Supporting Information

Boosting Oxygen Reduction Reaction with Metal Phthalocyanines: Altering Central Metals and Substituents

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Supplementary Note 1. Computational details.

The four-electron ORR mechanism in acidic medium was assumed as the following steps:

$$* + O_2 + H^+ + e^- \rightarrow OOH*$$

$$OOH* + H^+ + e^- \rightarrow O* + H_2O$$

$$O* + H^+ + e^- \rightarrow OH*$$

$$OH* + H^+ + e^- \rightarrow * + H_2O$$

where *, OOH*, O* and OH* stand for an active site, adsorbed OOH* intermediate, adsorbed O* intermediate and adsorbed OH* intermediate, respectively.

The binding energies (ΔE_{ads}) of OOH*, O* and OH* were calculated by:

$$\Delta E_{ads}(OOH*) = E_{MPc-OOH*} - E_{MPc} - (2E_{H_2O} - 3/2E_{H_2})$$

$$\Delta E_{ads}(O*) = E_{MPc-O*} - E_{MPc} - (E_{H_2O} - E_{H_2})$$

$$\Delta E_{ads}(OH*) = E_{MPc-OH*} - E_{MPc} - (E_{H_2O} - 1/2E_{H_2})$$

where $E_{MPc-OOH*}$, E_{MPc-O*}, $E_{MPc-OH*}$ present the ground state electronic energies of OOH*, O* and OH* intermediates adsorbed on MPc, respectively. E_{H_2O} and E_{H_2} are the calculated DFT energies of isolated H_2O and H_2 molecules.

Then the Gibbs free energies of adsorption (ΔG_{ads}) can be calculated by:

$$\Delta G_{ads} = \Delta E_{ads} + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH}$$

where ΔZPE denotes the corrections of zero-point energy, and $T\Delta S$ indicates the corrections of entropy. T is set as 298.15 K. ΔG_U presents the influence of the Gibbs free energies related to electrode potential U. ΔG_{pH} is the change of Gibbs free energies based on the concentration of H^+, $\Delta G_{pH} = k_B \times ln[H^+] = k_B \times pH \times ln\,10$, where k_B is the Boltzmann constant, and pH of an acidic medium is assumed be zero.

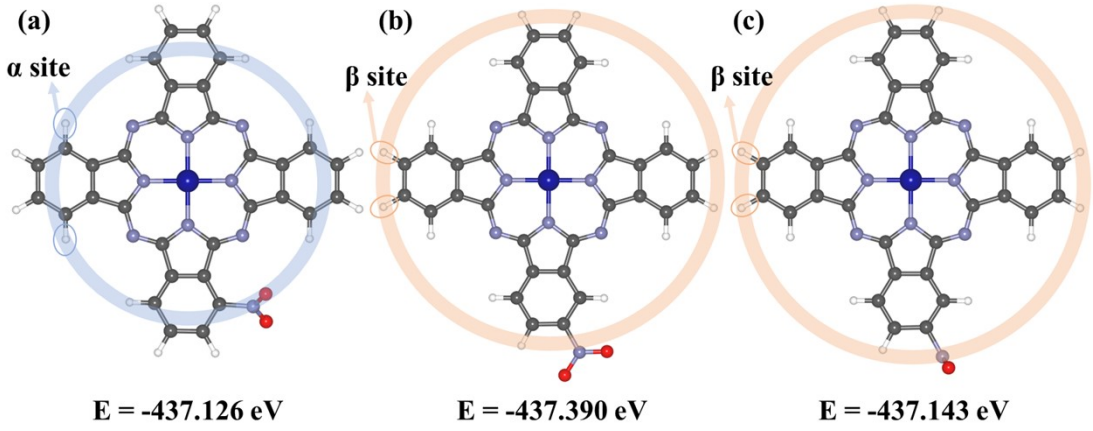

Figure S1. Structures of (a) the substituent positioned at the α site, (b) the substituent positioned at the β site, and (c) the substituent perpendicular to the macrocycle.

