Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Single-Atom Catalysts of TM-Porphyrin for Alkali Oxygen Battery: Reaction Mechanism and Universal Design Principle

Qian Wu, Shiying Shen, Rui Peng, Baibiao Huang, Ying Dai* and Yandong Ma*

School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Shandanan Str. 27, Jinan 250100, China

*Email: daiy60@sina.com (Y.D.); yandong.ma@sdu.edu.cn (Y.M.)

1. Adsorption energy

The consecutive adsorption energy (E_{ads}) of a newly added Li/Na or O_2 of Li/Na_xO_{2y} (x = 0–4, y = 0–2) intermediates on Fe/Co/Ni/Cu-porphyrin were calculated as

$$E_{ads}\ (Li/Na) = E_{Li/Na_xO_{2y}} - E_{Li/Na} - E_{Li/Na_{(x-1)}O_{2y}}$$

$$E_{ads}\ (O_2) = E_{Li/Na_xO_{2y}} - E_{O_2} - E_{Li/Na_xO_{2(y-1)}}$$

where $E_{Li/Na_xO_{2y}}$, $E_{Li/Na_{(x-1)}O_{2y}}$ and $E_{Li/Na_xO_{2(y-1)}}$ are the total energy of Li/Na_xO_{2y} or Li/$Na_{(x-1)}O_{2y}$ or Li/$Na_xO_{(2y-1)}$ adsorbed X-porphyrin (X = Fe/Co/Ni/Cu), $E_{Li/Na}$ is the energy of Li/Na atom in the bulk phase, E_{O_2} is the energy of O_2 molecule.

2. Equilibrium potential

The equilibrium potential can be obtained by the Nernst equation

$$U_{eq} = -\frac{\Delta G_f}{ne}$$

$$\Delta G_f = G_{Li/Na_xO_{2y}} - xG_{Li/Na} - yG_{O_2}$$

where ΔG_f is the standard formation energy of Li/Na_xO_{2y}, n is the number of transferred electrons during the reaction, and $G_{Li/Na_xO_{2y}}$, $G_{Li/Na}$ and G_{O_2} are the Gibbs free energies of Li/Na_xO_{2y}, Li atom of bulk phase and O_2 molecule, respectively.

3. Adsorption free energies for intermediates

The adsorption free energies of *Li, *LiO_2, *Li_2O_2, *Li_3O_2, *Li_4O_2 are calculated as following:

$\Delta G_{*Li} = \Delta G\ (* + Li^+ + e^- \rightarrow *Li)$

$= G_{*Li} - G_* - G_{Li}$

$= (E_{*Li} - E_* - E_{Li}) + (E_{ZPE(*Li)} - E_{ZPE(*)} - E_{ZPE(Li)}) - T \times (S_{*Li} - S_* - S_{Li})$

$\Delta G_{*LiO_2} = \Delta G\ (* + O_2 + Li \rightarrow *LiO_2)$

$= G_{*LiO_2} - G_* - G_{O_2} - G_{Li}$

$= (E_{*LiO_2} - E_* - E_{O_2} - E_{*Li}) + (E_{ZPE(*LiO_2)} - E_{ZPE(*)} - E_{ZPE(O_2)} - E_{ZPE(*Li)}) - T \times (S_{*LiO_2} - S_* - S_{O_2} - S_{*Li})$

$\Delta G_{*Li_2O_2} = \Delta G\ (* + O_2 + 2Li^+ + e^- \rightarrow *Li_2O_2)$

$= G_{*Li_2O_2} - G_* - G_{O_2} - 2G_{Li}$

$= (E_{*Li_2O_2} - E_* - E_{O_2} - 2E_{Li}) + (E_{ZPE(*Li_2O_2)} - E_{ZPE(*)} - E_{ZPE(O_2)} - 2E_{ZPE(Li)}) - T \times (S_{*Li_2O_2} - S_* - S_{O_2} - 2S_{Li})$

$\Delta G_{*Li_3O_2} = \Delta G\ (* + O_2 + 3Li^+ + e^- \rightarrow *Li_3O_2)$

$= G_{*Li_3O_2} - G_* - G_{O_2} - 3G_{Li}$

$= (E_{*Li_3O_2} - E_* - E_{O_2} - 3E_{Li}) + (E_{ZPE(*Li_3O_2)} - E_{ZPE(*)} - E_{ZPE(O_2)} - 3E_{ZPE(Li)}) - T \times (S_{*Li_3O_2} - S_* - S_{O_2} - 3S_{Li})$

$\Delta G_{*Li_4O_2} = \Delta G\ (* + O_2 + 4Li^+ + e^- \rightarrow *Li_4O_2)$

$= G_{*Li_4O_2} - G_* - G_{O_2} - 4G_{Li}$

$= (E_{*Li_4O_2} - E_* - E_{O_2} - 4E_{Li}) + (E_{ZPE(*Li_4O_2)} - E_{ZPE(*)} - E_{ZPE(O_2)} - 4E_{ZPE(Li)}) - T \times (S_{*Li_4O_2} - S_* - S_{O_2} - 4S_{Li})$

4. Reaction free energy

$$* + Li^+ + e^- + O_2 \rightarrow *LiO_2\ (1)$$

$$*LiO_2 + Li^+ + e^- \rightarrow *Li_2O_2\ (2)$$

$$*Li_2O_2 + Li^+ + e^- \rightarrow *Li_3O_2\ (3)$$

$$*Li_3O_2 + Li^+ + e^- \rightarrow *Li_4O_2\ (4)$$

$\Delta G_1 = G_{*LiO_2} - G_* - G_{Li} - G_{O_2}$

$= \Delta G_{*LiO_2}$

$\Delta G_2 = G_{*Li_2O_2} - G_{*LiO_2} - G_{Li}$

$= \Delta G_{*Li_2O_2} + G_* + G_{O_2} + 2G_{Li} - \Delta G_{*LiO_2} - G_* - G_{O_2} - G_{Li} - G_{Li}$

$= \Delta G_{*Li_2O_2} - \Delta G_{*LiO_2}$

$\Delta G_3 = G_{*Li_3O_2} - G_{*Li_2O_2} - G_{Li}$

$= \Delta G_{*Li_3O_2} + G_* + G_{O_2} + 3G_{Li} - \Delta G_{*Li_2O_2} - G_* - G_{O_2} - 2G_{Li} - G_{Li}$

$= \Delta G_{*Li_3O_2} - \Delta G_{*Li_2O_2}$

$\Delta G_4 = G_{*Li_4O_2} - G_{*Li_3O_2} - G_{Li}$

$= \Delta G_{*Li_4O_2} + G_* + G_{O_2} + 4G_{Li} - \Delta G_{*Li_3O_2} - G_* - G_{O_2} - 3G_{Li} - G_{Li}$

$= \Delta G_{*Li_4O_2} - \Delta G_{*Li_3O_2}$

Table S1. Optimized lattice constants of TM-porphyrin (TM = Fe/Co/Ni/Cu) during PBE, PBEsol and SCAN functionals. The unit is Å.

	Fe-porphyrin		Co-porphyrin		Ni-porphyrin		Cu-porphyrin	
	a	b	a	b	a	b	a	b
PBE	8.34	8.34	8.33	8.33	8.33	8.33	8.38	8.38
PBEsol	8.33	8.33	8.31	8.31	8.31	8.31	8.36	8.36
SCAN	8.26	8.26	8.24	8.24	8.24	8.24	8.29	8.29

Table S2. Computed total energies (E_{tot}), thermal correction to Gibbs free energies (zero-point energies (E_{ZPE}) and entropy (TS)), Gibbs free energies (G) and reaction Gibbs free energies (ΔG) of $*O_2$ (with side-on/end-on adsorption configurations), *Li and $*LiO_2$ (with side-on/end-on adsorption configurations of O_2 molecules) intermediates on Fe/Co/Ni/Cu-porphyrin for Li-O_2 battery.

