Supporting Information

Theoretical study on the ORR electrocatalytic activity of axial ligand modified polyphthalocyanine cobalt

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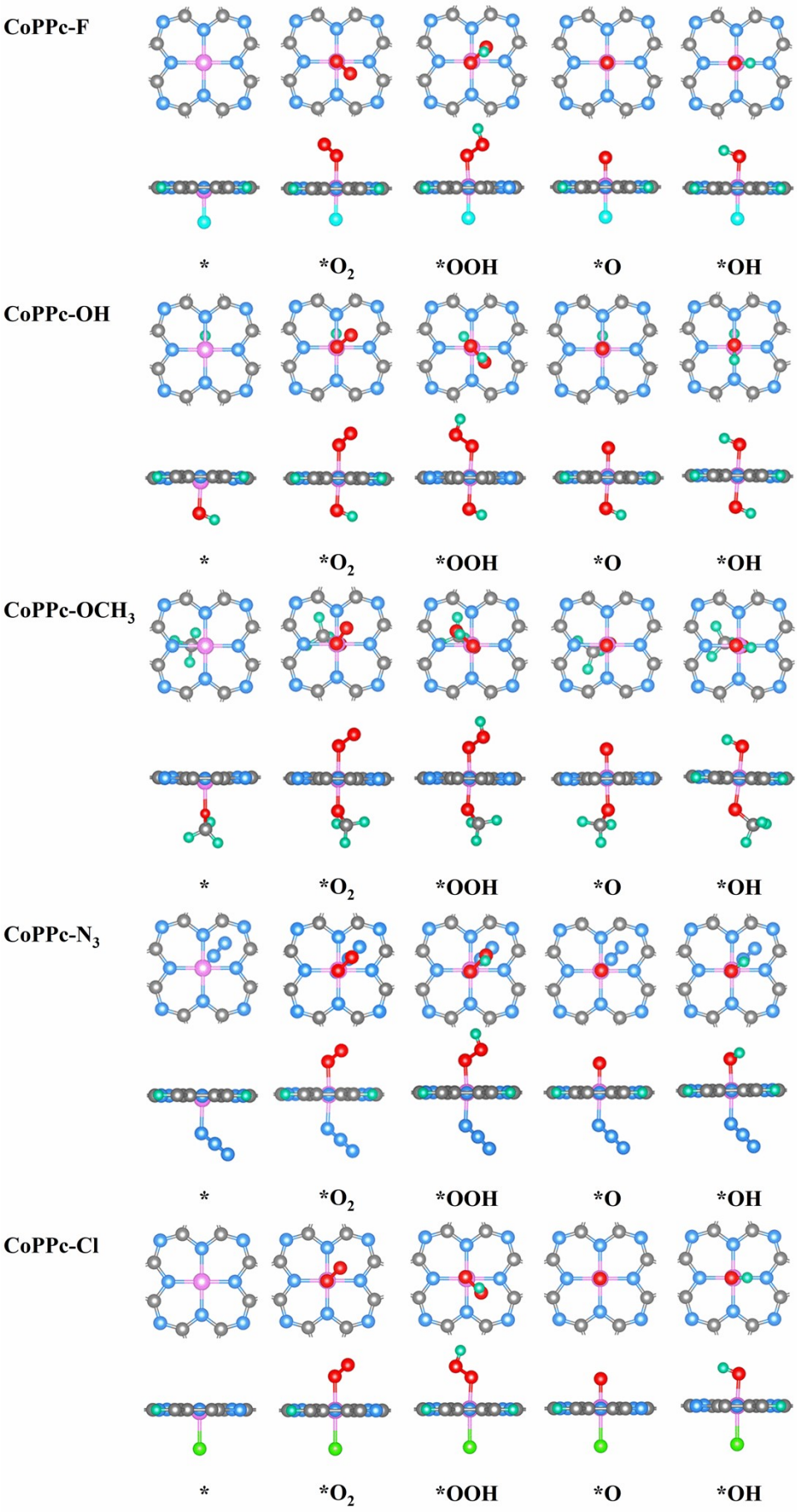
CoPPc-F
*
*O2
*OOH
*O
*OH
CoPPc-OH
*
*O2
*OOH
*O
*OH
CoPPc-OCH3
*
*O2
*OOH
*O
*OH
CoPPc-N3
*
*O2
*OOH
*O
*OH
CoPPc-Cl
*
*O2
*OOH
*O
*OH