For the positioning of the substituents (see **Figure S1**), using NO_2 substituents as an example, our energy calculations show that the β sites (**Figure S1 (b)**) are energetically more favorable than the α sites (**Figure S1 (a)**) by 0.264 eV. This energy difference indicates a higher likelihood of substituents being located at the β sites. Accordingly, we have specified in the manuscript that the substituents are positioned at the β sites.

Furthermore, we conducted an analysis comparing the stability of different configurations of the substituents relative to the macrocycle. Our findings indicate that when the substituents are in equilibrium with the macrocycle (**Figure S1 (b)**), the energy is 0.247 eV lower than when the substituents are perpendicular to the macrocycle (**Figure S1 (c)**). This suggests that the substituents are most stable when located at the β sites and in equilibrium with the macrocycle, supporting the proposed configuration.

Table S1. Free energies of adsorption of oxygenated intermediates on MPcs and cobalt phthalocyanine complexes.

ΔG_{ads} (eV)	$\Delta G_{(OOH^*)}$	$\Delta G_{(O^*)}$	$\Delta G_{(OH^*)}$
CrPc	3.49	0.54	0.19
MnPc	3.86	1.38	0.60
FePc	3.94	1.48	0.78
CoPc	4.22	2.76	1.18
NiPc	4.89	4.37	2.18
$CoPc(NO_2)_4$	4.05	2.84	1.22
$CoPc(NO_2)_3(NH_2)_1$	4.06	2.81	1.22
$CoPc(NO_2)_2(NH_2)_2$	4.06	2.79	1.21
$CoPc(NO_2)_1(NH_2)_3$	4.15	2.73	1.17
CoPc $(NH_2)_4$	4.20	2.70	1.14

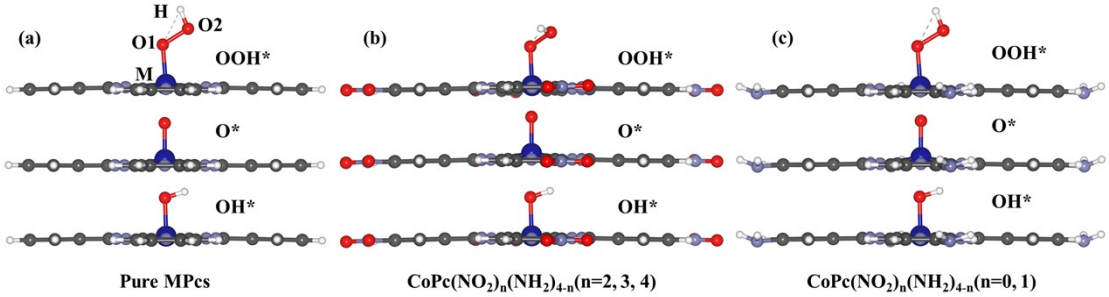

Figure S2 Structures of intermediates on (a) pure MPcs, (b) $CoPc(NO_2)_n(NH_2)_{4-n}$ (n=2, 3, 4) and (c) $CoPc(NO_2)_n(NH_2)_{4-n}$ (n=0, 1).

Table S2. Summary of structural parameters for intermediates on MPcs and their complexes.

MPc	intermediates	M-O1 bond (Å)	O1-O2 bond (Å)	O2-H bond (Å)
	OOH*	1.821	1.481	0.979
CrPc	O*	1.561		
	OH*	1.826		0.975
	OOH*	1.966	1.452	0.978
MnPc	O*	1.586		
	OH*	1.918		0.973
	OOH*	1.919	1.440	0.979
FePc	O*	1.642		
	OH*	1.788		0.980
	OOH*	1.897	1.429	0.981
CoPc	O*	1.734		
	OH*	1.840		0.978
	OOH*	2.202	1.393	0.984
NiPc	O*	1.936		
	OH*	2.016		0.977
	OOH*	1.858	1.408	0.984
$CoPc(NO_2)_4$	O*	1.733		
	OH*	1.838		0.978
	OOH*	1.856	1.411	0.984
$CoPc(NO_2)_3(NH_2)_1$	O*	1.733		
	OH*	1.840		0.978
	OOH*	1.857	1.413	0.983
$CoPc(NO_2)_2(NH_2)_2$	O*	1.733		
	OH*	1.841		0.978
	OOH*	1.905	1.430	0.981
$CoPc(NO_2)_1(NH_2)_3$	O*	1.733		

