Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Halogen Substitutions Leading to Enhance Oxygen Evolution and Oxygen Reduction Reactions in Metalloporphyrin Frameworks

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Table S1. Free energy corrections (G_{corr}), including, zero-point energy (ZPE), and entropic corrections (TS term) and solvent corrections (G_{solv}) to gasphase and adsorbed species taken from ref 17. All energies are in eV unit.

Species	ZPE	TS	G_{solv}	G_{corr}
$H_2O_{(l)}$	0.56	0.67	0.00	-0.11
$H_{2(g)}$	0.27	0.41	0.00	-0.14
*O	0.07	0.00	0.00	0.07
*OH	0.36	0.00	-0.30	0.06
*OOH	0.39	0.00	-0.30	0.09

Table S2. Free energies of the OER and ORR adsorbates, *OH, *O, and *OOH, in eV unit and overpotentials of the OER and ORR, in V unit, on the metalloporphyrin framework M-Por.

M	ΔG_{*OH}	ΔG_{*O}	ΔG_{*OOH}	$\Delta\Delta G$	ΔG_1	ΔG_2	ΔG_3	ΔG_4	η^{OER}	η^{ORR}
Cr	0.17	0.83	3.39	3.22	0.17	0.66	2.55	1.53	1.32	1.06
Mn	0.42	1.45	3.76	3.35	0.42	1.03	2.32	1.16	1.09	0.81
Fe	0.60	1.44	3.56	2.96	0.60	0.84	2.12	1.36	0.89	0.63
Co	0.93	2.75	3.88	2.95	0.93	1.82	1.14	1.04	0.59	0.30
Ni	2.04	4.35	4.86	2.82	2.04	2.31	0.51	0.06	1.08	1.17
Cu	2.64	4.62	5.08	2.45	2.64	1.98	0.46	-0.16	0.75	1.39
Zn	1.99	4.57	4.88	2.89	1.99	2.58	0.32	0.04	1.35	1.19
Ru	-0.05	0.64	2.91	2.96	-0.05	0.69	2.28	2.01	1.05	1.28
Rh	0.59	2.42	3.58	2.99	0.59	1.83	1.16	1.34	0.60	0.64
Pd	2.35	4.84	5.03	2.68	2.35	2.50	0.18	-0.11	1.27	1.34
Ag	2.47	5.00	5.00	2.53	2.47	2.53	0.00	-0.08	1.30	1.31
Ir	0.62	2.20	3.66	3.04	0.62	1.58	1.47	1.26	0.35	0.61
Pt	2.31	4.63	5.05	2.74	2.31	2.32	0.42	-0.13	1.09	1.36
Au	2.00	4.63	4.77	2.77	2.00	2.64	0.13	0.15	1.41	1.10

Table S3. Magnetic moment projected per metal site for each reaction step.

M	*	*OH	*O	*OOH
Cr	2.9	1.4	0.0	2.1
Mn	2.9	2.0	1.5	1.8
Fe	1.8	1.5	0.9	0.7
Co	0.9	0.0	1.2	0.0
Ni	0.0	0.5	0.5	0.3
Cu	0.6	0.0	0.7	0.5
Zn	0.0	0.0	0.0	0.0
Ru	1.0	0.5	0.4	0.4
Rh	0.5	0.0	0.2	0.0
Pd	0.0	0.3	0.0	0.1
Ag	0.4	0.3	0.2	0.3
Ir	0.4	0.0	0.2	0.0
Pt	0.0	0.2	0.0	0.0
Au	0.0	0.0	0.0	0.0

