threshold was set to 10⁻⁵ eV in electronic relaxation and 0.02 eV/Å in Hellmann-Feynman force on each atom. Considering the long-range van der Waals (vdW) interactions, we used the DFT-D3 method with Becke-Jonson damping.^{S5,S6} The vacuum layer thickness was set to 15 Å,

which is large enough to avoid interlayer interactions. Brillouin zone sampling was set to the Γ point only.

The DFT generation energies of OOH*, O* and OH* are calculated with reference to $H_2O(g)$ and $H_2(g)$ according to the following Equations (1)-(3):

$$\Delta E_{ads}(OOH^*) = E_{OOH^*} - E_{*} - (2E_{H_{2O}} - 3/2E_{H_2})$$
(1)

$$\Delta E_{ads}(O^*) = E_{O^*} - E_{*} - (E_{H2O} - E_{H2})$$
(2)

$$\Delta E_{ads}(OH^*) = E_{OH^*} - E_{*} - (E_{H2O} - 1/2E_{H2})$$
(3)

where the E_* , E_{OH^*} , E_{O^*} and E_{OOH^*} are the total energies of the catalyst substrate without and with the adsorption of OH, O or OOH, respectively. E_{H^2} and $E_{H^{2O}}$ represent the total energy of separating H_2 and H_2O . The Computational Hydrogen Electrode (CHE) model was applied to calculate the Gibbs free energy change of the adsorbate under acid conditions by Equation (4).

$$G = \Delta E + \Delta Z P E - T \Delta S + \Delta G_{pH} + \Delta G_U \tag{4}$$

where ΔE is the change in the reaction energy calculated directly from the DFT. ΔZEP and ΔS are the zero-point energy and entropy differences, respectively. T is the temperature (298.15K). ΔG_{pH} and ΔG_U are the changes in free energy caused, respectively, by the change in the H⁺ concentration and the free energy changes due to changes in electrode potential. In this study, the pH of the acidic medium is assumed to be zero. ΔG_U represents the amount of free energy correction introduced by the electrode potential difference. Thus, the following equation can be obtained: $\Delta G_U =$ *neU*, where n is the number of transferred electrons, e is the number of charges, and U is the applied electrode potential.

In acidic solutions, OER proceeds via a four-electron transfer pathway as follows:

$$* + H_2O \rightarrow OH^* + H^+ + e^-$$
 (a)

$$OH^* \rightarrow O^* + H^+ + e^-$$
 (b)

$$O^{*}+H_{2}O \rightarrow OOH^{*}+H^{+}+e^{-}$$
 (c)

$$OOH^* \rightarrow * + O_2 + H^+ + e^- \tag{d}$$

where * represents an active site on the catalyst surface, and OH*, O* and OOH* represent three different catalytic intermediates.

Finally, the overpotential (η) of OER can be evaluated by the following formula:

$$\eta = \max{\{\Delta Ga, \Delta Gb, \Delta Gc, \Delta Gd\}/e - 1.23 V}$$
(5)

Gaussian 09 program^{S7} was employed for density functional theory (DFT) calculations. All the optimized structures were performed using DFT method with Beck's three-parameter hybrid exchange functional,^{S8} Lee, and Yang and Parr correlation functional^{S9} B3LYP/6–31G (d,p) for non-metallic atoms and LANL2DZ for metallic atoms. The calculated electronic density plots were prepared using the Gaussview 5.0.8. The Multiwfn^{S10} and VMD^{S11} software were used for more detailed analysis.



Fig. S1. ¹H NMR spectrum of PM-TPDA in CDCl₃.



Fig. S2. ¹³C NMR spectrum of PM-TPDA in CDCl₃.



Fig. S3. FT-IR spectra of 2-PA, TPDA and PM-TPDA.

According to the supplementary **Fig. S3**, the imine-linkage between 2-PA and TPDA was confirmed. TPDA has N–H stretching vibration peaks at 3430 cm⁻¹ and 3346 cm⁻¹, and N–H bending vibration peak at 1620 cm⁻¹,^{S12,S13} and C–N stretching vibration peaks at 1257 cm⁻¹,^{S14} respectively. The peak at 1708 cm⁻¹ could be attributed

to C=O stretching vibration in 2-PA.^{S15} In the spectrum of PM-TPDA, the characteristic absorption peaks of amino and aldehyde groups disappear, and a new peak appears at 1621 cm⁻¹, which is the characteristic absorption peak after the formation of the aldehyde-amine condensation product. It confirms the successful condensation between amino and aldehyde groups.^{S16}



Fig. S4. Molecular electronic potential maps (ESP) of TPDA, PM-TPDA, CoPM-TPDA,

Co₃FePM-TPDA and FePM-TPDA.



Fig. S5. Fluorescence excitation spectrum for the prepared materials.



Fig. S6. The frontier molecular orbitals (HOMO and LUMO) energy gap of TPDA, PM-TPDA, CoPM-TPDA, Co₃FePM-TPDA and FePM-TPDA.



Fig. S7. Transient photocurrent responses of PM-TPDA, CoPM-TPDA, Co₃FePM-TPDA and

FePM-TPDA.