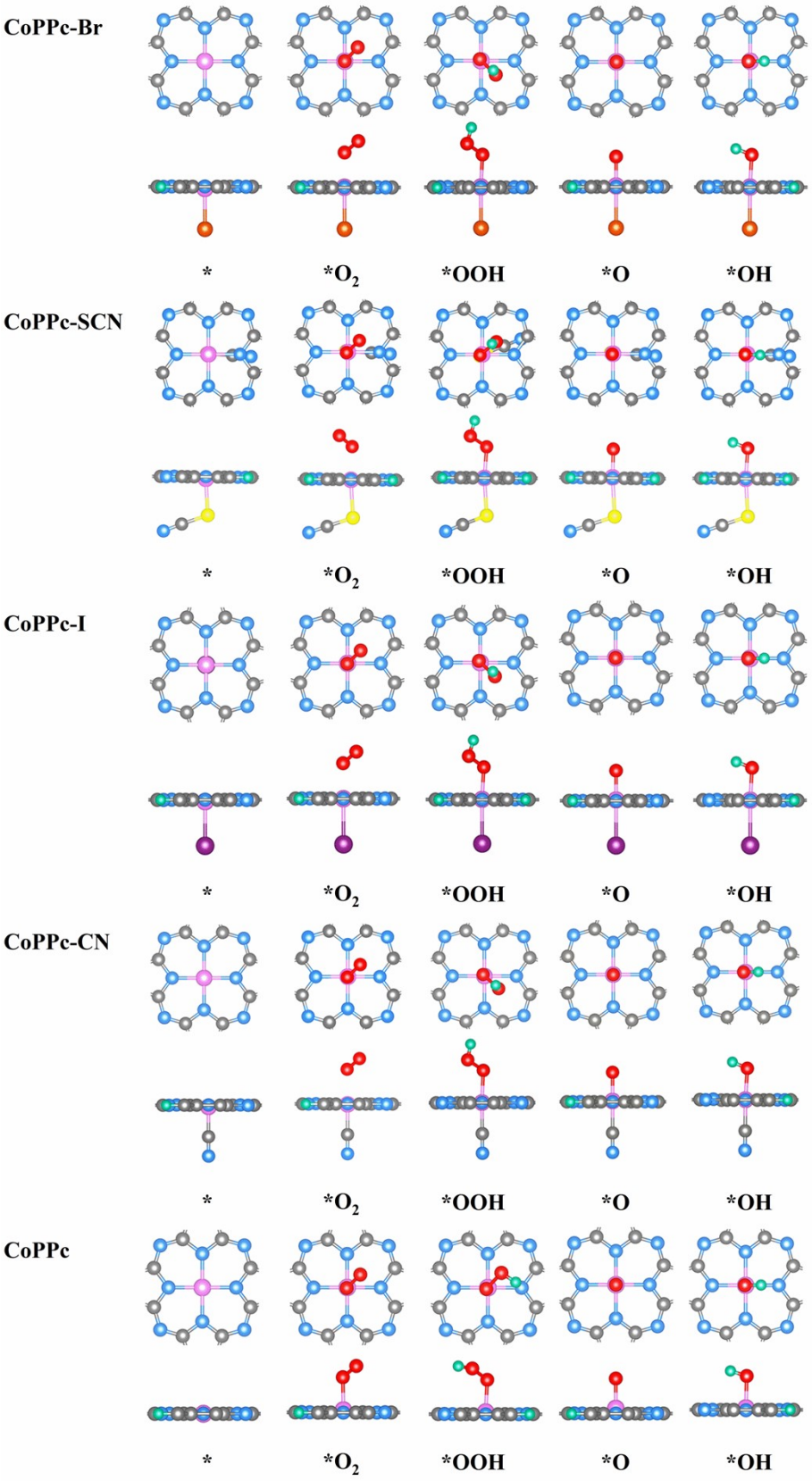

Fig.S1. Optimized geometric structure of the CoPPc and various CoPPc-L with top and side views. The green, gray, blue, pink, cyan, yellow, light green, orange and purple represent H, C, N, Co, F, S, Cl, Br and I atoms, respectively.