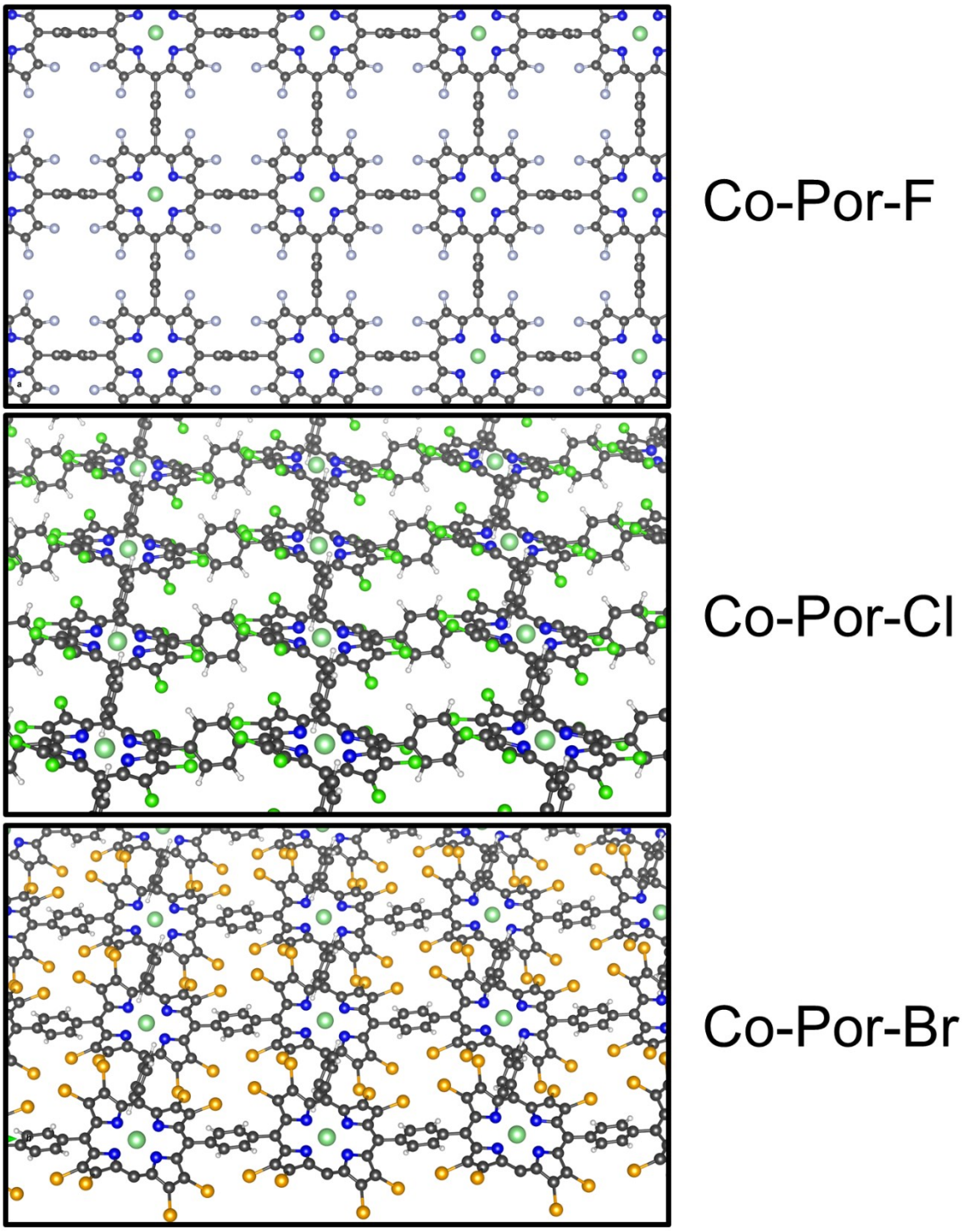

Figure S1. Flat 2D structure of Co-Por-F and distorted structure Co-Por-Cl and Co-Por-Br due to steric effect of Cl and Br atoms.

