Supplementary Information for

Theoretical study of covalent organic frameworks and heterojunctions for oxygen reduction reaction

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1. Computational details of the adsorption free energies

In the four-electron reduction pathway of ORR, the intermediates include $*O_2$, $*OOH$, $*OH$, and $*O$. The adsorption free energies (ΔG_{ads}) of these intermediates were calculated relative to H_2O and H_2 under conditions of $T = 298.15$ K and pH = 0 (vs. SHE) according to equations[1, 2]:

$*+2H_2O \rightarrow *O_2+2H_2$:

$$\Delta G_{*\mathrm{O}_2} = G_{*\mathrm{O}_2} + 2G_{\mathrm{H}_2} - G_{*} - 2G_{\mathrm{H_2O}} \qquad （1）$$

$*+2H_2O \rightarrow *OOH+3/2H_2$:

$$\Delta G_{*\mathrm{OOH}} = G_{*\mathrm{OOH}} + 3/2G_{\mathrm{H}_2} - G_{*} - 2G_{\mathrm{H_2O}} \qquad （2）$$

$*+H_2O \rightarrow *O+H_2$:

$$\Delta G_{*\mathrm{O}} = G_{*\mathrm{O}} + G_{\mathrm{H}_2} - G_{*} - G_{\mathrm{H_2O}} \qquad （3）$$

$*+H_2O \rightarrow *OH+1/2H_2$:

$$\Delta G_{*\mathrm{OH}} = G_{*\mathrm{OH}} + 1/2G_{\mathrm{H}_2} - G_{*} - G_{\mathrm{H_2O}} \qquad （4）$$

where * represents the Fe-TCPP and Fe-(mIM)$_n$ (n=2-3) adsorption sites. The G of each intermediate is calculated from the total DFT ground state energy (E_{total}) corrected by the thermodynamic correction according to equation:

$$G = E_{\mathrm{total}} + E_{\mathrm{ZPE}} + \Delta H_{0\rightarrow T} - TS \qquad （5）$$

where E_{ZPE} is zero-point energy calculated from the DFT frequency analysis. $\Delta H_{0\rightarrow T}$ is defined as the enthalpy variation by temperature and calculated as $\int_{0\mathrm{K}}^{298\mathrm{K}} C_{\mathrm{p}}\mathrm{d}T$ (C_p represents the heat capacities). S is the entropy at 298.15 K.

2. Computational details of the reaction free energy

The reaction free energy (ΔG) of each ORR elemental step was calculated according to equation:

$$\Delta G = \Delta\Delta G_{\mathrm{ads}} + \Delta G_{\mathrm{pH}} + \Delta G_{\mathrm{U}} \qquad (6)$$

where ΔG of each ORR elemental step was calculated based on the computational hydrogen electrode (CHE) model developed by Nørskov et al[3]. $\Delta\Delta G_{\mathrm{ads}}$ is the adsorption free energy variation between the reactants and products according to equations (1)-(4). $\Delta G_{\mathrm{pH}} = -kT\ln[\mathrm{H}^+] = \mathrm{pH}\cdot kT\cdot\ln 10$ is used to correct the free energy of $\mathrm{H}^+ + \mathrm{e}^-$ referenced by a standard hydrogen electrode (SHE) at various pH values. $\Delta G_{\mathrm{U}} = -neU$ is the free energy change resulting from an extra applied potential U *vs.* SHE.

The theoretical ORR overpotentials (η_{ORR}, *vs.* SHE) associated with different active sites were calculated according to equation

$$\eta_{\mathrm{ORR}} = 1.23\ \mathrm{V} + \Delta G_{\mathrm{max}}/\mathrm{e} \qquad (7)$$

where 1.23 V is defined as the equilibrium potential of the overall 4-electron ORR at the standard state and ΔG_{max} represents the most positive free energy variation associated with the proton-electron-transfer (PET) steps.

