

## Supplement Information

# Bimetallic conjugated metal-organic frameworks as bifunctional electrocatalysts for overall water splitting

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## Additional computational details for DFT calculations

For OER, the absorption energies of all reaction intermediates OH\*, O\*, OOH\* were calculated follows:

$$\Delta E_{OH^*} = E_{OH^*} - E_T - E_{H_2O} + \frac{1}{2}E_{H_2} \quad (S1)$$

$$\Delta E_{O^*} = E_{O^*} - E_T - E_{H_2O} + E_{H_2} \quad (S2)$$

$$\Delta E_{OOH^*} = E_{OOH^*} - E_T - 2E_{H_2O} + \frac{3}{2}E_{H_2} \quad (S3)$$

where  $E_T$ ,  $E_{OH^*}$ ,  $E_{O^*}$ ,  $E_{OOH^*}$  are the total energy of the studied catalyst without adsorbed intermediate, and that adsorbed by OH\*, O\* and OOH\* intermediates, respectively.  $E_{H_2O}$  and  $E_{H_2}$  are the energies of H<sub>2</sub>O and H<sub>2</sub> molecule in the gas phase. The correction added to the adsorption energy to obtain the free energy is 0.05, 0.35, and 0.40 eV for adsorbed O, OH, and OOH, respectively.<sup>1</sup> the Gibbs free energy charges  $\Delta G_{OER}$  (OER = OH\*, O\*, OOH\*) are defined as following equation:

$$\Delta G_{OH^*} = \Delta E_{OH^*} - 0.35 \text{ eV} \quad (S4)$$

$$\Delta G_{O^*} = \Delta E_{O^*} - 0.05 \text{ eV} \quad (S5)$$

$$\Delta G_{OOH^*} = \Delta E_{OOH^*} - 0.4 \text{ eV} \quad (S6)$$

where  $\Delta G_{OH^*}$ ,  $\Delta G_{O^*}$ , and  $\Delta G_{OOH^*}$  denote the free energy changes of the studied catalyst with adsorbed OH\*, O\*, and OOH\* intermediates, respectively. Each step of reaction free energy charges  $\Delta G_i$  ( $i = 1, 2, 3, 4$ ) can be determined by the following equation:

$$\Delta G_1 = \Delta G_{OH^*} - \Delta G_{H_2O} \quad (S7)$$

$$\Delta G_2 = \Delta G_{O^*} - \Delta G_{OH^*} \quad (S8)$$

$$\Delta G_3 = \Delta G_{OOH^*} - \Delta G_{O^*} \quad (S9)$$

$$\Delta G_4 = \Delta G_{O_2} - \Delta G_{OOH^*} \quad (S10)$$

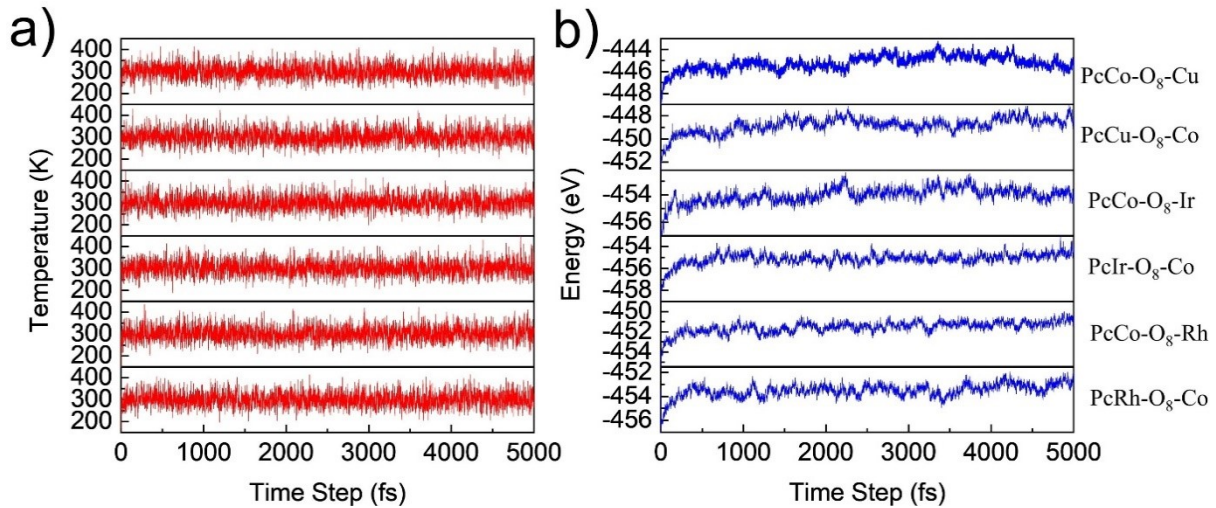
where  $\Delta G_1$ ,  $\Delta G_2$ ,  $\Delta G_3$  and  $\Delta G_4$  are the Gibbs free energy change for the four OER steps:  $OH^*$  formation by dissociative adsorption of  $H_2O$ ,  $O^*$  formation by deprotonation,  $O^*$  oxidation to  $OOH^*$ ,  $O_2$  formation and release.