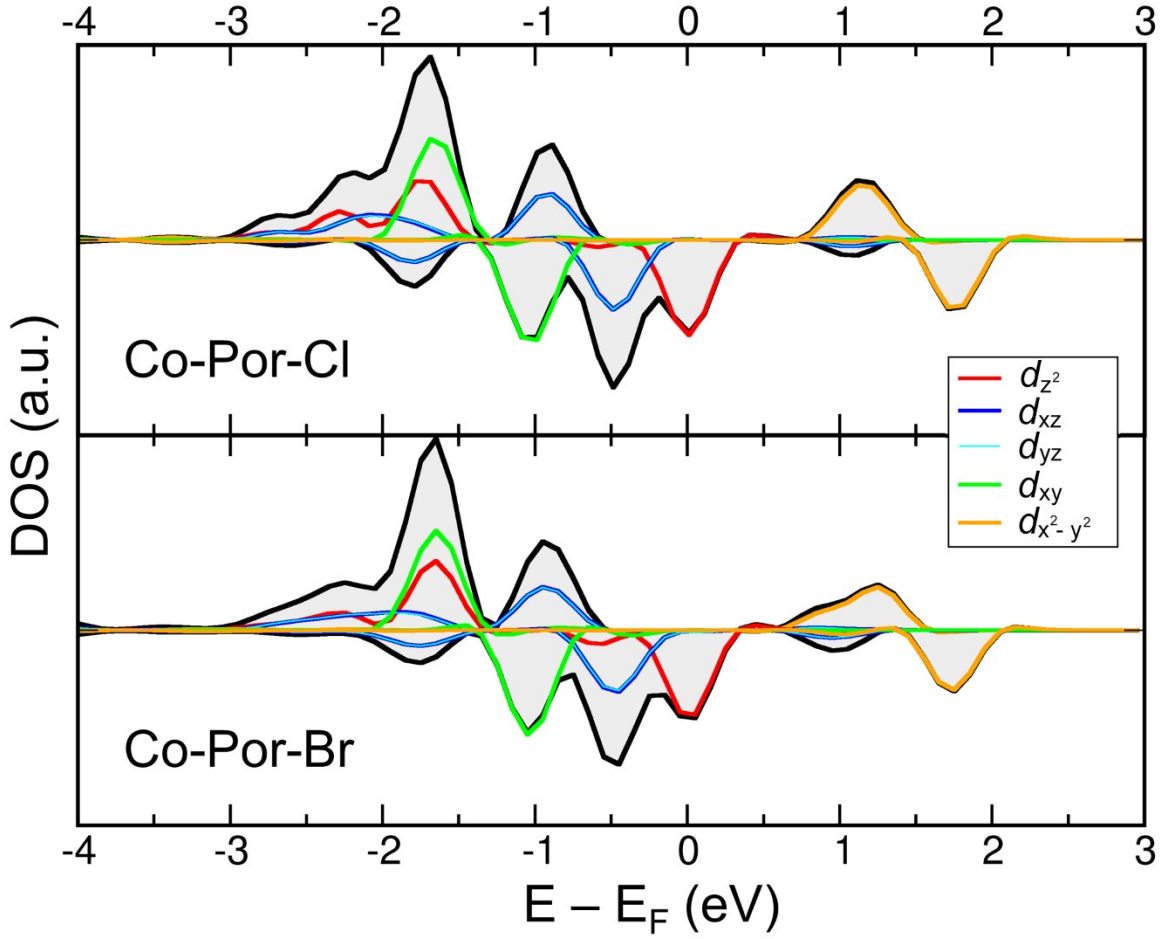

Figure S2. Projected density of state of each d-component of Co atom on Co-Por-Cl and Co-Por-Br