	E_{tot} (eV)	ZPE-TS (eV)	G (eV)	ΔG (eV)
Fe-porphyrin/$*O_2$ (side-on)	-235.58	0.06	-235.52	-0.59
Fe-porphyrin/$*O_2$ (end-on)	-235.56	0.07	-235.49	-0.56
Fe-porphyrin/*Li	-227.64	0.04	-227.60	-1.17
Fe-porphyrin/$*LiO_2$ (side-on)	-239.35	0.11	-239.24	-1.24
Fe-porphyrin/$*LiO_2$ (end-on)	-239.37	0.12	-239.25	-1.25
Co-porphyrin/$*O_2$ (side-on)	-234.03	0.06	-233.97	0.08
Co-porphyrin/$*O_2$ (end-on)	-233.52	0.04	-233.48	0.57
Co-porphyrin/*Li	-226.91	0.05	-226.86	-1.31
Co-porphyrin/$*LiO_2$ (side-on)	-237.93	0.09	-237.84	-0.58
Co-porphyrin/$*LiO_2$ (end-on)	-237.93	0.08	-237.85	-0.59
Ni-porphyrin/$*O_2$ (side-on)	-232.15	-0.04	-232.19	0.37
Ni-porphyrin/$*O_2$ (end-on)	-232.14	0.01	-232.13	0.43
Ni-porphyrin/*Li	-225.37	0.05	-225.32	-1.26
Ni-porphyrin/$*LiO_2$ (side-on)	-236.01	0.04	-235.97	-0.25

Ni-porphyrin/*LiO_2 (end-on)	-236.01	0.05	-235.96	-0.24
Cu-porphyrin/*O_2 (side-on)	-229.42	-0.04	-229.46	0.16
Cu-porphyrin/*O_2 (end-on)	-229.18	-0.02	-229.20	0.42
Cu-porphyrin/*Li	-222.64	0.05	-222.59	-1.47
Cu-porphyrin/*LiO_2 (side-on)	-233.30	0.08	-233.22	-0.23
Cu-porphyrin/*LiO_2 (end-on)	-233.31	0.02	-233.29	-0.30

Table S3. Calculated O-O bond length and atomic charges of adsorbed O_2 molecule at the active site with (w) or without (w/o) Li of Fe/Co/Ni/Cu-porphyrin.

	Fe-porphyrin	Co-porphyrin	Ni-porphyrin	Cu-porphyrin
O-O bond length (w) (Å)	1.35	1.33	1.30	1.30
O-O bond length (w/o) (Å)	1.28	1.27	1.24	1.24
charge of O_2 (w) (e)	0.67	0.59	0.44	0.46
charge of O_2 (w/o) (e)	0.32	0.25	0.07	0.03

Table S4. Computed total energies (E_{tot}), thermal correction to Gibbs free energy (zero-point energies (E_{ZPE}) and entropy (TS)), Gibbs free energy (G) and reaction Gibbs free energies (ΔG) of *Li_3O_2, *Li_2O_4, *Li_4O_2 and *Li_3O_4 intermediates on Fe/Co/Ni/Cu-porphyrin for Li-O_2 battery.

	E_{tot} (eV)	ZPE-TS (eV)	G (eV)	ΔG (eV)
Fe-porphyrin/*Li_3O_2	-247.73	0.17	-247.56	-2.45
Fe-porphyrin/*Li_2O_4	-254.15	0.08	-254.07	-0.46
Fe-porphyrin/*Li_4O_2	-251.61	0.25	-241.36	-1.90
Fe-porphyrin/*Li_3O_4	-257.64	0.17	-257.47	0.49
Co-porphyrin/*Li_3O_2	-245.90	0.18	-245.72	-1.91
Co-porphyrin/*Li_2O_4	-252.77	0.10	-252.67	-0.36
Co-porphyrin/*Li_4O_2	-250.21	0.26	-249.75	-2.13

Co-porphyrin/*Li_3O_4	-255.77	0.20	-255.57	0.55
Ni-porphyrin/*Li_3O_2	-244.15	0.18	-243.97	-1.92
Ni-porphyrin/*Li_2O_4	-250.54	0.13	-250.41	0.09
Ni-porphyrin/*Li_4O_2	-247.70	0.23	-247.47	-1.65
Ni-porphyrin/*Li_3O_4	-254.93	0.20	-254.73	-0.36
Cu-porphyrin/*Li_3O_2	-241.49	0.20	-241.29	-1.97
Cu-porphyrin/*Li_2O_4	-247.62	0.25	-247.37	0.45
Cu-porphyrin/*Li_4O_2	-245.08	0.30	-244.78	-1.59
Cu-porphyrin/*Li_3O_4	-251.40	0.17	-251.23	0.46

Table S5. Optimized TM-N bond lengths with and without absorbents (*Li/*LiO_2/*Li_2O_2/*Li_3O_2/*Li_4O_2) of TM-porphyrin (TM = Fe/Co/Ni/Cu).

	TM-N1 (Å)	TM-N2 (Å)	TM-N3 (Å)	TM-N4 (Å)	magnetic moment of TM (μB)	oxidation state of TM
Fe-porphyrin	1.96	1.96	1.96	1.96	2.10	1.1
Fe-porphyrin/*Li	1.94	1.94	1.97	1.97	1.81	-0.23
Fe-porphyrin/*LiO_2	1.96	1.97	2.00	2.00	0.11	0.32
Fe-porphyrin/*Li_2O_2	1.98	1.96	1.98	2.00	1.00	0.01
Fe-porphyrin/*Li_3O_2	1.98	1.98	2.00	2.00	1.47	0.13
Fe-porphyrin/*Li_4O_2	1.98	1.97	2.02	2.03	2.00	-0.02
Co-porphyrin	1.95	1.95	1.95	1.95	0.62	0.97
Co-porphyrin/*Li	1.97	1.97	1.94	1.94	0.78	-0.15
Co-porphyrin/*LiO_2	1.98	1.98	1.96	1.96	1.04	0.24
Co-porphyrin/*Li_2O_2	1.97	1.97	1.97	1.96	0.91	0.02
Co-porphyrin/*Li_3O_2	1.96	1.98	1.99	1.96	0.37	-0.03

Co-porphyrin/*Li_4O_2	1.96	2.01	2.00	1.96	1.38	-0.02
Ni-porphyrin	1.96	1.96	1.96	1.96	0.06	0.93
Ni-porphyrin/*Li	1.94	1.98	1.98	1.94	0.00	-0.12
Ni-porphyrin/*LiO_2	1.95	1.97	1.97	1.95	0.08	0.08
Ni-porphyrin/*Li_2O_2	1.95	1.96	1.97	1.96	0.14	0.02
Ni-porphyrin/*Li_3O_2	1.97	1.96	1.96	1.96	0.00	-0.1
Ni-porphyrin/*Li_4O_2	1.96	1.97	1.96	1.97	0.03	-0.05
Cu-porphyrin	2.01	2.01	2.01	2.01	0.56	0.96
Cu-porphyrin/*Li	1.97	2.03	2.03	1.97	0.51	-0.06
Cu-porphyrin/*LiO_2	1.98	2.01	2.01	1.98	0.55	-0.03
Cu-porphyrin/*Li_2O_2	1.99	2.01	1.99	1.97	0.52	-0.02
Cu-porphyrin/*Li_3O_2	1.99	2.00	2.01	2.00	0.51	-0.03
Cu-porphyrin/*Li_4O_2	2.01	2.00	2.01	2.02	0.43	-0.06

Table S6. Computed total energies (E_{tot}), thermal correction to Gibbs free energy (zero-point energies (E_{ZPE}) and entropy (TS)), Gibbs free energy (G) and reaction Gibbs free energies (ΔG) of *Na, *NaO_2 (with side-on/end-on adsorption configurations of O_2 molecules), *Na_3O_2, *Na_2O_4, *Na_4O_2 and *Na_3O_4 intermediates on Fe/Co/Ni/Cu-porphyrin for Na-O_2 battery.