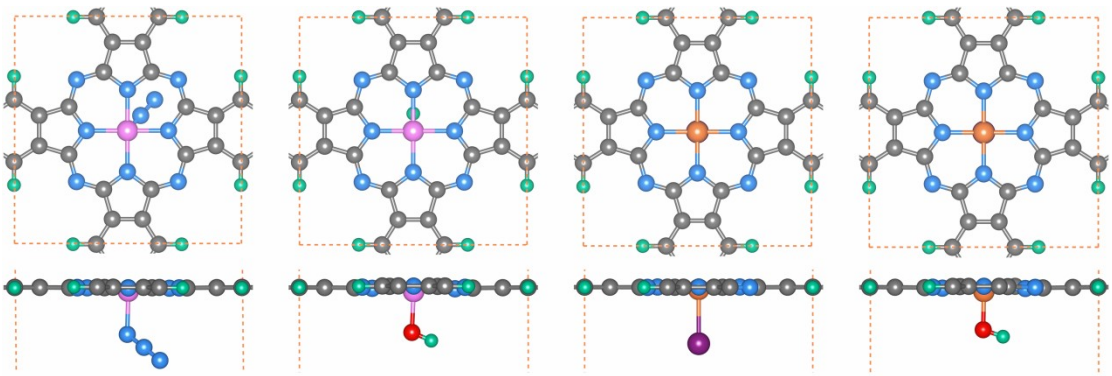

Fig.S2.(a)-(d) Top view and side view of the unit cell of CoPPc-N_3, CoPPc-OH, FePPc-I and FePPc-OH, respectively. The green, gray, blue, red, purple, pink and orange represent H, C, N, O, I, Co and Fe atoms, respectively.