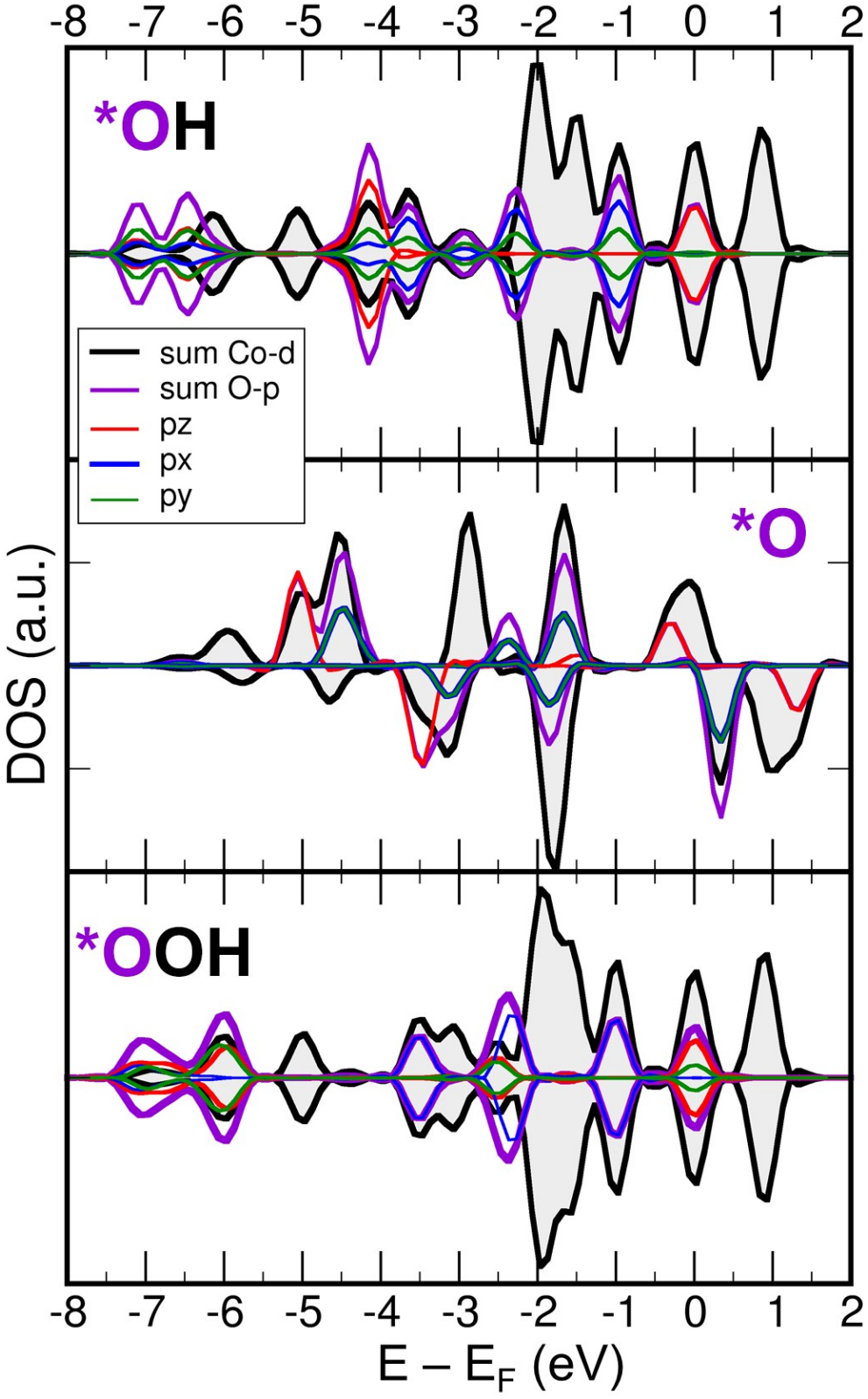

Figure S3 Projected density of states of *p*-components of O atom at intermediate adsorbing states on the Co-Por catalyst. Spin up and down states are shown.