	OH*	1.842		0.978
	OOH*	1.896	1.436	0.980
$CoPc(NH_2)_4$	O*	1.733		
	OH*	1.844		0.978

Structural diagrams of the intermediates are presented in **Figure S2** and **Table S2**. The data show that the M-O1 bond lengths in $CoPc(NO_2)_n(NH_2)_{4-n}$ (n = 2, 3, 4) are approximately 1.857 Å, 1.733 Å, and 1.840 Å when adsorbed with OOH*, O*, and OH*, respectively. For other MPcs, the M-O1 bond lengths range between 1.821 and 2.202 Å with OOH* adsorption, between 1.561 and 1.936 Å with O* adsorption, and between 1.788 and 2.016 Å with OH* adsorption. These results suggest that $CoPc(NO_2)_n(NH_2)_{4-n}$ (n = 2, 3, 4) exhibits moderate M-O1 bond lengths compared to other MPcs, which are more favorable for the electrochemical reaction process.

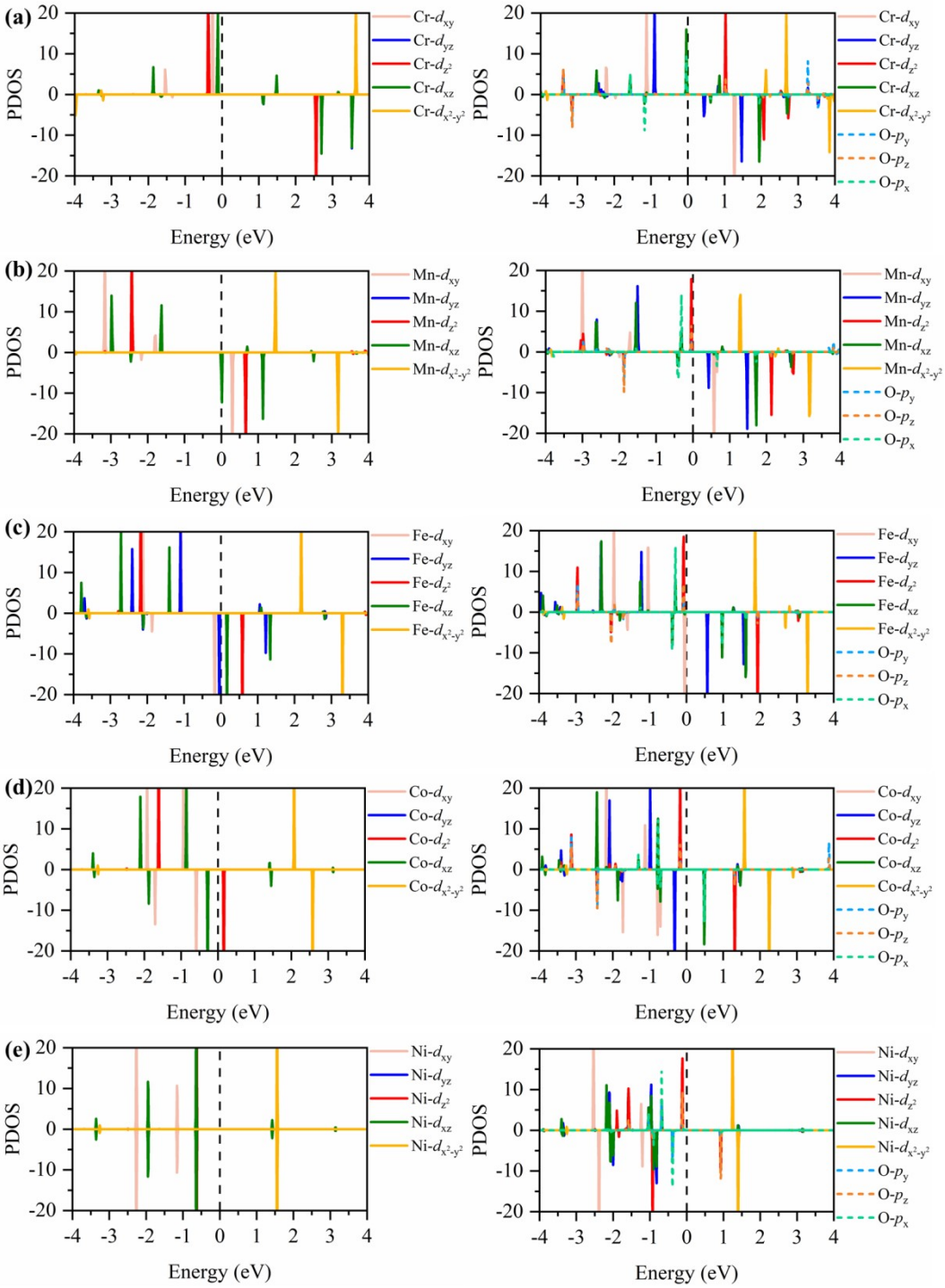

Figure S3. (a-e) Projected density of states (PDOS) for MPc and OOH* adsorbed on MPc. (M=Cr, Mn, Fe, Co, Ni).

