

## Supporting Information

**A novel two-dimensional cobaltporphyrin-based organic framework as a promising electrocatalyst for CO<sub>2</sub> reduction reaction: a computational study**

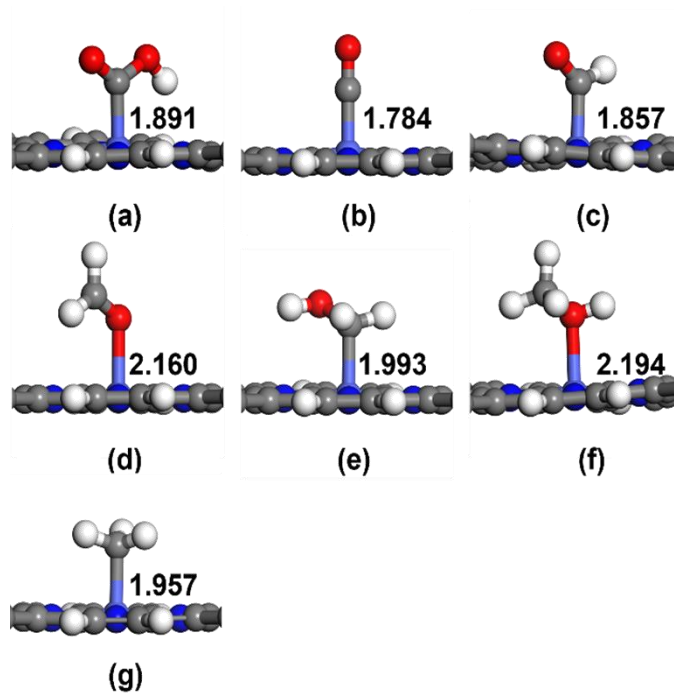
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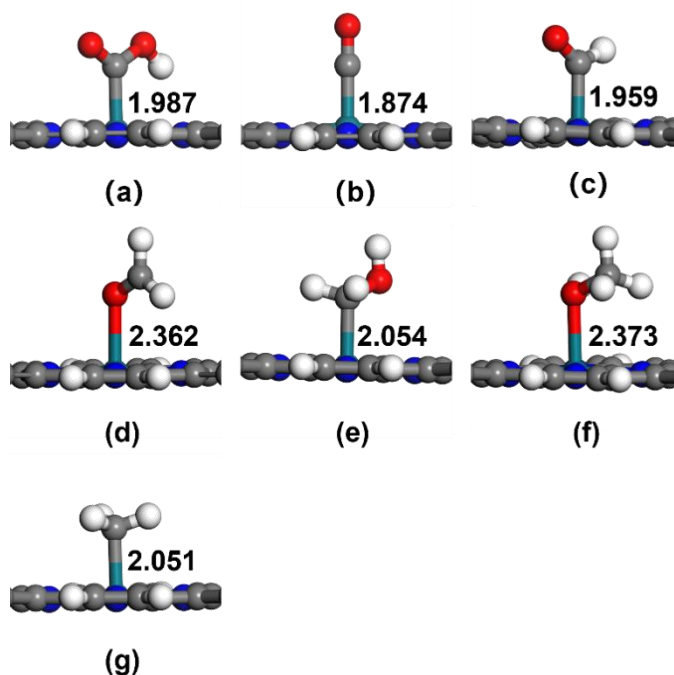
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## Computational details

The adsorption energy ( $E_{\text{ads}}$ ) for \*CO intermediate on the 2D TM-PMOF was defined as  $E_{\text{ads}} = E_{\text{TM-PMOF-CO}} - E_{\text{TM-PMOF}} - E_{\text{CO}}$ , where  $E_{\text{TM-PMOF-CO}}$ ,  $E_{\text{TM-PMOF}}$ , and  $E_{\text{CO}}$  are the total energy for the \*CO adsorbed on the 2D TM-PMOF, the pure 2D TM-PMOF, and the CO molecule, respectively. A negative value of the  $E_{\text{ads}}$  suggests favorable adsorption. The change in Gibbs free energy ( $\Delta G$ ) of every elemental step was acquired by applying the computational hydrogen electrode (CHE) model proposed by Nørskov et al.<sup>1,2</sup> In detail, the Gibbs free energy change is defined as  $\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_{\text{pH}} + \Delta G_{\text{U}}$ , where  $\Delta E$  is the electronic energy difference directly obtained by DFT calculations,  $\Delta E_{\text{ZPE}}$  is the zero-point energy change,  $T$  is set at room temperature (298.15 K), and  $\Delta S$  is the entropy change. The zero-point energies and entropies of adsorbed species were calculated from the vibrational frequencies, in which only the vibrational modes of adsorbate were calculated explicitly, while the catalyst substrate was fixed.<sup>3-5</sup> The entropies and vibrational frequencies of the free molecules were taken from the NIST database.<sup>6</sup> At the same time, the calculated energies, ZPE, and TS of these free molecules are listed in Table S1.  $\Delta G_{\text{pH}}$  is the free energy correction of pH, calculated by  $\Delta G_{\text{pH}} = 2.303k_{\text{B}}T\text{pH}$  ( $k_{\text{B}}$  is the Boltzmann constant, and the pH value was set to zero for all the calculations here).  $\Delta G_{\text{U}}$  is the free energy contribution related to electrode potential (U), which can be determined as  $\Delta G_{\text{U}} = -neU$ , where  $n$  is the number of electrons transferred and  $U$  is the applied electrode potential.