For HER, the absorption energies of  $H^*$  was calculated follows:

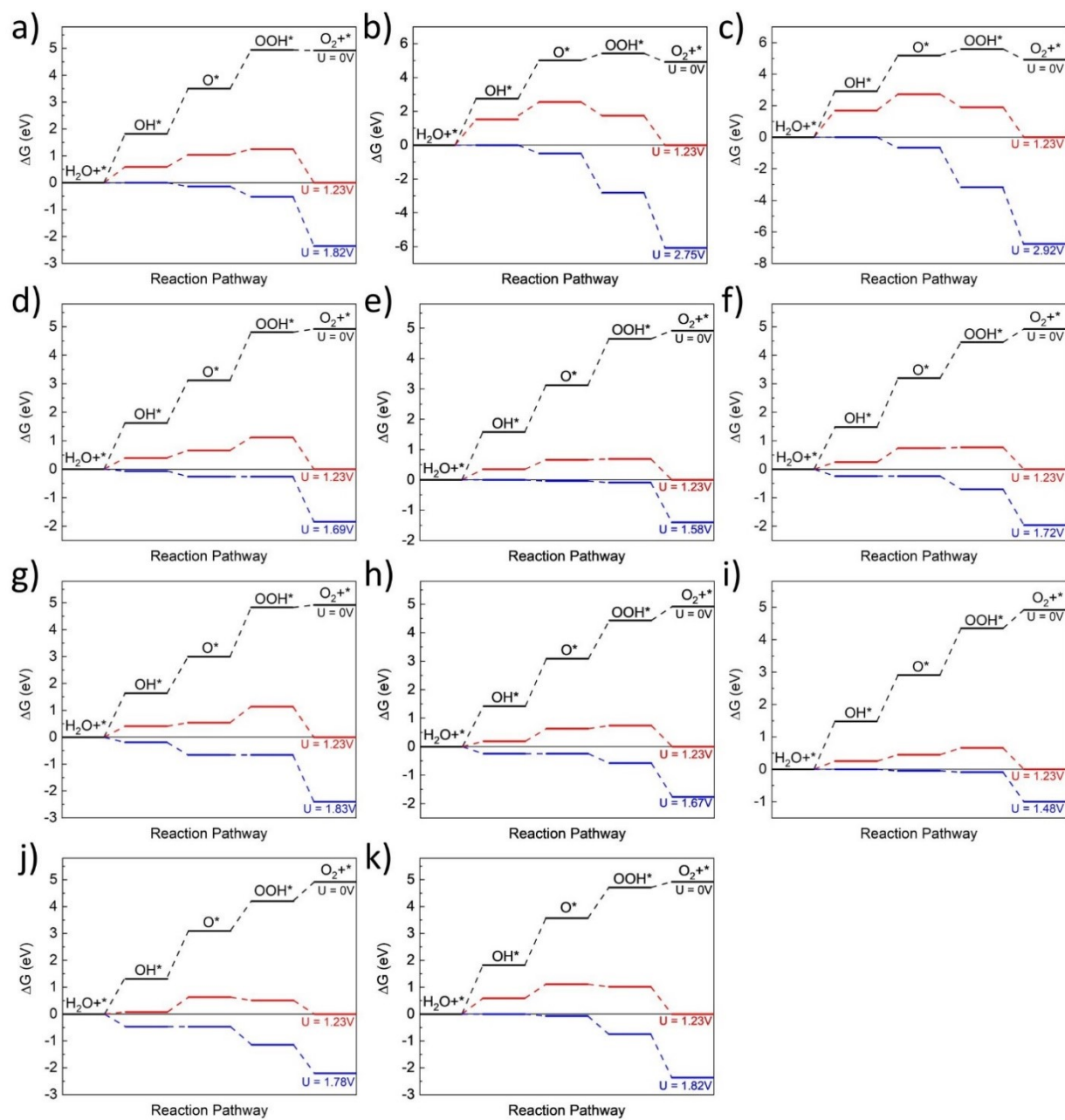
$$\Delta E_{H^*} = E_{H^*} - E_T - \frac{1}{2}E_{H_2} \quad (S11)$$