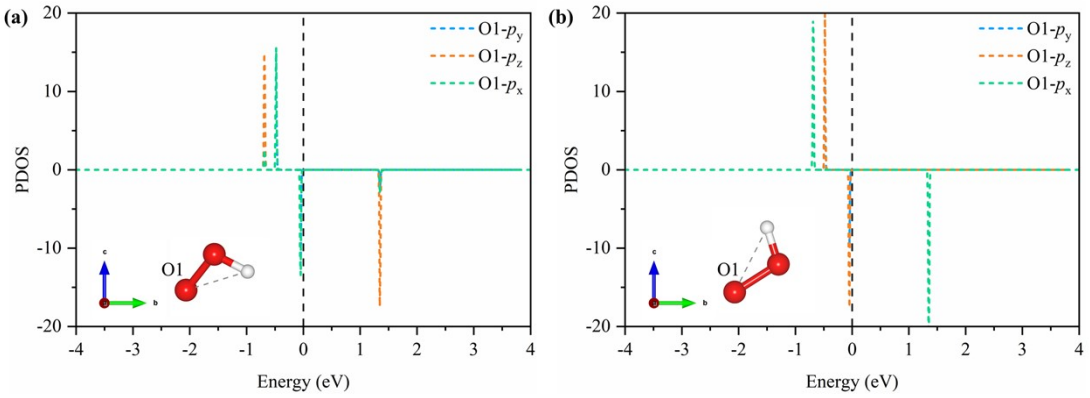

Figure S4. PDOS of OOH molecule in (a) Cycle I and (b) Cycle II.

For Cycle I, our calculations reveal that the p_z orbital of the OOH molecule is distinct in energy from the p_x and p_y orbitals, which remain degenerate. In contrast, in Cycle II, the p_x orbital is no longer degenerate with the other p orbitals, while the p_y and p_z orbitals exhibit degeneracy. These findings indicate that the orbital degeneracies in the OOH molecule are sensitive to the initial configuration and the orientation of the coordinate axes. Depending on whether the configuration corresponds to Cycle I or Cycle II, one p orbital may not degenerate, while the other two p orbitals exhibit degeneracy.

Table S3. ICOHP values for Metal-O bond of OOH* adsorbed on different MPcs.