**Figure S1.** The optimized structures of intermediates corresponding to the optimal CO<sub>2</sub>RR on the 2D Co-PMOF: (a) \*COOH, (b) \*CO, (c) \*CHO, (d) \*OCH<sub>2</sub>, (e) \*CH<sub>2</sub>OH, (f) \*OHCH<sub>3</sub>, (g) \*CH<sub>3</sub>.



**Figure S2.** The optimized structures of intermediates corresponding to the optimal CO<sub>2</sub>RR on the 2D Rh-PMOF: (a) \*COOH, (b) \*CO, (c) \*CHO, (d) \*OCH<sub>2</sub>, (e) \*CH<sub>2</sub>OH, (f) \*OHCH<sub>3</sub>, (g) \*CH<sub>3</sub>.

**Table S1.** Change in Gibbs free energies ( $\Delta G$ , eV) for all possible elementary steps for CO<sub>2</sub>RR on Co-PMOF. The computed results corresponding to the optimal reduction path are marked in yellow.

Reaction pathway	$\Delta G$ /(eV)
* + CO <sub>2</sub> + H <sup>+</sup> + e <sup>-</sup> → *COOH	0.07
* + CO <sub>2</sub> + H <sup>+</sup> + e <sup>-</sup> → *OCHO	0.73
*COOH + H <sup>+</sup> + e <sup>-</sup> → *CO + H <sub>2</sub> O	0.53
*CO + H <sup>+</sup> + e <sup>-</sup> → *CHO	-0.13
*CO + H <sup>+</sup> + e <sup>-</sup> → *COH	1.59
*CHO + H <sup>+</sup> + e <sup>-</sup> → *OCH <sub>2</sub>	0.25
*CHO + H <sup>+</sup> + e <sup>-</sup> → *CHOH	0.80
*CH <sub>2</sub> O + H <sup>+</sup> + e <sup>-</sup> → *CH <sub>2</sub> OH	-0.39
*CH <sub>2</sub> O + H <sup>+</sup> + e <sup>-</sup> → *OCH <sub>3</sub>	0.35
*CH <sub>2</sub> OH + H <sup>+</sup> + e <sup>-</sup> → *OHCH <sub>3</sub>	-0.18
*CH <sub>2</sub> OH + H <sup>+</sup> + e <sup>-</sup> → *CH <sub>2</sub> + H <sub>2</sub> O	1.32
*OHCH <sub>3</sub> + H <sup>+</sup> + e <sup>-</sup> → *CH <sub>3</sub> + H <sub>2</sub> O	-0.34
*CH <sub>3</sub> + H <sup>+</sup> + e <sup>-</sup> → * + CH <sub>4</sub>	-0.51

**Table S2.** Change in Gibbs free energies ( $\Delta G$ , eV) for all possible elementary steps for CO<sub>2</sub>RR on Rh-PMOF. The computed results corresponding to the optimal reduction path are marked in yellow.

Reaction pathway	$\Delta G$ /(eV)
* + CO <sub>2</sub> + H <sup>+</sup> + e <sup>-</sup> → *COOH	-0.03
* + CO <sub>2</sub> + H <sup>+</sup> + e <sup>-</sup> → *OCHO	0.89
*COOH + H <sup>+</sup> + e <sup>-</sup> → *CO + H <sub>2</sub> O	0.63
*CO + H <sup>+</sup> + e <sup>-</sup> → *CHO	-0.63
*CO + H <sup>+</sup> + e <sup>-</sup> → *COH	1.43
*CHO + H <sup>+</sup> + e <sup>-</sup> → *OCH <sub>2</sub>	0.98
*CHO + H <sup>+</sup> + e <sup>-</sup> → *CHOH	1.00
*CH <sub>2</sub> O + H <sup>+</sup> + e <sup>-</sup> → *CH <sub>2</sub> OH	-0.51
*CH <sub>2</sub> O + H <sup>+</sup> + e <sup>-</sup> → *OCH <sub>3</sub>	1.146
*CH <sub>2</sub> OH + H <sup>+</sup> + e <sup>-</sup> → *OHCH <sub>3</sub>	-0.15
*CH <sub>2</sub> OH + H <sup>+</sup> + e <sup>-</sup> → *CH <sub>2</sub> + H <sub>2</sub> O	1.01
*OHCH <sub>3</sub> + H <sup>+</sup> + e <sup>-</sup> → *CH <sub>3</sub> + H <sub>2</sub> O	-0.56
*CH <sub>3</sub> + H <sup>+</sup> + e <sup>-</sup> → * + CH <sub>4</sub>	-0.29

**Table S3.** The charge states analyzed by Hirshfeld charge of the three moieties for 2D Co-PMOF along the optimal reaction pathway. The moieties 1, 2, and 3 represent the Co-PMOF substrate, the CoN<sub>4</sub> unit, and the adsorbed \*C<sub>x</sub>O<sub>y</sub>H<sub>z</sub>, respectively. 1, 2, 3, 4, 5, 6, 7, and 8 illustrate the CO<sub>2</sub>, \*COOH, \*CO, \*CHO, \*CH<sub>2</sub>O, \*CH<sub>2</sub>OH, \*OHCH<sub>3</sub>, and \*CH<sub>3</sub> intermediates along the reaction pathway.

<b>Reaction step</b>	<b>Moiety 1</b>	<b>Moiety 2</b>	<b>Moiety 3</b>
1	0.2887	-0.2857	0.0030
2	0.3786	-0.2386	-0.1389
3	0.2004	-0.2282	0.0331
4	0.2837	-0.2304	-0.0504
5	0.0703	-0.2384	0.1718
6	0.1523	-0.2275	0.079
7	0.0533	-0.2144	0.1647
8	0.2175	-0.1826	-0.0306

### Supplementary References

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