where  $E_{H^*}$  is the total energy of the studied catalyst with  $H^*$  intermediate. The correction added to the adsorption energy to obtain the free energy is 0.24 eV for adsorbed H intermediate.<sup>2</sup> This means that

$$\Delta G_{H^*} = \Delta E_{H^*} + 0.24 \text{ eV} \quad (S12)$$



**Fig. S1** The variations of temperature and energy versus the time for AIMD simulations of all designed PcTM-O<sub>8</sub>-TM' 2D c-MOFs under 300 K for 5000 fs.



**Fig. S2** Reaction diagram of the OER on the PcTM-O<sub>8</sub>-TM' 2D c-MOFs. The structure of a) PcCo-O<sub>8</sub>-Cu-A, b) PcCo-O<sub>8</sub>-Cu-B, c) PcCu-O<sub>8</sub>-Co-A, d) PcCu-O<sub>8</sub>-Co-B, e) PcCo-O<sub>8</sub>-Ir-A, f) PcIr-O<sub>8</sub>-Co-A, g) PcIr-O<sub>8</sub>-Co-B, h) PcCo-O<sub>8</sub>-Rh-A, i) PcCo-O<sub>8</sub>-Rh-B, j) PcRh-O<sub>8</sub>-Co-A, k) PcRh-O<sub>8</sub>-Co-B. The value of onset potential is marked in diagram.

**Table S1.** Reaction free energies  $\Delta G_i$  ( $i = 1, 2, 3, 4$ ) of intermediate steps ( $U = 0V$ ) at oxygen active sites. The values in the bracket and red denote the chemical reaction process on the B site and the largest energy difference, respectively.

Systems	$\Delta G_1$	$\Delta G_2$	$\Delta G_3$	$\Delta G_4$
PcCo-O <sub>8</sub> -Cu	1.82 (2.75)	1.68 (2.26)	1.44 (0.42)	-0.02 (-0.51)
PcCu-O <sub>8</sub> -Co	2.92 (1.62)	2.25 (1.50)	0.41 (1.69)	-0.67 (0.11)
PcCo-O <sub>8</sub> -Ir	1.58 (N/A)	1.54 (N/A)	1.53 (N/A)	0.27 (N/A)
PcIr-O <sub>8</sub> -Co	1.48 (1.64)	1.72 (1.36)	1.26 (1.83)	0.46 (-0.04)
PcCo-O <sub>8</sub> -Rh	1.42 (1.48)	1.67 (1.43)	1.34 (1.44)	0.49 (0.57)
PcRh-O <sub>8</sub> -Co	1.31 (1.82)	1.78 (1.75)	1.11 (1.14)	0.72 (0.21)

**Table S2.** Electron transfer ( $e$ ) of TM, N, and O atoms at PcTM-O<sub>8</sub>-TM'. ( $Q_{TM}$ ,  $Q_{TM'}$ ,  $Q_N$ , and  $Q_O$  in  $e$  per unit cell)

Systems	$Q_{TM}$	$Q_{TM'}$	$Q_N$	$Q_O$
PcCo-O <sub>8</sub> -Cu	-0.94	-0.91	+0.43/+0.38 +0.37/+0.42	+0.80/+0.77 +0.85/+0.75