MPcs	**CrPc**	**MnPc**	**FePc**	**CoPc**	**NiPc**
ICOHP-UP	-2.584	-1.775	-1.767	-1.573	-1.133
d_{z^2}-p_z(up)	-0.629	-0.234	-0.196	-0.061	-0.043
d_{xz}-p_x(up)	-0.196	-0.004	-0.003	0.002	-0.003
d_{yz}-p_y(up)	-0.148	-0.047	-0.048	-0.047	-0.005
ICOHP-DOWN	-2.817	-2.589	-2.708	-2.699	-1.465
d_{z^2}-p_z(dw)	-0.549	-0.525	-0.561	-0.564	-0.323
d_{xz}-p_x(dw)	-0.481	-0.325	-0.358	-0.354	-0.004
d_{yz}-p_y(dw)	-0.166	-0.082	-0.091	-0.069	-0.007
TOT	-5.401	-4.364	-4.475	-4.272	-2.598

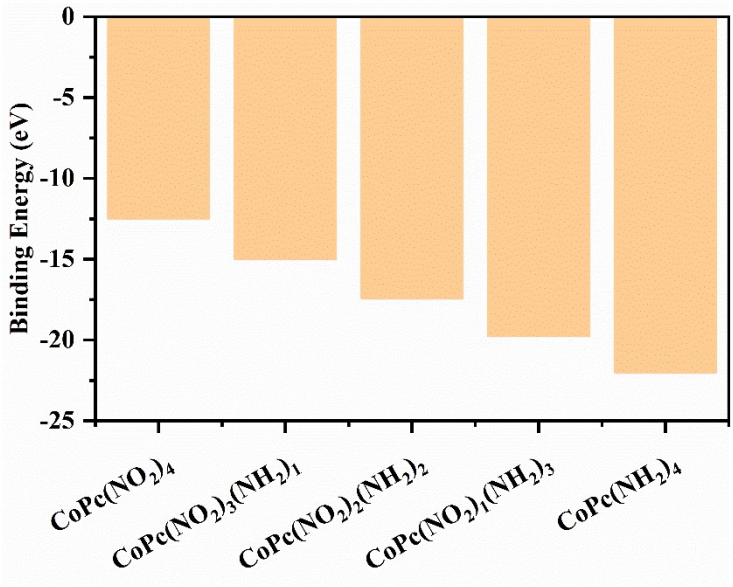

Figure S5. Calculated binding energy of cobalt phthalocyanine complexes.

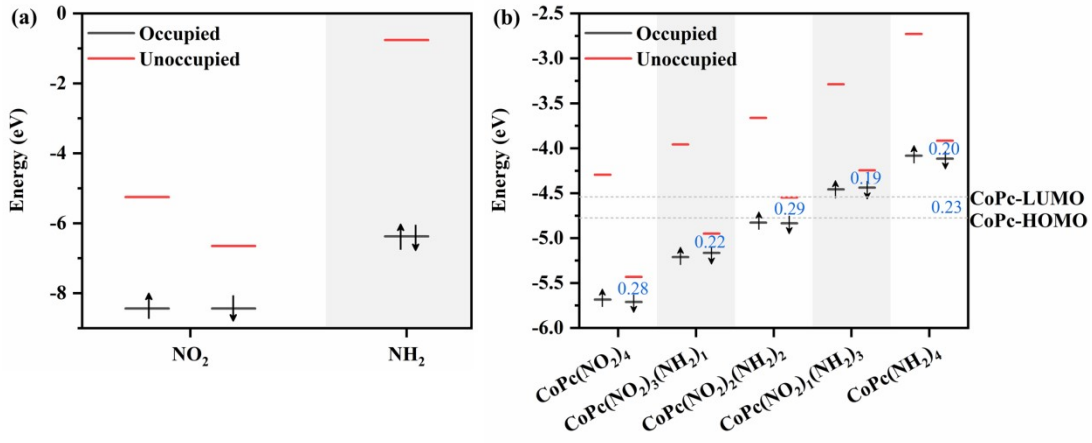

Figure S6. (a) HOMO and LUMO of isolated NO_2 and NH_2. (b) Effects of NO_2 and NH_2 on HOMO and LUMO energy on cobalt phthalocyanine complexes.