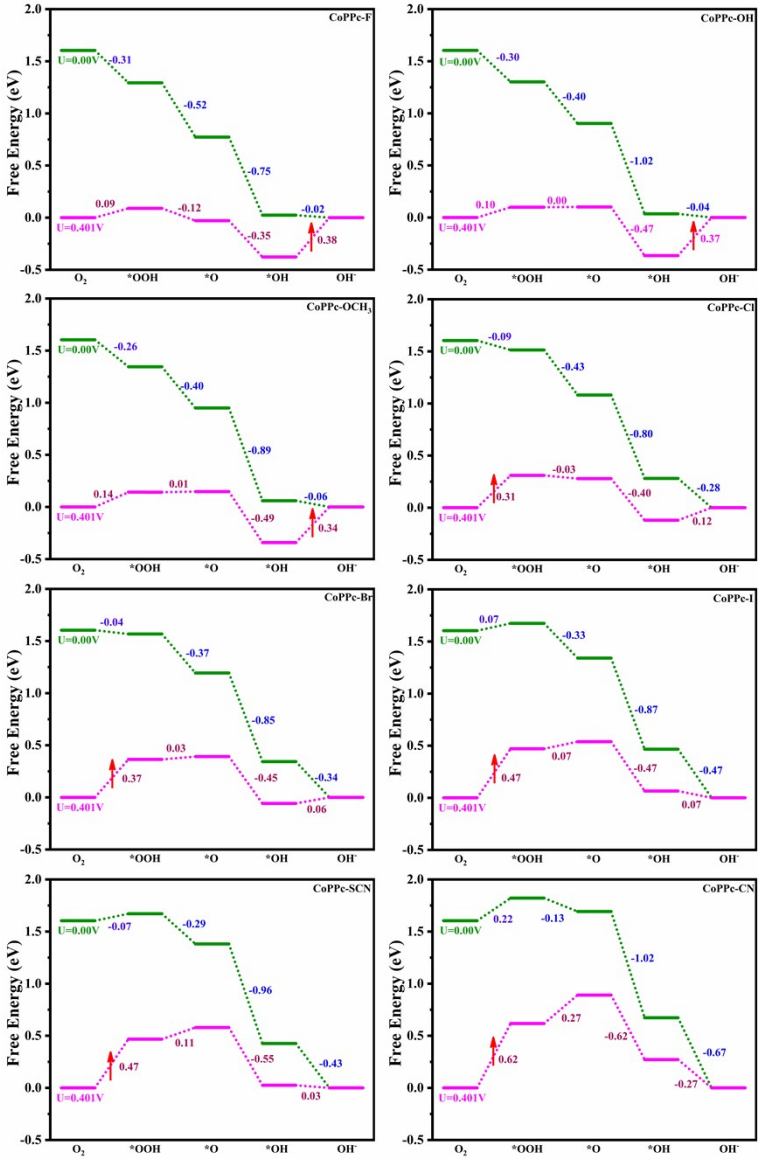

Fig.S3. Free energy change of ORR on CoPPc-L, respectively. The calculated working potential is marked by the green line. η denotes the overpotential of ORR.

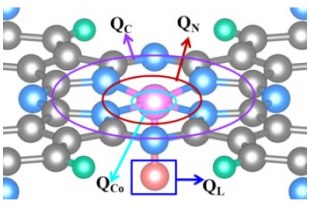

Fig.S4. Q_{Co}, Q_N, Q_C and Q_L represent bader charge of cobalt atom (Cyan circle), total bader charge of four N atoms directly connected with cobalt atom (red circle), total bader charge of eight C atoms directly connected with these four N atoms (purple circle) and bader charge of axial ligands (blue circle) in the Coppc-L, respectively.

Table S1. Lattice parameters of CoPPc and CoPPc-L (in Å).

Structure	**Lattice parameters**	**Lattice parameters**
CoPPc-F	a=16.630	b=16.630
CoPPc-OH	a=16.640,	b=16.636
CoPPc-OCH_3	a=16.641	b=16.637
CoPPc-N_3	a=16.636	b=16.636
CoPPc-Cl	a=16.628	b=16.628
CoPPc-Br	a=16.628	b=16.628
CoPPc-SCN	a=16.628	b=16.631
CoPPc-I	a=16.628	b=16.628
CoPPc-CN	a=16.627	b=16.627
CoPPc	a=16.632	b=16.632

Table S2. Q_{Co}, Q_N, Q_C and Q_L represent Bader charge of cobalt atom, total Bader charge of four N atoms directly connected with the Co atom, total Bader charge of eight C atoms directly connected with the four N atoms and Bader charge of axial ligands in CoPPc and the Coppc-L, respectively.

Structure	**Q_{Co} (|e|)**	**Q_N (|e|)**	**Q_C (|e|)**	**Q_L (|e|)**
CoPPc-F	1.28	-4.51	8.30	-0.64
CoPPc-OH	1.21	-4.54	8.23	-0.39
CoPPc-OCH_3	1.16	-4.40	7.92	-0.32
CoPPc-N_3	1.10	-4.67	8.48	-0.41
CoPPc-Cl	1.08	-4.49	8.20	-0.35
CoPPc-Br	1.09	-4.52	8.19	-0.31
CoPPc-SCN	1.06	-4.55	8.20	-0.28
CoPPc-I	0.98	-4.54	8.17	-0.14
CoPPc-CN	1.05	-4.49	8.20	-0.31
CoPPc	1.13	-4.73	8.12	---