Fig. S8. (a) The OER LSV curves and (b) Tafel plots of Co₃FePM-TPDA, Co₂Fe₂PM-TPDA and

CoFe₃PM-TPDA.



Fig. S9. Cyclic voltammograms in the double-layer region of the electrodes loaded with (a) Co₃FePM-TPDA, (b) CoPM-TPDA, (c) FePM-TPDA, and (d) PM-TPDA in 1.0 M KOH.



Fig. S10. Energy-dispersive spectroscopy elemental mapping images of Co₃FePM-TPDA after



Fig. S11. XPS spectra of Co₃FePM-TPDA, CoPM-TPDA, and FePM-TPDA before and after

OER tests (a) Fe 2p, (b) Co 2p.



Fig. S12. Cyclic voltammograms in the double-layer region of the electrodes loaded with (a) Co₃FePM-TPDA, (b) CoPM-TPDA, (c) FePM-TPDA, and (d) PM-TPDA in simulated seawater electrolyte (1.0 M KOH + 0.5 M NaCl).



Fig. S13. The most stable configurations of top view and side view of Co₃FePM-TPDA. N atoms are in dark blue, C atoms in grey, H atoms in white, Fe atom in purple, and Co atoms in light blue, respectively.



Fig. S14. The Cl⁻ adsorption structure model of Co₃FePM-TPDA and CoPM-TPDA.



Fig. S15. Adsorption energy of Cl⁻ on Co₃FePM-TPDA and CoPM-TPDA surfaces.

Electrocatalysts	Current	Overpotential	Electrolyte	Ref.
	density			
Co ₃ FePM-TPDA	10 mA cm ⁻²	298 mV	1 M KOH	This work
COF-CNT	10 mA cm ⁻²	389 mV	0.1 M KOH	S17
COF-C ₄ N	10 mA cm ⁻²	349 mV	1 M KOH	S18
BP-CN-c	10 mA cm ⁻²	350 mV	1 M KOH	S19
Co TPP/CNT	10 mA cm ⁻²	407 mV	1 M KOH	S20
Fe/Ni-BTC@NF	10 mA cm ⁻²	270 mV	1M KOH	S21
Co-TAPP-COF-Fe	10 mA cm ⁻²	416 mV	1 M KOH	S22
S/N-CMF@Fe _x Co _y Ni _{1-x-}	10 mA cm ⁻²	296 mV	1 M KOH	S23
_y -MOF				
Co-TAPP-COF	10 mA cm ⁻²	473 mV	1 M KOH	S24
Ni-BDC/Ni(OH) ₂	10 mA cm ⁻²	320 mV	1 M KOH	S25
O–Co–N/C	10 mA cm ⁻²	290 mV	1 M KOH	S26

 Table S1 Comparison of activity data for non-noble metal-based OER electrocatalysts in alkaline solution.

References

[S1] G. Kresse and J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comp. Mater. Sci.*, 1996, **6**, 15–50.

[S2] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B*, 1999, **59**, 1758–1775.

[S3] J. P. Perdew, K. Burke and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.*, 1996, 77, 3865.

[S4] P. E. Blöchl, Projector augmented-wave method, Phys. Rev. B, 1994, 50, 17953–17979.

[S5] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.*, 2010, **132**, 154104.

[S6] S. Grimme, Semiempirical GGA-type density functional constructed with a long-range

dispersion correction, J. Comput. Chem., 2006, 27, 1787–1799.

[S7] H. Huang, Y. X. Wang, B. Wang, S. Q. Zhuang, B. Pan, X. Yang, L. Wang and C. L. Yang, Controllably tunable phenanthroimidazole–carbazole hybrid bipolar host materials for efficient green electrophosphorescent devices, *J. Mater. Chem. C*, 2013, 1, 5899–5908.

[S8] S. Chen, Y. K. Wu, Y. Zhao and D. N. Fang, Deep blue organic light-emitting devices enabled by bipolar phenanthro[9,10-*d*]imidazole derivatives, *RSC Adv.*, 2015, **5**, 72009–72018.

[S9] Y. Yuan, J. X. Chen, F. Lu, Q. X. Tong, Q. D. Yang, H. W. Mo, T. W. Ng, F. L. Wong, Z. Q. Guo, J. Ye, Z. Chen, X. H. Zhang and C. S. Lee, Bipolar phenanthroimidazole derivatives containing bulky polyaromatic hydrocarbons for nondoped blue electroluminescence devices with high efficiency and low efficiency roll-off, *Chem. Mater.*, 2013, 25, 4957–4965.

[S10] T. Lu and F. W. Chen, Multiwfn: A multifunctional wavefunction analyzer, *J. Comput. Chem.*, 2012, **33**, 580–592.

[S11] W. Humphrey, A.w Dalke and K. Schulten, VMD: Visual molecular dynamics, J. Mol. Graph., 1996, 14, 33–38.