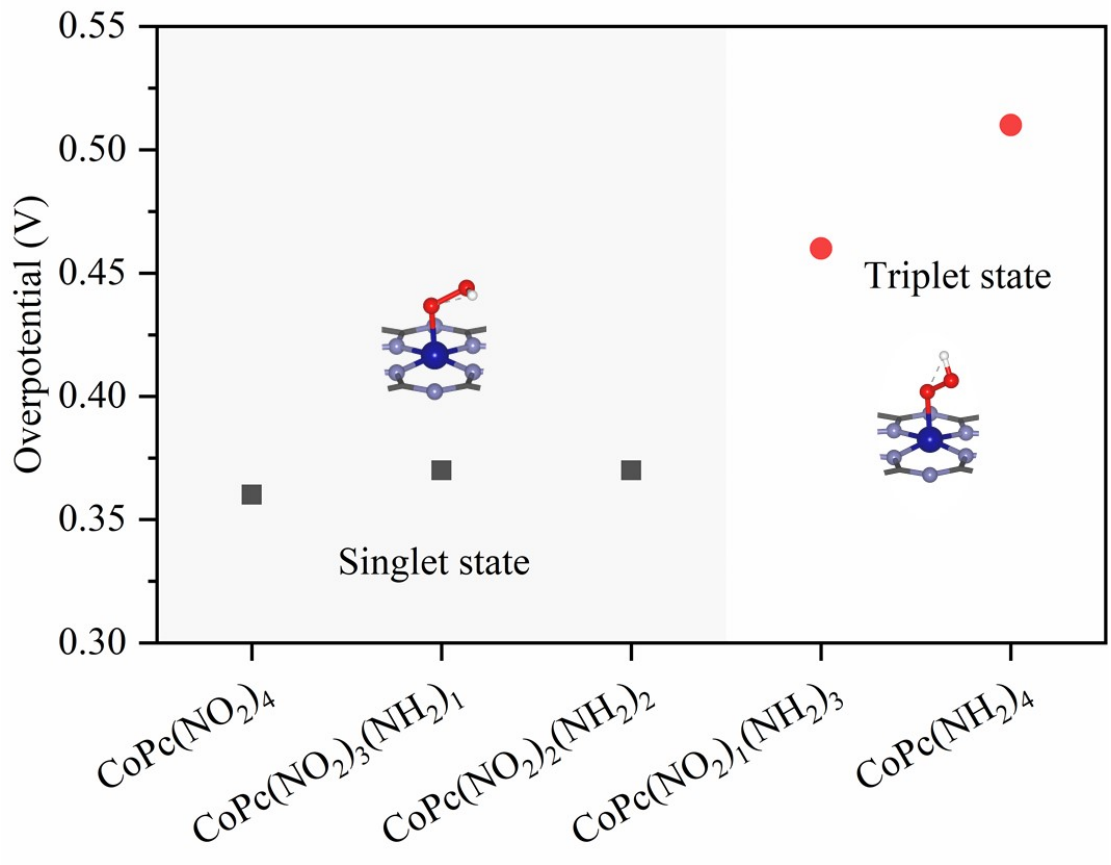

Figure S7. Overpotentials of CoPc complexes with different spin states when OOH* adsorbed.