	E_{tot} (eV)	ZPE-TS (eV)	G (eV)	ΔG (eV)
Fe-porphyrin/*Na	-227.11	-0.02	-227.13	-1.29
Fe-porphyrin/*NaO_2 (side-on)	-238.76	0.05	-238.71	-1.18
Fe-porphyrin/*NaO_2 (end-on)	-238.76	0.04	-238.72	-1.19
Fe-porphyrin/*Na_3O_2	-244.51	0.01	-244.50	-1.34
Fe-porphyrin/*Na_2O_4	-253.06	0.04	-253.02	-0.77
Fe-porphyrin/*Na_4O_2	-248.19	-0.01	-248.20	-2.39
Fe-porphyrin/*Na_3O_4	-256.01	0.02	-255.99	-1.09

Co-porphyrin/*Na	-226.21	-0.02	-226.23	-1.27
Co-porphyrin/*NaO_2 (side-on)	-237.04	-0.01	-237.05	-0.42
Co-porphyrin/*NaO_2 (end-on)	-237.08	0.05	-237.03	-0.40
Co-porphyrin/*Na_3O_2	-242.72	0.01	-242.71	-1.21
Co-porphyrin/*Na_2O_4	-251.37	0.02	-251.35	-0.76
Co-porphyrin/*Na_4O_2	-244.78	-0.04	-244.82	-0.80
Co-porphyrin/*Na_3O_4	-254.25	-0.02	-254.27	-1.16
Ni-porphyrin/*Na	-224.66	-0.02	-224.68	-1.21
Ni-porphyrin/*NaO_2 (side-on)	-235.24	0.02	-235.22	-0.14
Ni-porphyrin/*NaO_2 (end-on)	-235.24	-0.05	-235.29	-0.21
Ni-porphyrin/*Na_3O_2	-241.15	-0.04	-241.19	-1.34
Ni-porphyrin/*Na_2O_4	-249.44	-0.05	-249.49	-0.55
Ni-porphyrin/*Na_4O_2	-243.49	-0.06	-243.55	-1.05
Ni-porphyrin/*Na_3O_4	-251.55	-0.04	-251.59	0.00
Cu-porphyrin/*Na	-221.90	-0.02	-221.92	-1.39
Cu-porphyrin/*NaO_2 (side-on)	-232.51	-0.03	-232.54	-0.22
Cu-porphyrin/*NaO_2 (end-on)	-232.51	-0.02	-232.53	-0.21
Cu-porphyrin/*Na_3O_2	-238.43	-0.04	-238.47	-1.43
Cu-porphyrin/*Na_2O_4	-246.72	-0.02	-246.74	-0.61
Cu-porphyrin/*Na_4O_2	-240.86	0.01	-240.85	-1.07
Cu-porphyrin/*Na_3O_4	-250.18	-0.02	-250.20	-1.33

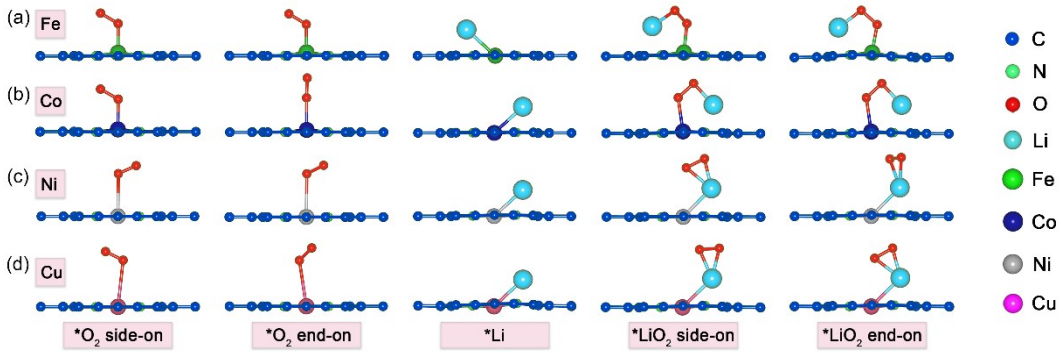

Figure S1. Optimized structures of the possible configurations of $*O_2$ (side/end-on), *Li, $*LiO_2$ (side/end-on) adsorbed on (a) Fe-porphyrin, (b) Co-porphyrin, (c) Ni-porphyrin and (d) Cu-porphyrin.

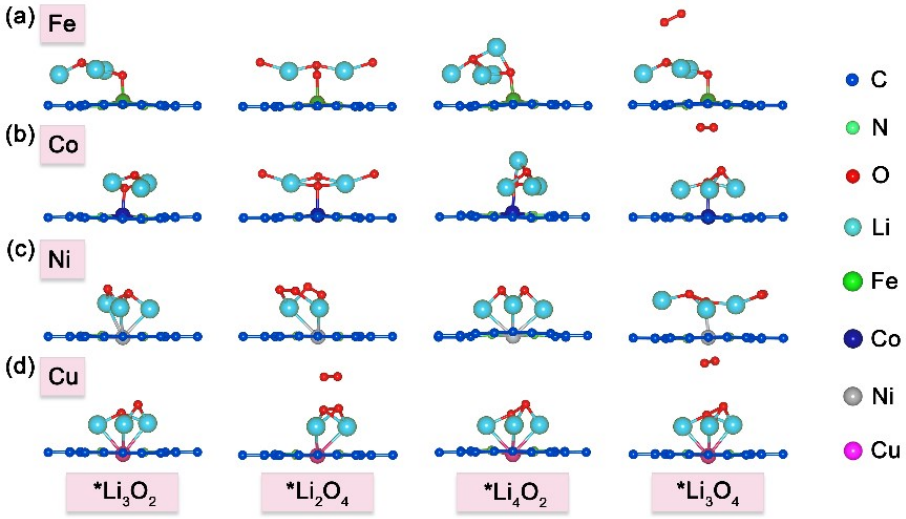

Figure S2. Optimized structures of the possible configurations of intermediates ($*Li_3O_2$, $*Li_2O_4$, $*Li_4O_2$ and $*Li_3O_4$) adsorbed on (a) Fe-porphyrin, (b) Co-porphyrin, (c) Ni-porphyrin and (d) Cu-porphyrin.

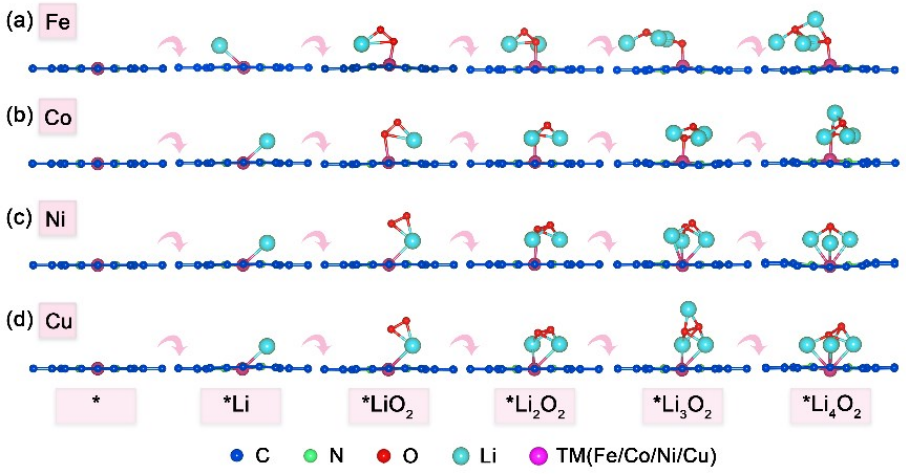

Figure S3. Optimized structures of all the favorable intermediates for Li-O_2 battery on (a) Fe-porphyrin, (b) Co-porphyrin, (c) Ni-porphyrin and (d) Cu-porphyrin.