PcCu-O <sub>8</sub> -Co	-0.82	-1.17	+0.72/+0.89	+0.51/+0.52
			+0.82/+0.89	+0.52/+0.52
PcCo-O <sub>8</sub> -Ir	-0.93	-1.86	+0.42/+0.38	+0.68/+0.68
			+0.38/+0.42	+0.69/+0.69
PcIr-O <sub>8</sub> -Co	-1.68	-1.18	+0.56/+0.60	+0.52/+0.51
			+0.59/+0.60	+0.52/+0.52
PcCo-O <sub>8</sub> -Rh	-0.93	-1.48	+0.42/+0.37	+0.59/+0.60
			+0.38/+0.43	+0.61/+0.60
PcRh-O <sub>8</sub> -Co	-1.33	-1.18	+0.49/+0.52	+0.52/+0.52
			+0.51/+0.52	+0.52/+0.52

**Table S3.** Reaction free energies  $\Delta G_i$  ( $i = 1, 2, 3, 4$ ) of intermediate steps ( $U = 0V$ ) at PcCo-O<sub>8</sub>-Rh under tensile strain. The values in the bracket and red denote the chemical reaction process on the B site and the largest energy difference, respectively.

Stain (%)	$\Delta G_1$	$\Delta G_2$	$\Delta G_3$	$\Delta G_4$
0	1.42	1.67	1.34	0.49
	(1.48)	(1.43)	(1.44)	(0.57)
1	1.70	1.35	1.23	0.64
	(1.59)	(0.86)	(1.50)	(0.97)
2	1.72	1.28	1.23	0.69
	(1.62)	(0.82)	(1.43)	(1.05)
3	1.74	1.22	0.23	0.73
	(1.64)	(0.76)	(1.42)	(1.10)

Table S4. The intermediates adsorptions on the PcCo-O<sub>8</sub>-Rh-B under the synergetic effect with the A site: Gibbs free energy change of OH\*, O\*, OOH\*, H\* intermediate of OER and HER ( $\Delta G_{\text{OH}^*}$ ,  $\Delta G_{\text{O}^*}$ ,  $\Delta G_{\text{OOH}^*}$ ,  $\Delta G_{\text{H}^*}$  in eV), overpotential ( $\eta_{\text{OER}}$  in V), onset potential ( $U_{\text{HER}}$  and  $U_{\text{OER}}$  in V).

	$\Delta G_{\text{OH}^*}$	$\Delta G_{\text{O}^*}$	$\Delta G_{\text{OOH}^*}$	$\Delta G_{\text{H}^*}$	$\eta_{\text{OER}}$	$U_{\text{HER}}$	$U_{\text{OER}}$
PcCo-O <sub>8</sub> -Rh-B (synergetic)	1.51	2.51	3.57	-0.17	0.28	-0.17	1.51
PcCo-O <sub>8</sub> -Rh-B (un-synergetic)	1.48	2.91	4.35	-0.19	0.25	-0.19	1.48

Table S5. Electron transfer of Co, Rh, N and O atoms at PcCo-O<sub>8</sub>-Rh under tensile strain. ( $Q_{\text{Co}}$ ,  $Q_{\text{Rh}}$ ,  $Q_{\text{N}}$ ,  $Q_{\text{O}}$  in e per unit cell)

Stain (%)	$Q_{\text{Co}}$	$Q_{\text{Rh}}$	$Q_{\text{N}}$	$Q_{\text{O}}$
0	-0.93	-1.48	+0.42/+0.37	+0.59/+0.60
			+0.38/+0.43	+0.61/+0.60
1	-0.88	-1.19	+0.40/+0.35	+0.58/+0.58
			+0.36/+0.41	+0.60/+0.59
2	-0.78	-1.12	+0.38/+0.33	+0.56/+0.57
			+0.35/+0.39	+0.58/+0.57
3	-0.70	-0.94	+0.36/+0.30	+0.54/+0.56
			+0.33/+0.37	+0.56/+0.55

## References

1. J. Rossmeisl, Z.-W. Qu, H. Zhu, G.-J. Kroes and J. K. Nørskov, *J. Electroanal. Chem.*, 2007, **607**, 83-89.
2. J. K. Nørskov, T. Bligaard, A. Logadottir, J. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *J. Electrochem. Soc.*, 2005, **152**, J23.