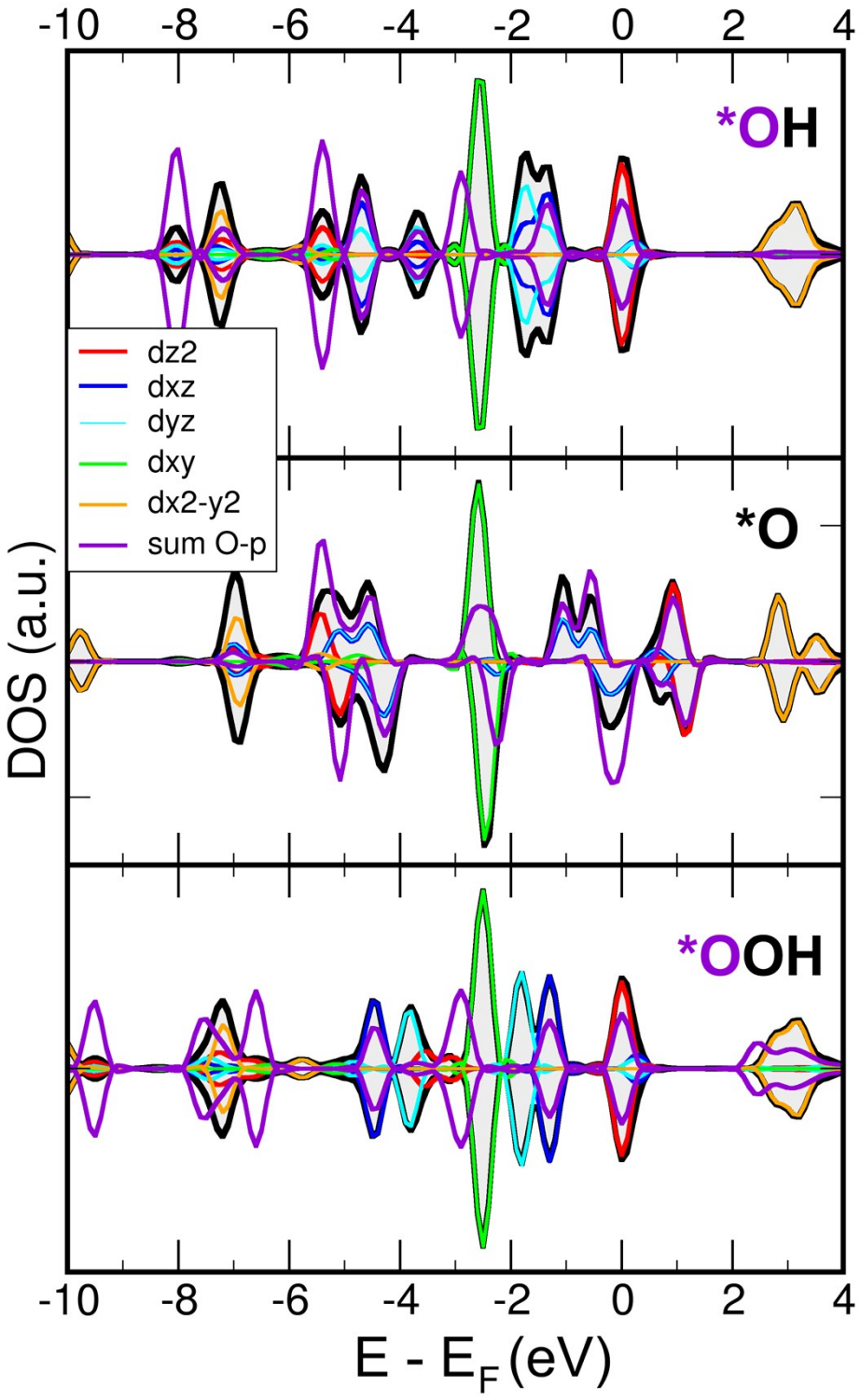

Figure S4. Projected density of states (PDOS) of the *d*-components of the Ir atom and of the *p*-components of the O atom of intermediate adsorbing states on the Ir-Por catalyst. Spin up and down states are shown.