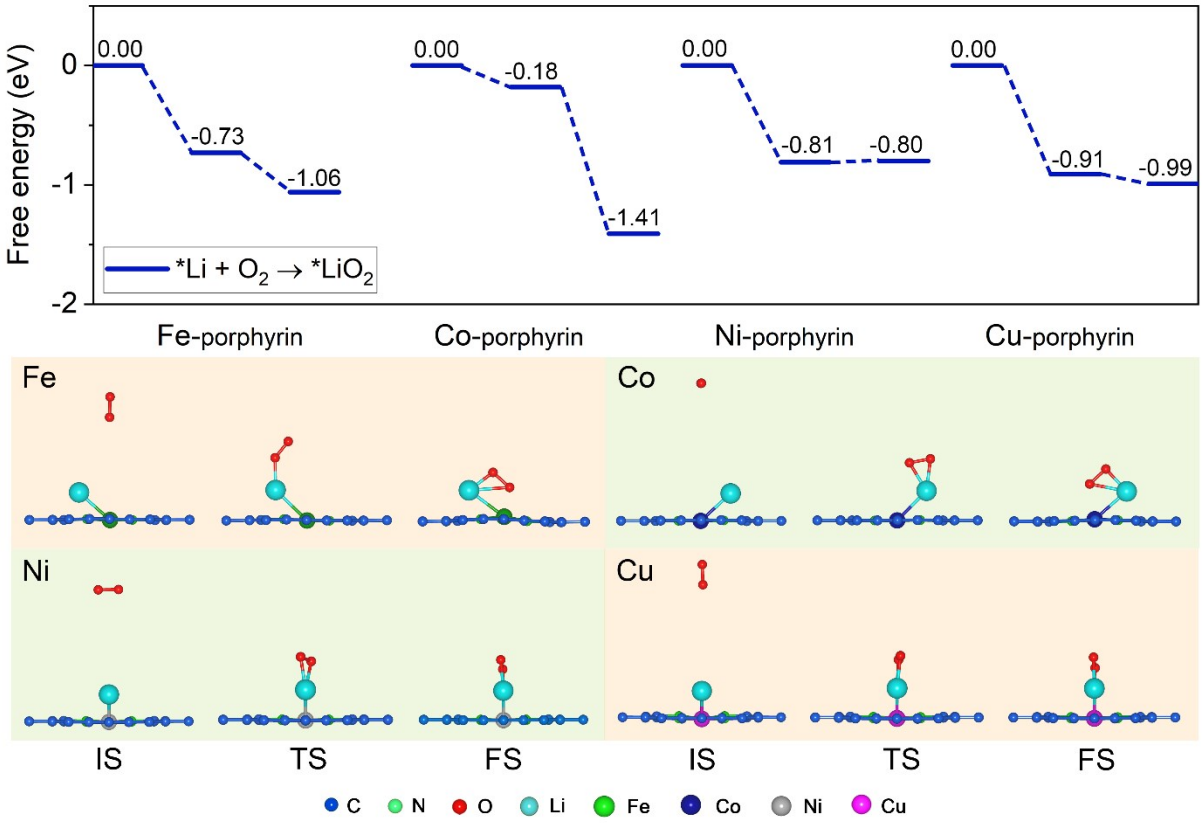

Figure S4. Calculated kinetic barriers and optimized structures for the reaction step of *Li + O_2 → *LiO_2 on Fe/C/Ni/Cu-porphyrin.

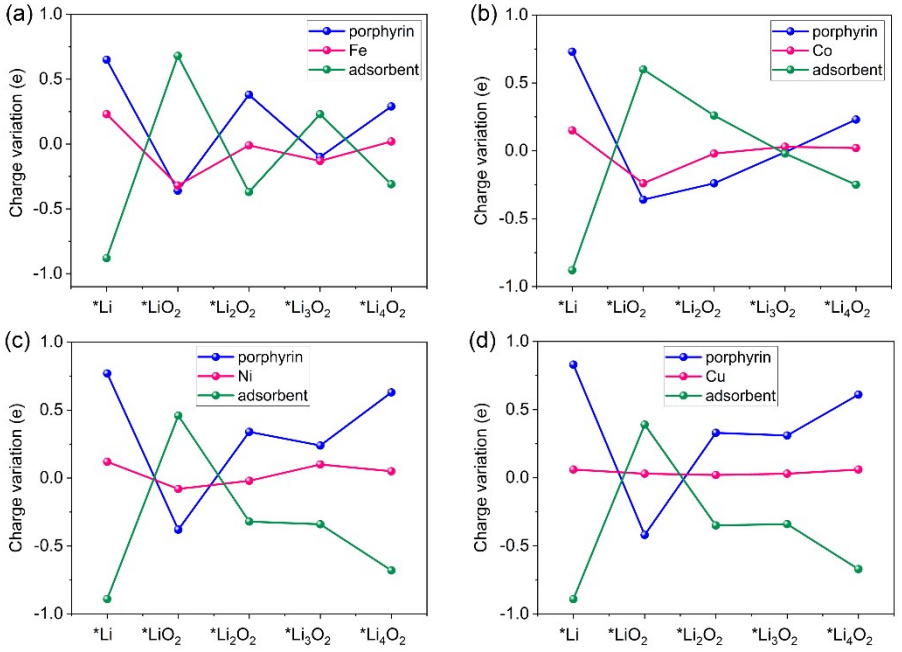

Figure S5. Bader charge variation of each reduction step during the most favorable pathway for Li-O_2 battery.

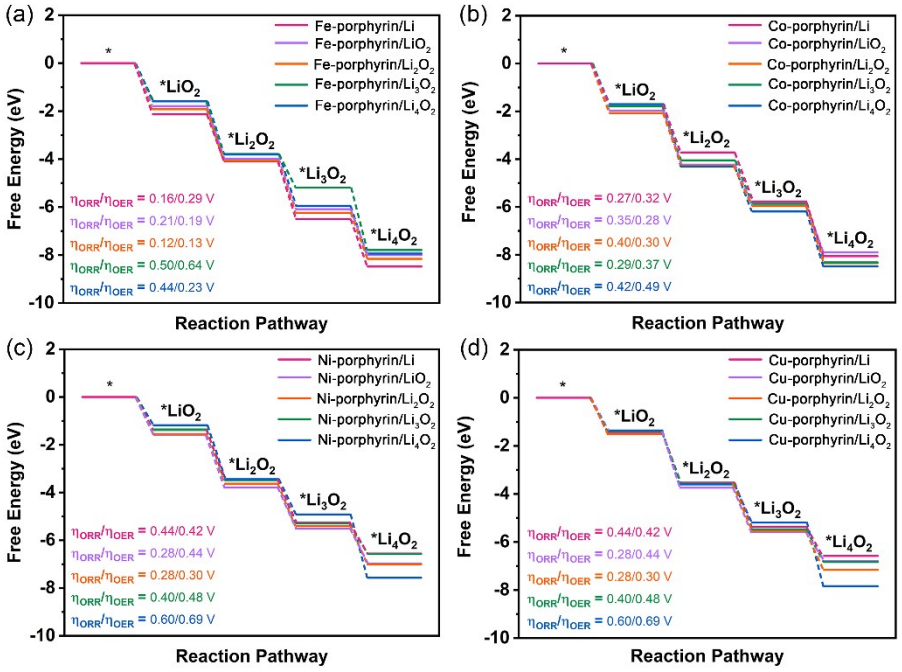

Figure S6. Calculated energetic profiles of the reaction pathway of (a) Fe-porphyrin, (b) Co-porphyrin, (c) Ni-porphyrin and (d) Cu-porphyrin with the regulation of possible axial ligand (-Li/LiO_2/Li_2O_2/Li_3O_2/Li_4O_2) for Li-O_2 battery.