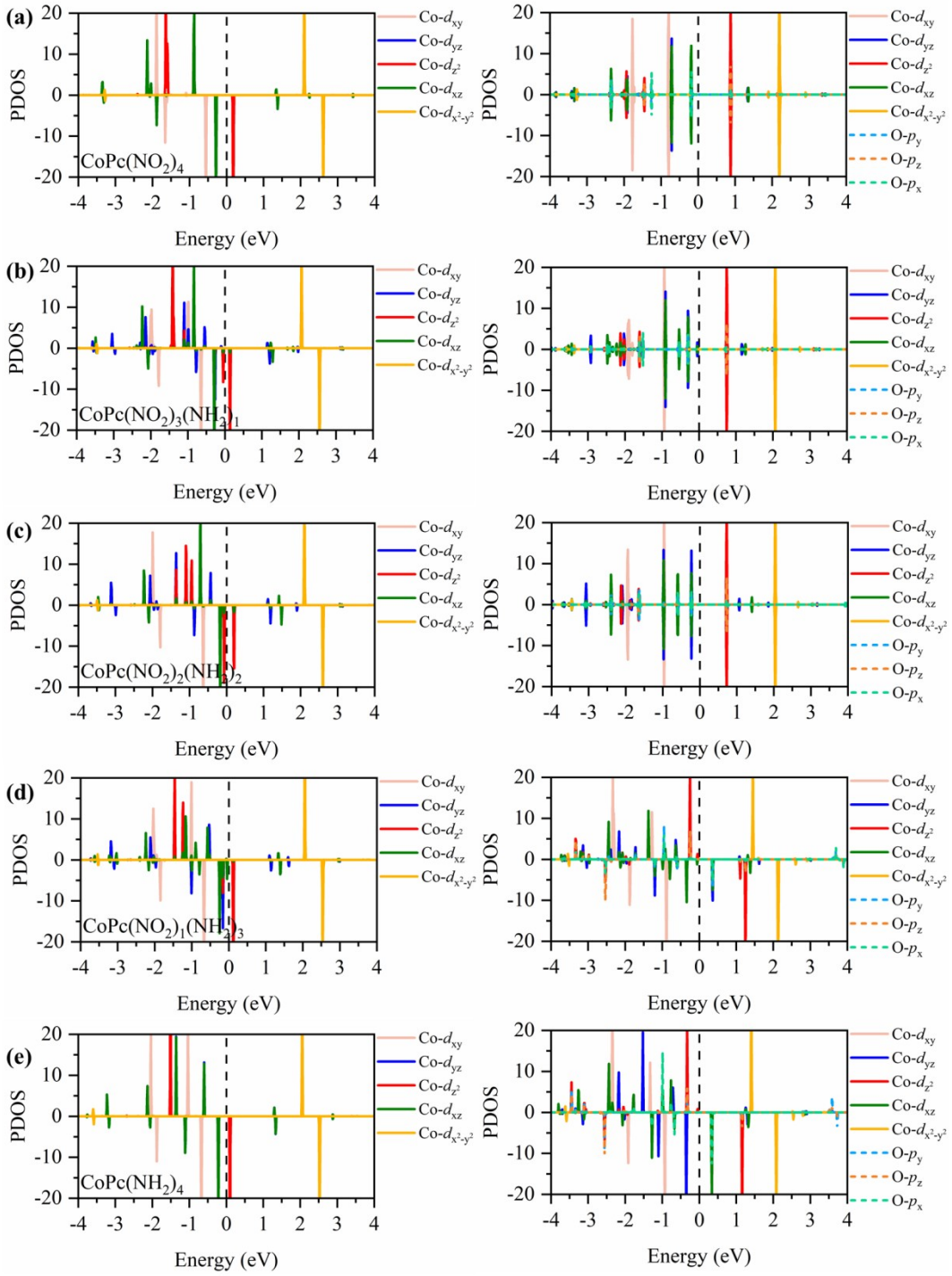

Figure S8. (a-e) Projected density of states (PDOS) for $CoPc(NO_2)_n(NH_2)_{4-n}$ (n=0, 1, 2, 3, 4) and OOH* adsorbed on $CoPc(NO_2)_n(NH_2)_{4-n}$.

Table S4. ICOHP values for Co-O bond of OOH* adsorbed on different substituted cobalt phthalocyanine complexes.

$CoPc(NO_2)_n(NH_2)_{4-n}$	n=4	n=3	n=2	n=1	n=0
ICOHP-UP	-2.483	-2.468	-2.444	-1.531	-1.549
d_z^2-p_z(up)	-0.640	-0.645	-0.647	-0.047	-0.052
d_{xz}-p_x(up)	-0.040	-0.044	-0.031	-0.026	0.002
d_{yz}-p_y(up)	-0.051	-0.046	-0.044	-0.020	-0.048
ICOHP-DOWN	-2.482	-2.468	-2.445	-2.651	-2.681
d_z^2-p_z(dw)	-0.640	-0.645	-0.647	-0.588	-0.567
d_{xz}-p_x(dw)	-0.040	-0.044	-0.030	-0.186	-0.349
d_{yz}-p_y(dw)	-0.051	-0.046	-0.044	-0.223	-0.073
TOT	-4.965	-4.936	-4.889	-4.183	-4.230