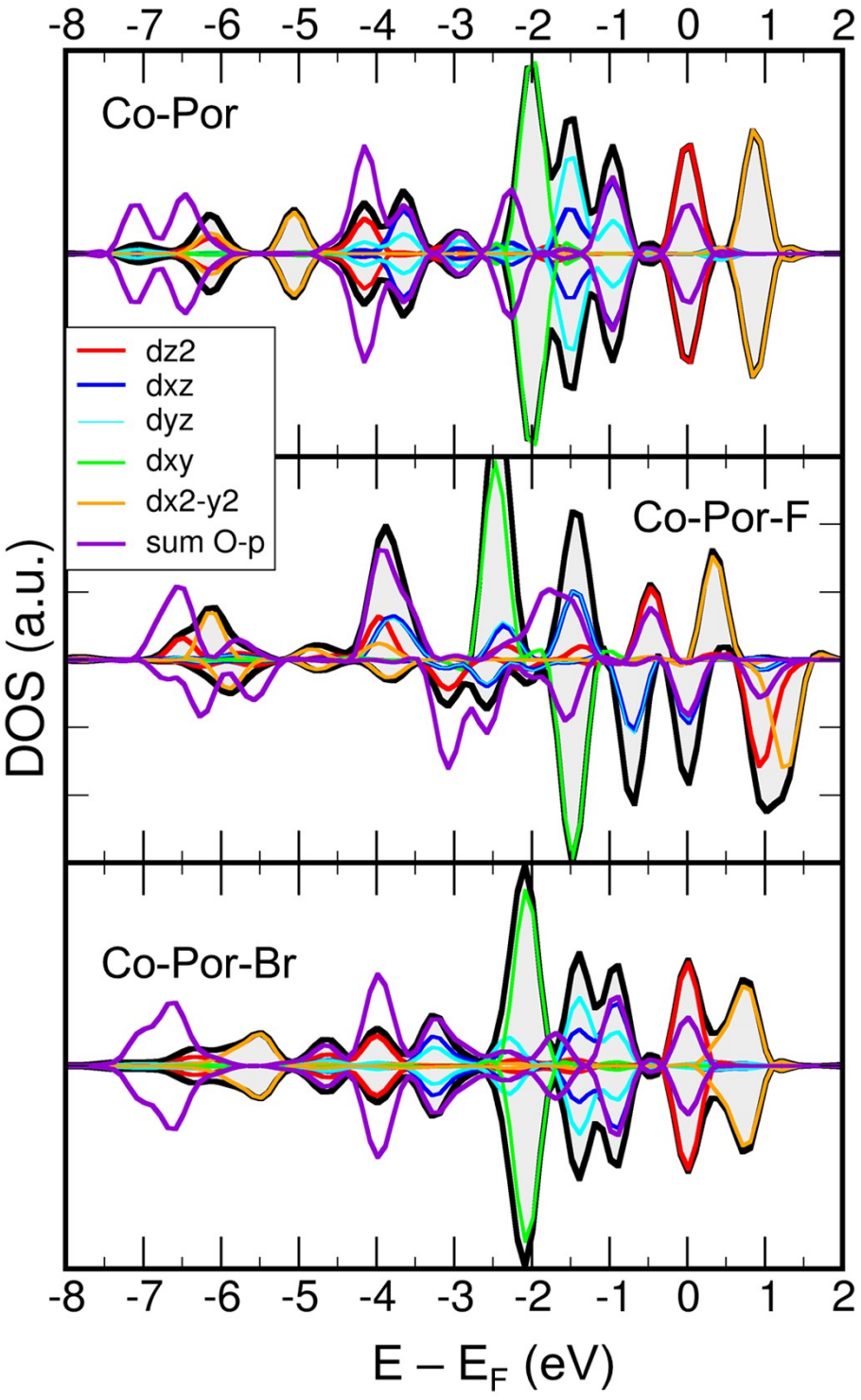

Figure S5 Projected density of states of *d*-components of Co atom and *p*-components of O atom of *OH adsorbing states on the Co-Por, Co-Por-F, and Co-Por-Br catalyst. Spin up and down states are shown.