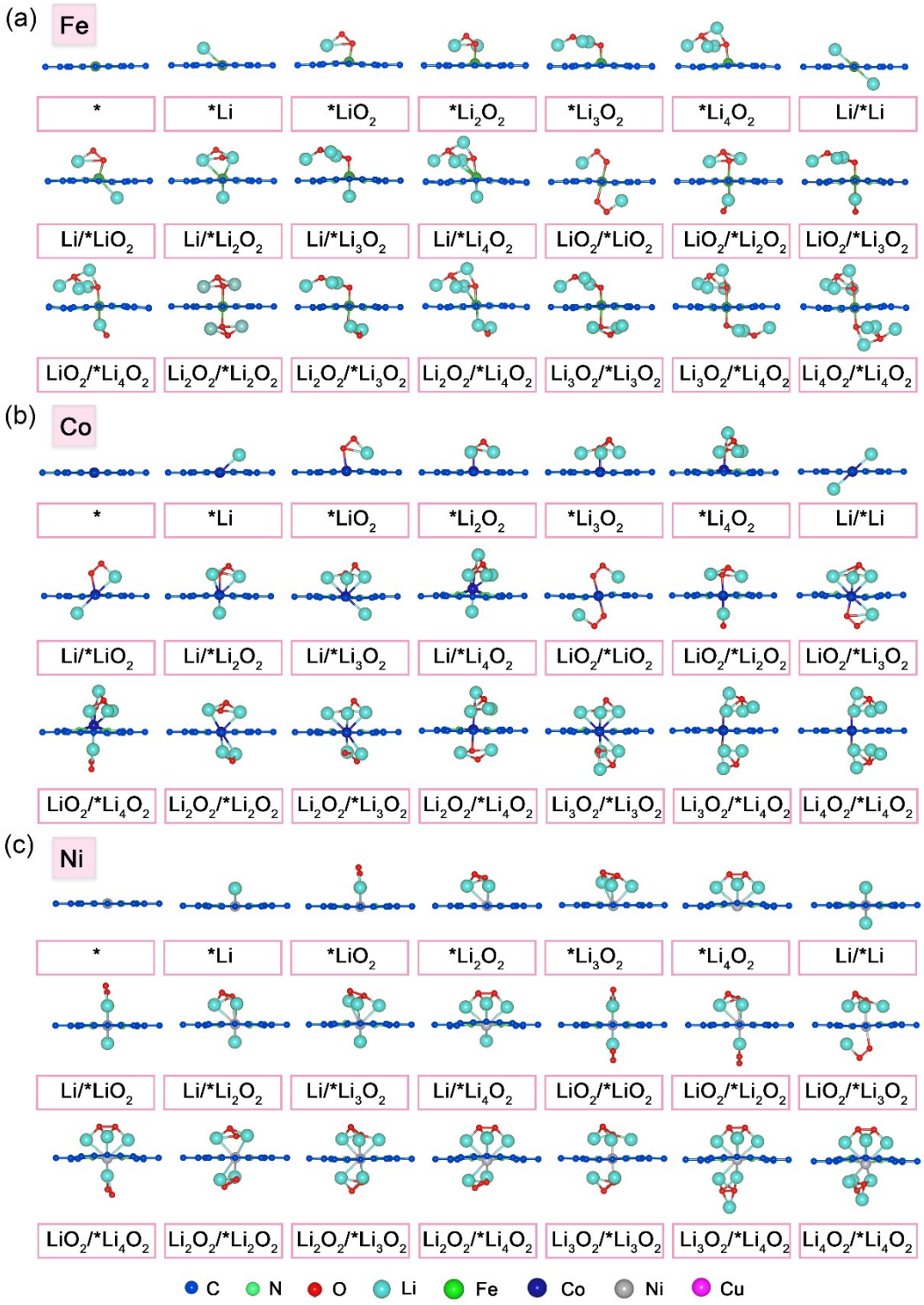

Figure S7. Optimized structures of the various intermediates on (a) Fe-porphyrin, (b) Co-porphyrin, (c) Ni-porphyrin and (d) Cu-porphyrin with the regulation of possible axial ligand (-Li/LiO_2/Li_2O_2/Li_3O_2/Li_4O_2) for Li-O_2 battery.

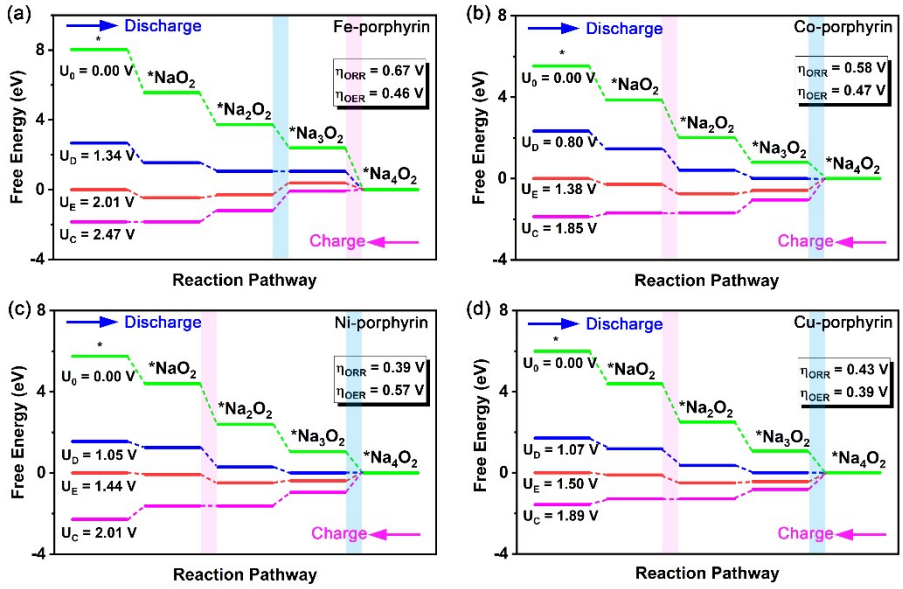

Figure S8. Calculated energetic profiles of the most favorable reaction pathway of (a) Fe-porphyrin, (b) Co-porphyrin, (c) Ni-porphyrin and (d) Cu-porphyrin for Na-O_2 battery under different potentials. The rate determining steps for ORR and OER are marked with blue and pink shadows, respectively.

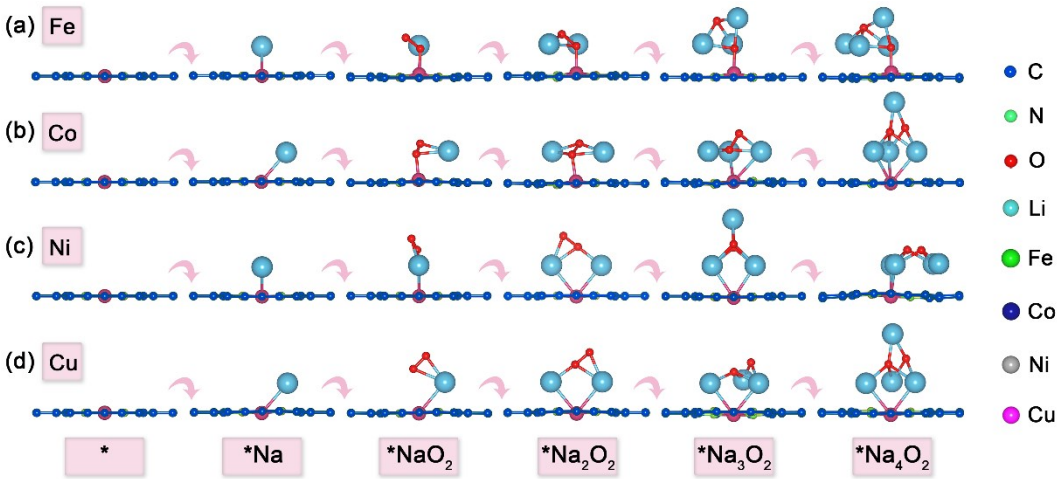

Figure S9. Optimized structures of all the favorable intermediates for Na-O_2 battery on (a) Fe-porphyrin, (b) Co-porphyrin, (c) Ni-porphyrin and (d) Cu-porphyrin.

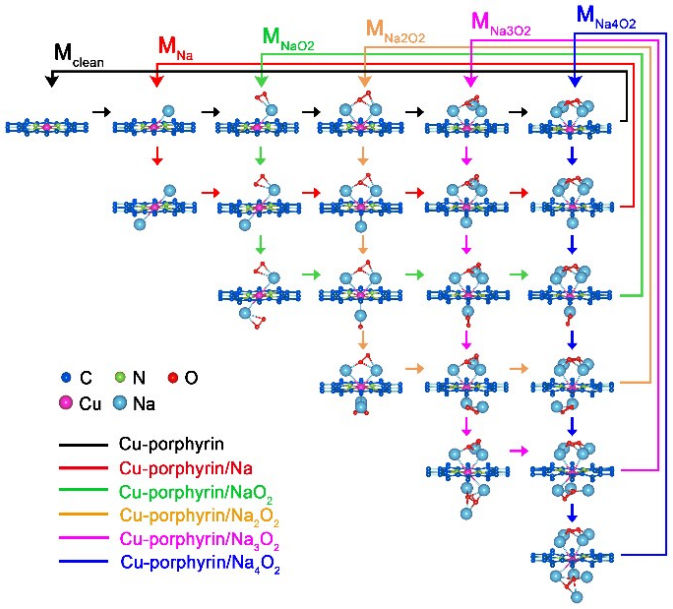

Figure S10. Schematic diagram of charge and discharge mechanisms for Na-O_2 battery of Cu-porphyrin under the axial ligand effect.