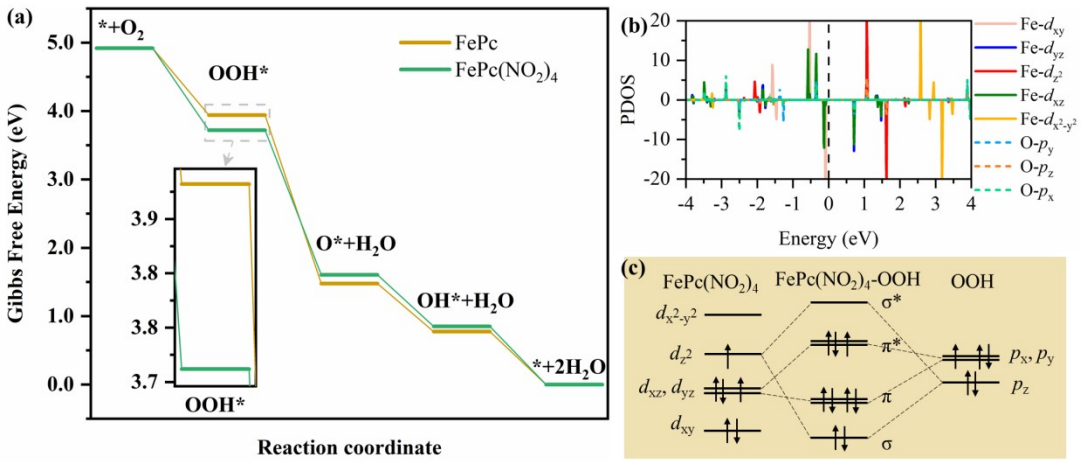

Figure S9. (a) Gibbs free energy diagrams for ORR on substituted iron phthalocyanine complexes at U = 0 V. (b) Projected density of states (PDOS) for OOH* adsorbed on $FePc(NO_2)_4$. (c) Orbital interaction between the cobalt atom of $FePc(NO_2)_4$ and OOH* when the OOH* adsorbed.

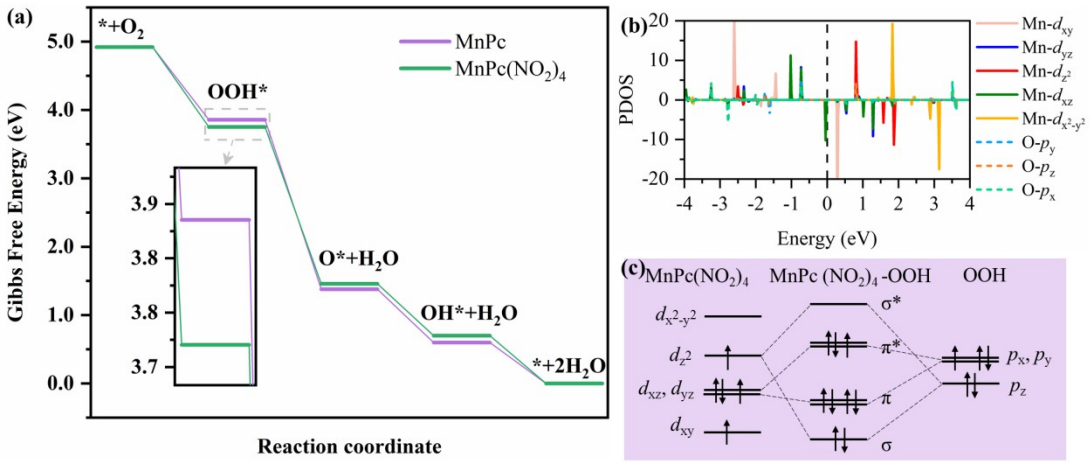

Figure S10. (a) Gibbs free energy diagrams for ORR on substituted manganese phthalocyanine complexes at U = 0 V. (b) Projected density of states (PDOS) for OOH* adsorbed on $MnPc(NO_2)_4$. (c) Orbital interaction between the cobalt atom of $MnPc(NO_2)_4$ and OOH* when the OOH* adsorbed.