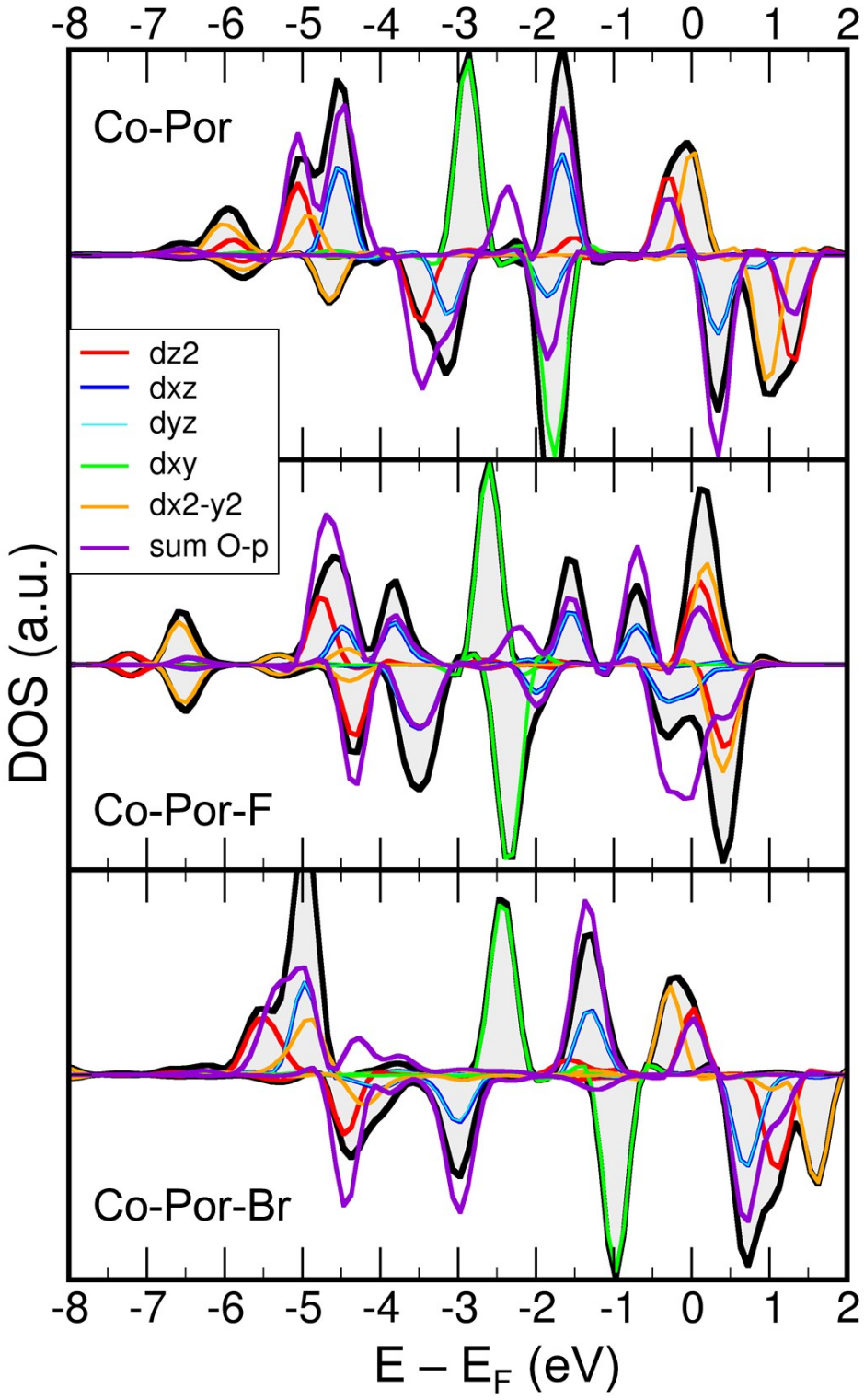

Figure S6 Projected density of states of *d*-components of Co atom and *p*-components of O atom of *O adsorbing states on the Co-Por, Co-Por-F, and Co-Por-Br catalyst. Spin up and down states are shown.