3. The total density of states (TDOS) of COFs

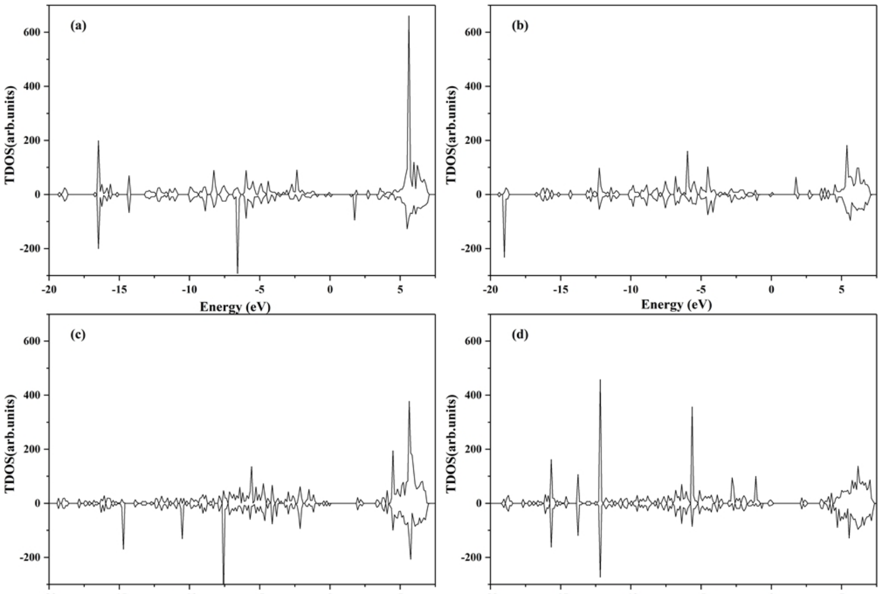

Figure S1. Total density of states (TDOS) of (a) Pc-PBBA COF_Fe, (b) COF-366_Fe, (c) Pc-PBBA COF_Co and (d) COF-366_Co structures.

4. Summary of the adsorption free energies and overpotential of the key intermediates of all materials

Table S1. Summary of adsorption free energy (eV) and overpotentials (V) of the key intermediates.

Structures	ΔG_{*O_2}	ΔG_{*OOH}	ΔG_{*O}	ΔG_{*OH}	η^{ORR}
Pc-PBBA COF_Fe	4.49	4.25	1.75	1.02	0.55
COF-366_Fe	5.23	4.35	2.53	1.48	0.69
Pc-PBBA COF_Co	4.70	4.37	2.89	1.52	0.66
COF-366_Co	4.39	4.18	2.65	1.15	0.49
Pc-PBBA COF_Fe@GP	4.39	3.99	1.58	0.84	0.49
COF-366_Fe@GP	4.47	3.97	1.54	0.87	0.55
Pc-PBBA COF_Co@GP	4.62	4.15	2.67	1.25	0.46
COF-366_Co@GP	4.49	4.28	2.68	1.36	0.31
Pc-PBBA COF_Fe@C_3N_4	4.32	4.20	3.16	1.49	0.51
COF-366_Fe@C_3N_4	4.50	4.11	2.65	1.38	0.42
Pc-PBBA COF_Co@C_3N_4	4.37	4.25	3.30	1.46	0.56
COF-366_Co@C_3N_4	4.27	4.10	2.65	1.39	0.41

5.Spin moments of the transition metal (Fe or Co) sites

Table S2. Spin moments (μ_B) of the transition metal (Fe or Co) sites.

Structures	Slab	$*O_2$	*OOH	*O	*OH
Pc-PBBA COF_Fe	2.015	2.501	2.169	1.426	1.006
Pc-PBBA COF_Fe@GP	2.011	1.438	2.517	-1.401	2.599
Pc-PBBACOF_Fe@C_3N_4	2.023	1.240	2.530	1.282	2.605
Pc-PBBA COF_Co	-1.020	-0.880	1.437	0.409	1.300
Pc-PBBA COF_Co@GP	-1.006	0.740	-0.049	0.373	1.559
Pc-PBBACOF_Co@C_3N_4	-1.046	0.691	-1.263	0.485	1.505
COF-366_Fe	2.024	2.068	2.271	1.269	2.438
COF-366_Fe@GP	2.025	1.309	1.086	1.489	2.674
COF-366_Fe@C_3N_4	2.289	2.374	-1.110	1.462	2.611
COF-366_Co	2.656	0.382	0.063	2.367	0.006
COF-366_Co@GP	-1.043	-0.519	1.540	2.380	0.003
COF-366_Co@C_3N_4	1.042	0.473	1.522	1.823	1.612

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