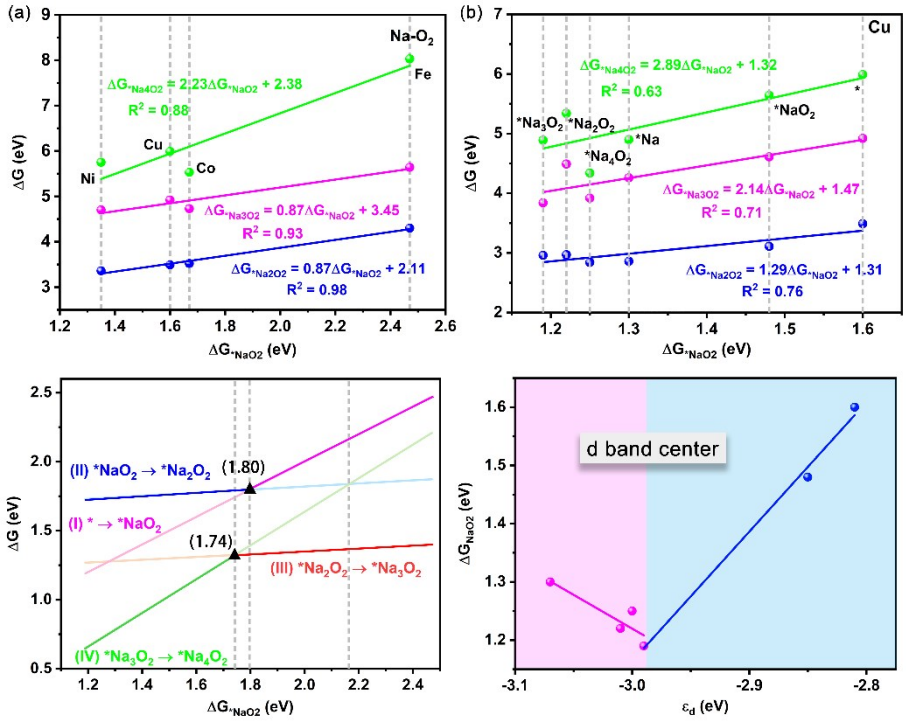

Figure S11. Scaling relationships between the adsorption free energies of *Na_2O_2($\Delta G_{*Na_2O_2}$) (blue line)/*Na_3O_2 ($\Delta G_{*Na_3O_2}$) (mauve line)/*Na_4O_2 ($\Delta G_{*Na_4O_2}$) (green line) and *NaO_2 (ΔG_{*NaO_2}) for (a) TM-porphyrin without axial ligands and (b) Cu-porphyrin with axial ligands. (c) Linear fitting relationships between the Gibbs free energies for each reaction steps and ΔG_{*NaO_2} for TM-porphyrin without axial ligands and Cu-porphyrin with axial ligands, the RDS is highlight in bold lines. (d) $\Delta G_{*Na_2O_2}$ v.s. *d* band center for TM-porphyrin without axial ligands and Cu-porphyrin with axial ligands.

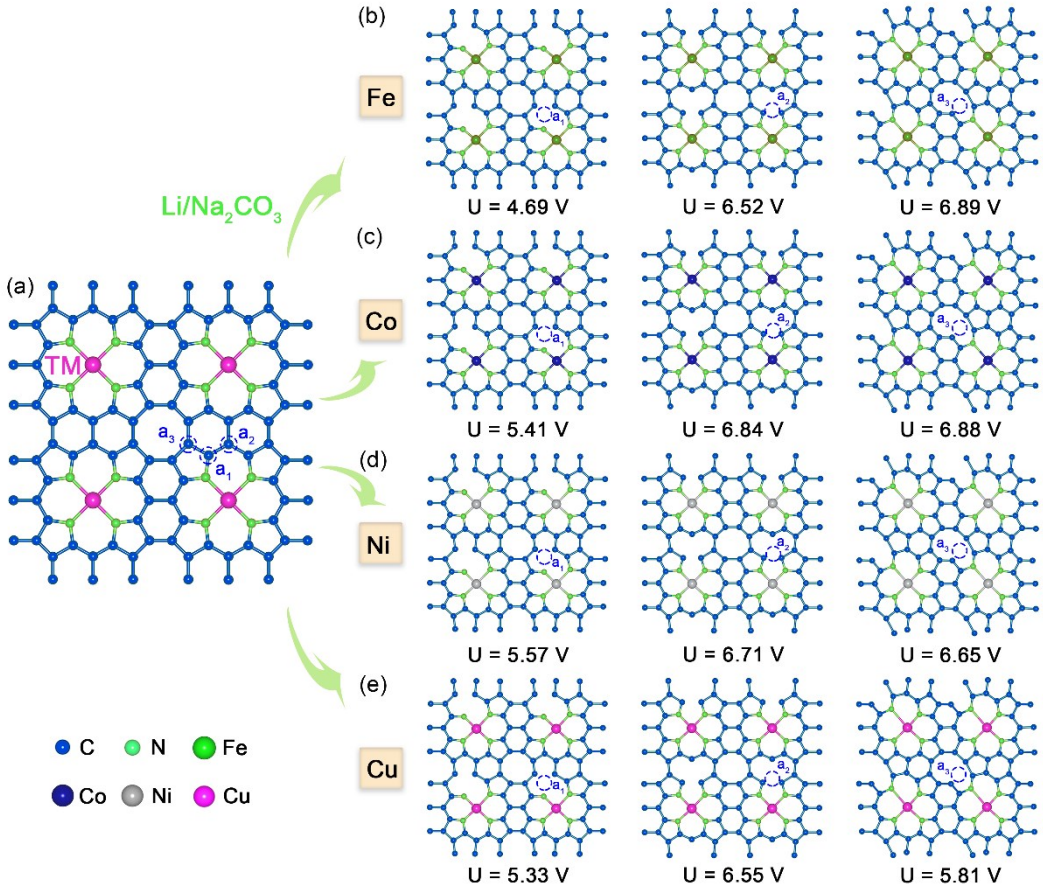

Figure S12. Possible decompose mechanism of C atom on (a) Fe-porphyrin, (b) Co-porphyrin, (c) Ni-porphyrin and (d) Cu-porphyrin during Li/Na-O_2 battery. All the possible decomposition sites and the decompose energies of C atom are presented.

Geometrical coordinates for Fe/Co/Ni/Cu-porphyrin

(1) Fe-porphyrin

Fe

1.00000000000000

8.3393881215521724 0.0000486951705568 -0.0010601483020709

0.0000487032686134 8.3426253931376220 0.0027173978865331

-0.0025398124304948 0.0065118589676466 19.9995389544333193

C N Fe

20 4 1

Direct

0.8385397494807114 0.6435639793966684 0.5355314221480639

0.9205731548765586 0.4973023236830370 0.5355532939441661

0.0935960628444251 0.4972795718262578 0.5356030508406995

0.1756607314589791 0.6435509588875703 0.5355684431533704

0.0911196248076074 0.7922055996845621 0.5356000023359424

0.9231151259647671 0.7922019647180711 0.5355543393021787

0.1756942853493212 0.3510754652976009 0.5355585819420057

0.0911008645458540 0.2024203588388155 0.5355821935992869

0.9230859617759289 0.2024349317517738 0.5355522928433886
0.8385025299008527 0.3510878547518351 0.5355012421588142
0.2122037128066573 0.9132811502243497 0.5355663707592802
0.2122163633137314 0.0813965596563095 0.5355657528715890
0.6534144074072853 0.8288973492224507 0.5353897810560290
0.5071325992402785 0.9108932130300327 0.5353946403431528
0.3608321909325127 0.8288923933735882 0.5354709285960325
0.3608155925487218 0.1657954763886970 0.5354720029490295
0.6533804849680911 0.1658017922117680 0.5353967763653524
0.5071050026062478 0.0838453499381526 0.5353920997784575
0.8020553856166825 0.9132895873808811 0.5354049200589054
0.8019974505580999 0.0814036433504143 0.5354236679325621
0.3410323124340265 0.6633696089214539 0.5353698195279798
0.6731576728884242 0.3312938931083115 0.5355097387811922
0.3410383286012932 0.3312923693740141 0.5353740503260526
0.6731845849381835 0.6633812642856362 0.5355143519538376
0.5071018201347572 0.4973395188002361 0.5354102364326205