[S12] D. J. Fa, J. Y. Yuan, G. Y. Feng, S. B. Lei and W. P. Hu, Regulating the synergistic effect in bimetallic two-dimensional polymer oxygen evolution reaction catalysts by adjusting the coupling strength between metal centers, *Angew. Chem. Int. Ed.*, 2023, **62**, e202300532.

[S13] S. Trenker, L. Grunenberg, T. Banerjee, G. Savasci, L. M. Poller, K. I. M. Muggli, F. Haase, C. Ochsenfeld and B. V. Lotsch, A flavin-inspired covalent organic framework for photocatalytic alcohol oxidation, *Chem. Sci.*, 2021, **12**, 15143–15150.

[S14] M. L. Luo, QL Yang, K. W. Liu, H. M. Cao and H. J. Yan, Boosting photocatalytic H₂ evolution on g-C₃N₄ by modifying covalent organic frameworks (COFs), *Chem. Commun.*, 2019, 55, 5829–5832.

[S15] X. Q. Ye, J. C. Fan, Y. L. Min, P. H. Shi and Q. J. Xu, Synergistic effect of Co/CoO nanoparticles on imine-based covalent organic framework for enhanced OER performance, *Nanoscale*, 2021, **13**, 14854–14865.

[S16] B. Zhang, H. Y. Qin, L. C. Diao, N. Q. Zhao, C. S. Shi, E. Z. Liu and C. N. He, Strongly coupled hollow-oxide/phosphide hybrid coated with nitrogen-doped carbon as highly efficient electrocatalysts in alkaline for hydrogen evolution reaction, *J. Catal.*, 2019, **377**, 582–588.

[S17] C. Liu, F. Liu, H. Li, J. S. Chen, J. Y. Fei, Z. X. Yu, Z. W. Yuan, C. J. Wang, H. L. Zheng,

Z. W. Liu, M. Y. Xu, G. Henkelman, L. Wei and Y. Chen, One-dimensional van der Waals heterostructures as efficient metal-free oxygen electrocatalysts, *ACS Nano*, 2021, 15, 3309–3319.
[S18] C. H. Yang, Z. D. Yang, H. Dong, N. Sun, Y. Lu, F. M. Zhang and G. L. Zhang, Theory-

driven design and targeting synthesis of a highly-conjugated basal-plane 2D covalent organic framework for metal-free electrocatalytic OER, *ACS Energy Lett.*, 2019, **4**, 2251–2258.

[S19] X. Wang, R. K. M. Raghupathy, C. J. Querebillo, Z. Q. Liao, D. Q. Li, K. Lin, M. Hantusch, Z. Sofer, B. H. Li, E. Zschech, I. M. Weidinger, T. D. Kühne, H. Mirhosseini, M. H. Yu and X. L. Feng, Interfacial covalent bonds regulated electron-deficient 2D black phosphorus for electrocatalytic oxygen reactions, *Adv. Mater.*, 2021, **33**, 2008752.

[S20] H. N. Qin, Y. Z. Wang, B. Wang, X. G. Duan, H. T. Lei, X. P. Zhang, H. Q. Zheng, W. Zhang and R. Cao, Cobalt porphyrins supported on carbon nanotubes as model catalysts of metal-N₄/C sites for oxygen electrocatalysis, *J. Energy Chem.*, 2021, **53**, 77–81.

[S21] D. Zhou, H. Fu, J. Long, K. Shen and X. Gou, Novel fusiform core-shell-MOF derived intact metal@carbon composite: An efficient cathode catalyst for aqueous and solid-state Zn-air batteries, *J. Energy Chem.*, 2022, 64, 385–394.

[S22] G. M. Cai, L. H. Zeng, L. Q. He, S. J. Sun, Y. X. Tong and J. Y. Zhang, Imine gels based on ferrocene and porphyrin and their electrocatalytic property, *Chem. –Asian J.*, 2020, **15**, 1963–1969.

[S23] Y. Zhao, X. F. Lu, Z. P. Wu, Z. Pei, D. Luan and X. W. D. Lou, Supporting trimetallic metalorganic frameworks on S/N-doped carbon macroporous fibers for highly efficient electrocatalytic oxygen evolution, *Adv. Mater.*, 2023, **35**, e2207888.

[S24] Y. Liu, X. D. Yan, T. Li, W. D. Zhang, Q. T. Fu, H. S. Lu, X. Wang and Z. G. Gu, Threedimensional porphyrin-based covalent organic frameworks with tetrahedral building blocks for single-site catalysis, *New J. Chem.*, 2019, **43**, 16907–16914.

[S25] D. D. Zhu, J. L. Liu, L. Wang, Y. Du, Y. Zheng, K. Davey and S. Z. Qiao, A 2D metal–organic framework/Ni(OH)₂ heterostructure for an enhanced oxygen evolution reaction, *Nanoscale*, 2019, 11, 3599–3605.

[S26] W. Zhang, C. H. Xu, H. Zheng, R. Li and K. Zhou, Oxygen-rich cobalt-nitrogen-carbon porous nanosheets for bifunctional oxygen electrocatalysis, *Adv. Funct. Mater.*, 2022, **32**, 2200763.