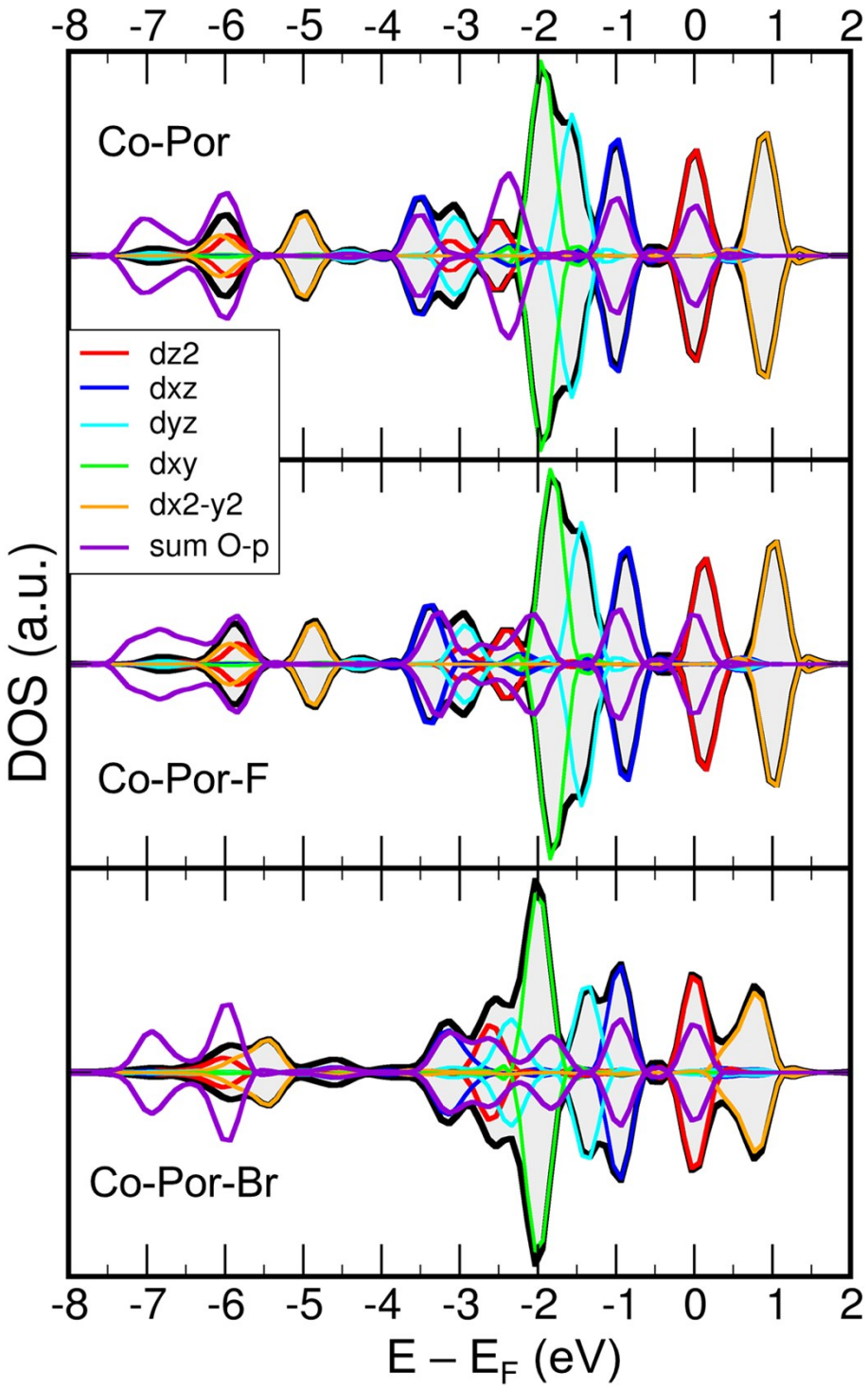

Figure S7 Projected density of states of *d*-components of Co atom and *p*-components of O atom of *OOH adsorbing states on the Co-Por, Co-Por-F, and Co-Por-Br catalyst. Spin up and down states are shown.