(2) Co-porphyrin

Co

1.00000000000000

8.3276921900413114 0.0000489941825582 -0.0000941693172639

0.0000489631194576 8.3278674461090780 0.0015445827515630

-0.0002264172095754 0.0037148252037095 20.0631170759865540

C N Co

20 4 1

Direct

0.8381061757933923 0.6432376075887892 0.5355717044512590
0.9205628548278422 0.4973062722640707 0.5355579519950097
0.0936102208709977 0.4972883146729682 0.5355769597597922
0.1761066072305340 0.6432204939071833 0.5355968734209766
0.0910763706086664 0.7920002537090820 0.5356100779911586
0.9231734458061447 0.7920155964183065 0.5355945163739616
0.1761575033860963 0.3514191857441738 0.5354768012872647
0.0910660400185709 0.2026381990480867 0.5355146786617548
0.9231385644233117 0.2026488000431344 0.5355270251359379
0.8380559245104708 0.3514272998428539 0.5354638513548354
0.2124098564917961 0.9133658644008041 0.5355256081950234
0.2124311390784807 0.0813145472025345 0.5354730360095709
0.6530135470597945 0.8283282184090771 0.5354951694422623
0.5071136570942490 0.9108534057365772 0.5354413032811445
0.3612153137725592 0.8283176409290758 0.5355048876774262
0.3612071258363417 0.1663547220326262 0.5354014778033165
0.6529940956529683 0.1663499835209847 0.5353848715104256
0.5070926994397073 0.0838692210177011 0.5353658439081775
0.8018351577434107 0.9133643234071970 0.5355111551944636
0.8017917451636695 0.0813144436968233 0.5354779949483682
0.3415125298723442 0.6629137373808400 0.5355183757993639
0.6726630057457909 0.3317385167852470 0.5353628256052561

0.3415271942714849 0.3317439764839304 0.5353910647764136
0.6726969907588214 0.6629314981170814 0.5355033006874933
0.5070982345425535 0.4973340557433044 0.5354126447293057

(3) Ni-porphyrin

Ni

1.00000000000000

8.3296107454396431 0.0000197176849619 -0.0000585273027794
0.0000196820682479 8.3294162501871867 0.0013273997226290
-0.0001405024564793 0.0031905497768735 20.0547660102743599

C N Ni

20 4 1

Direct

0.8380258740056095 0.6431948400081359 0.5355095916540797
0.9205997504215412 0.4973050811872239 0.5355909092609693
0.0935729628993571 0.4972888668893273 0.5356170391263391
0.1761859436779578 0.6431864667411906 0.5355362208564513
0.0912627937615296 0.7923964423908958 0.5355516132305007
0.9229782560001061 0.7923870702131870 0.5355420980945230
0.1762418252187176 0.3514534960973817 0.5355913075217804
0.0912492273922400 0.2022418580863715 0.5355952416922475
0.9229547855830026 0.2022570872164611 0.5356072559896804
0.8379597736029829 0.3514576419223240 0.5355732393482353
0.2120146932334335 0.9131821485324775 0.5354445349688265
0.2120471924201200 0.0814987079050356 0.5354963725239269
0.6529740035182511 0.8282497079751981 0.5353665542842156
0.5071216390600312 0.9108920832546907 0.5353383012586287
0.3612652375542786 0.8282324180920368 0.5353724344834671
0.3612588686173854 0.1664347064502361 0.5354882018892470
0.6529449086957402 0.1664442095003835 0.5354721838087146
0.5071006190465882 0.0838356656545672 0.5354090451630751
0.8022257776591737 0.9131835295740462 0.5354515374619064
0.8021647022231368 0.0815034722362043 0.5355186855134166
0.3409306323795090 0.6635009941258386 0.5353940156431498
0.6732451390153478 0.3311602694798314 0.5354796901866655
0.3409455818127217 0.3311515311614293 0.5355202442435981
0.6732859091118414 0.6635199063813049 0.5353786346045237
0.5070999030893816 0.4973379770266809 0.5354150471918231

(4) Cu-porphyrin

Cu

1.00000000000000

8.3816465665531226 0.0000892177061530 -0.0011605339425849
0.0000815787466574 8.3825274800040006 0.0185431496603946
-0.0022046308077294 0.0488699581444734 18.2452837848878886

C N Cu

20 4 1

Direct

0.8395803124943699 0.6445350727520905 0.5354882060087433
0.9207344549504869 0.4973582359911677 0.5354766033746579

0.0934824233731108 0.4973399438569953 0.5355572600781666
0.1746673958905885 0.6445161040311774 0.5355798081369528
0.0904966006036218 0.7934409595851383 0.5354715086932872
0.9237167988368695 0.7934895453442459 0.5354644767520639
0.1746545780670793 0.3501476555215501 0.5355691158576800
0.0904812907090826 0.2011393941475397 0.5355016761943503
0.9236967595011125 0.2011984465848733 0.5353886472209619
0.8395577520762741 0.3501977345231709 0.5354192840172327
0.2109019019401109 0.9138733609952172 0.5355208351688765
0.2108993571612590 0.0807061103395671 0.5355267063577200
0.6543170024827930 0.8298609804383630 0.5354504689940556
0.5071099507382848 0.9109852281261865 0.5354362386477205
0.3599167183950289 0.8298066671593202 0.5355688490807906
0.3598916057742955 0.1648072273326350 0.5355153499852190
0.6542920548459349 0.1648264478857699 0.5353600778769699
0.5070945490696779 0.0836922326759059 0.5354149818391950
0.8033134022369744 0.9139298509445084 0.5354414818801387
0.8033067789204588 0.0807598350625574 0.5353477320687312
0.3372991162275666 0.6671636083466336 0.5356769714091975
0.6769298646638209 0.3274897231579251 0.5354344376856320
0.3372649850724301 0.3274698317714237 0.5355568876034323
0.6769415608928830 0.6672095638664233 0.5354804583428965
0.5071087850758558 0.4973524176620882 0.5356119367253328

(5) Co-porphyrin/*Li

Li

1.00000000000000

8.3418200000000002 0.0000000000000000 0.0000000000000000
0.0000000000000000 8.3399999999999999 0.0000000000000000
0.0000000000000000 0.0000000000000000 20.0000000000000000

Li C N Co

1 20 4 1

Direct

0.5073792803983252 0.7040629901864293 0.6195145455099507
0.8390570541400209 0.6352615327720628 0.5387607692884586
0.9207299139290157 0.4889602146166538 0.5388389696093654
0.0935878388671725 0.4889539513331442 0.5388825768782866
0.1753171939099971 0.6352457103813833 0.5388728934670084
0.0918211103855029 0.7840648538457913 0.5380299369243673
0.9225444488163319 0.7840849908476315 0.5379624736222368
0.1762677740918548 0.3430793286723031 0.5377347945441073
0.0916600024365408 0.1942754581570583 0.5373160348293524
0.9226599822101562 0.1942958245463657 0.5373009861359535
0.8380499478961383 0.3430976942282982 0.5377012593243933
0.2113736389766459 0.9049132373165207 0.5366571508358220
0.2117928666950348 0.0740574218796723 0.5365259902426374
0.6542713151254205 0.8213842313671975 0.5356746054663404
0.5071832601945161 0.9033410083828315 0.5356298630305645
0.3601007310644064 0.8213773384590581 0.5357702753132045

0.3608709814321998 0.1581338849195149 0.5362868454037795
0.6534569947937570 0.1581400174298722 0.5362470865561733
0.5071607072156255 0.0764919985229966 0.5360129080953868
0.8029926765963822 0.9049427568315025 0.5365819233799698
0.8025578434444114 0.0740981843180606 0.5364879916595413
0.3413258913121666 0.6542795058055262 0.5378562171150634
0.6728568011384723 0.3232122275027436 0.5368942726235559
0.3414697096764243 0.3232090270498631 0.5369327320176467
0.6730570498978992 0.6542923262994762 0.5377350629219819
0.5071894235759444 0.4860774251933080 0.5364691319416934

(6) Co-porphyrin/*LiO_2

LiO2

1.00000000000000

8.3418200000000002 0.0000000000000000 0.0000000000000000
0.0000000000000000 8.3399999999999999 0.0000000000000000
0.0000000000000000 0.0000000000000000 20.0000000000000000

Li C N O Co
1 20 4 2 1

Direct

0.5072331690201182 0.7150687219405470 0.6225314498860449
0.8390410682380784 0.6335163313619375 0.5362831832398697
0.9209338689830200 0.4871479723668574 0.5363574399747918
0.0937982953494992 0.4871351815064920 0.5363541096752021
0.1757062817630871 0.6334930487082989 0.5362445448755288
0.0916261718808389 0.7821583419470782 0.5344111437855501
0.9231197180253312 0.7821594004785001 0.5344510087054305
0.1761979975193124 0.3409533743346963 0.5343154974939688
0.0913579410977058 0.1920372485350490 0.5332673441483484
0.9233837944807137 0.1920501675939513 0.5332947983302627
0.8385431957170009 0.3409633821993181 0.5343379525899865
0.2113887752329727 0.9032098024092713 0.5323541539533067
0.2117788007221110 0.0714536043585062 0.5318681158575398
0.6543405236080279 0.8193041507592140 0.5324052957564711
0.5073775948272629 0.9013695190811014 0.5317888252781545
0.3604206953293331 0.8192896179270880 0.5322858310225268
0.3608411997180650 0.1558649342078511 0.5317025782995352
0.6538949480153778 0.1558766397323035 0.5317973614930389
0.5073826847433789 0.0743995939054096 0.5315742039604200
0.8033782740219253 0.9032304952566897 0.5324972103923807
0.8029511534548727 0.0714689354506283 0.5319956494933562
0.3409791664621897 0.6536189779906549 0.5355928023381231
0.6743557637840915 0.3201301473174620 0.5329545151900547
0.3403730768649922 0.3201184559018587 0.5328888548323399
0.6737628617800298 0.6536229250554699 0.5356651256742595
0.5069672704249799 0.4484588550749367 0.6449292280003646
0.5057659608994718 0.5652941391760848 0.6898450269189147
0.5073673859303165 0.4844525287449897 0.5385755321117145

(7) Co-porphyrin/*Li_2O_2

Li2O2

1.00000000000000

8.3418199999999985	0.0000000000000000	0.0000000000000000
0.0000000000000000	8.3399999999999999	0.0000000000000000
0.0000000000000000	0.0000000000000000	30.0000000000000000

Li	C	N	O	Co
2	20	4	2	1

Direct

0.4659016030162778	0.7059190790422216	0.4223065157992276
0.7222228042214496	0.4501576361027722	0.4222417166193276
0.8283976826056282	0.6273800947431741	0.3584186642644710
0.9110249940222666	0.4807614518886002	0.3587497980363660
0.0839986874161406	0.4809805167656881	0.3591659671825195
0.1652559239869109	0.6275908492421114	0.3587839808951888
0.0812417919305965	0.7764736146589026	0.3582841634576850
0.9123831069120013	0.7763141751271128	0.3584073668598753
0.1661958974483046	0.3347505154417924	0.3589353483722011
0.0819358470957915	0.1855421539752904	0.3584057887916944
0.9132936975972407	0.1846619532601697	0.3580328262823541
0.8295594007301625	0.3336539018331421	0.3578050743927957
0.2009072623853753	0.8970929108949171	0.3580409895385541
0.2017765792137974	0.0657463312022002	0.3584205866370694
0.6435735335578440	0.8121662583425734	0.3584418701757384
0.4969764821525317	0.8948067249658139	0.3587779892600961
0.3498763090350647	0.8133415712935198	0.3578219107508333
0.3509452765069154	0.1500180224722021	0.3589413369636256
0.6437819544474881	0.1490627977195011	0.3587678953266936
0.4971620309115126	0.0678436136561180	0.3591698565102993
0.7924629329371596	0.8961760687628920	0.3584214905503377
0.7926148569392207	0.0650285618926554	0.3582849986038925
0.3301482399063093	0.6476903353348320	0.3585062587521498
0.6639258266155559	0.3139750308753764	0.3584891047254912
0.3305268756591814	0.3143713314375597	0.3591417880107446
0.6634619116352466	0.6472145816903402	0.3581525666351609
0.4978872514988618	0.4817781250564927	0.4315977493341794
0.6076647537054553	0.5915133955009028	0.4545459435390872
0.4963889130908272	0.4801994252479957	0.3621671478280512

(8) Co-porphyrin/*Li_3O_2

Li3O2

1.00000000000000

8.3418199999999985	0.0000000000000000	0.0000000000000000
0.0000000000000000	8.3399999999999999	0.0000000000000000
0.0000000000000000	0.0000000000000000	30.0000000000000000

Li	C	N	O	Co
3	20	4	2	1

Direct

0.6114407655728087	0.6831466654956094	0.4352009299799545
0.6805878655456390	0.4061701578155559	0.4372707059111916

0.9637827446847910 0.6322674482424026 0.4246213414849735
0.8085095041189329 0.6333799903791392 0.3569040737779722
0.8913339551958596 0.4868645293273915 0.3577029457155629
0.0644397948139984 0.4869144599499608 0.3586517855008432
0.1469308071104603 0.6335776997760674 0.3591453776989101
0.0626424957737963 0.7831717272647402 0.3597902457686139
0.8926747712982110 0.7827708581013748 0.3584842212409788
0.1468859893499475 0.3405290479961119 0.3599185397389253
0.0630636502586576 0.1914896336292349 0.3603249256988737
0.8936424807354473 0.1912154144650718 0.3604795287769911
0.8096514805718925 0.3403397655911839 0.3599117223999533
0.1824429311525766 0.9027932536256303 0.3614806601859741
0.1827115356508017 0.0720906489888685 0.3615622946717306
0.6242401762474578 0.8189766006663254 0.3602750813390456
0.4776376365981084 0.9007442697748577 0.3623708384504349
0.3313230997935877 0.8184120883703582 0.3614643589221403
0.3318492743230294 0.1562612804933626 0.3622041380690027
0.6246927683229512 0.1553575909729706 0.3628328286402136
0.4779050097463545 0.0738183675776872 0.3632361759173001
0.7733312604241248 0.9023670738470182 0.3606593012923435
0.7738395821458524 0.0718794987042681 0.3618068448968524
0.3110143893720037 0.6541118166724892 0.3595415994887612
0.6449077492452542 0.3203085809082470 0.3618477817573897
0.3112914094721599 0.3209164433720073 0.3605179142829315
0.6438799015229965 0.6539362407926685 0.3572701993358932
0.4856434242567699 0.5026841029023142 0.4248292936341633
0.7886131613554269 0.5824023986216649 0.4529143442813509
0.4759020424544274 0.4883377529123265 0.3658663149545738

(9) Co-porphyrin/*Li_4O_2

Li4O2

1.00000000000000

8.3418199999999985 0.0000000000000000 0.0000000000000000
0.0000000000000000 8.3399999999999999 0.0000000000000000
0.0000000000000000 0.0000000000000000 30.0000000000000000

Li C N O Co

4 20 4 2 1

Direct

0.6202807002749583 0.6884307111681465 0.4272690353759063
0.7089254383748642 0.4345129537036381 0.4245344407550605
0.9527335936144378 0.6408928767567756 0.4265420853582361
0.6043897416131138 0.5301153136376906 0.4844019916515530
0.8087758267168585 0.6321429531758286 0.3565854312314782
0.8912356815057568 0.4853648562814235 0.3581032716431918
0.0640680622821872 0.4853174728131870 0.3604253763515020
0.1463708921416951 0.6320214060627853 0.3614848095310043
0.0623605766437854 0.7815031522455648 0.3607549533002671
0.8927023816217112 0.7812994742394048 0.3580401910151779
0.1463439019365496 0.3388148102531917 0.3609594540494608

0.0625564820358811	0.1896803458536425	0.3599520718037041
0.8933793876315602	0.1893495537073559	0.3589298881749037
0.8094432379193297	0.3381926846651335	0.3583021719282679
0.1822455687504953	0.9011662242598862	0.3619892741833964
0.1823001032321864	0.0703012452111322	0.3614834161833261
0.6240001287974383	0.8180411086157183	0.3583108636010324
0.4773698239160389	0.8993312943750132	0.3617353803331246
0.3309818829505984	0.8165401202795466	0.3626048536689243
0.3312712120324910	0.1545818639567618	0.3626713799255149
0.6242094064715570	0.1535348849586146	0.3609942932893249
0.4774939345921188	0.0720870469066077	0.3624848482082693
0.7729735663486138	0.9010382585957354	0.3587302195898860
0.7731606302341412	0.0703063802515887	0.3596360889019935
0.3101798573520085	0.6524175924638341	0.3625777780740234
0.6443216221747704	0.3181908367125613	0.3605068321694272
0.3102658616046060	0.3188543852669253	0.3624663570721862
0.6439292245084414	0.6524795594616495	0.3567955276123964
0.4944571396762308	0.5002736555965853	0.4324706899787817
0.7839324046817754	0.5974852967320446	0.4589593690738072
0.4749606573680606	0.4856621246410837	0.3684244074134366