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Supplementary Information

Advancing Oxygen Evolution Reaction Efficiency in Iron Phthalocyanines: Axial Coordination as a Key to Structural and Electronic Tuning

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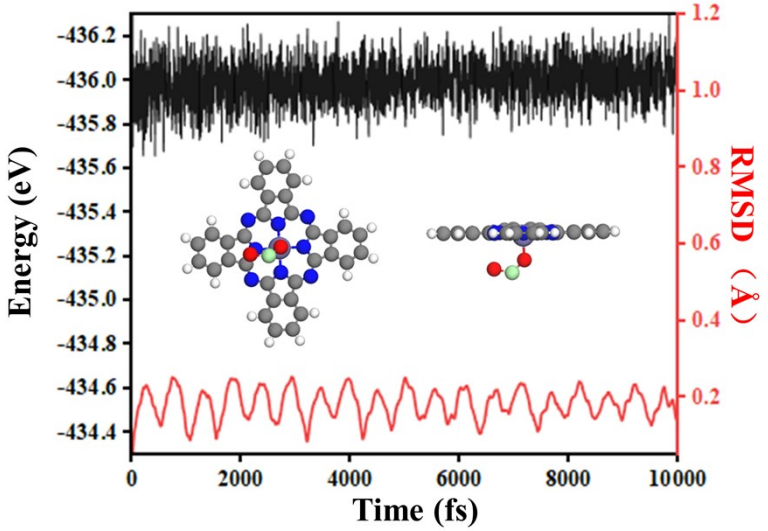
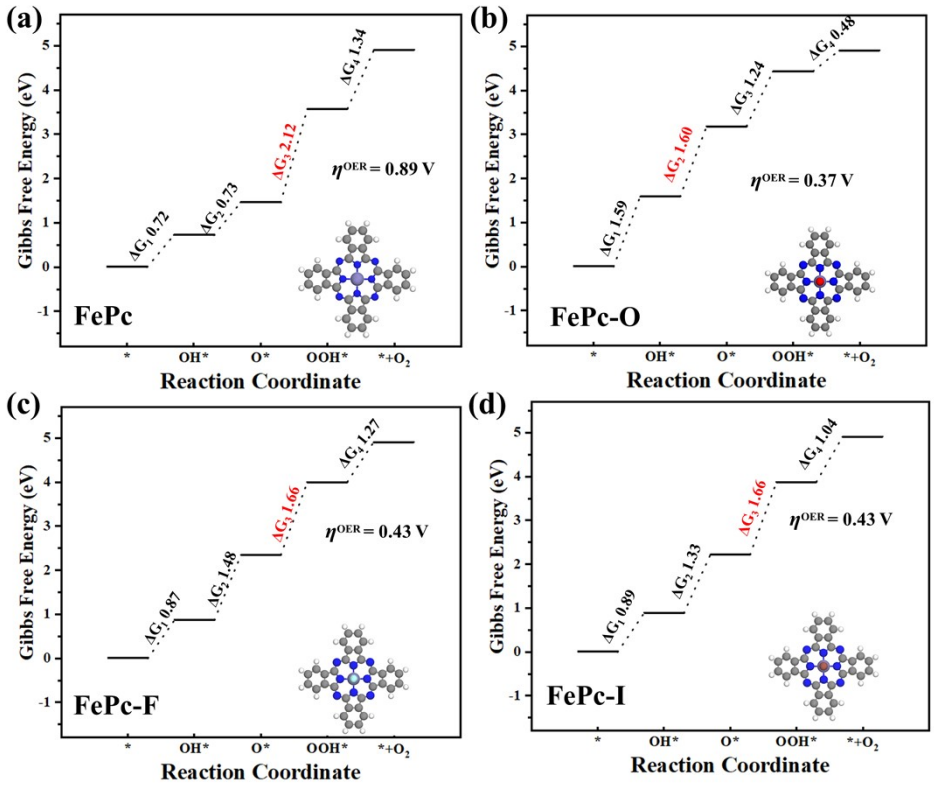
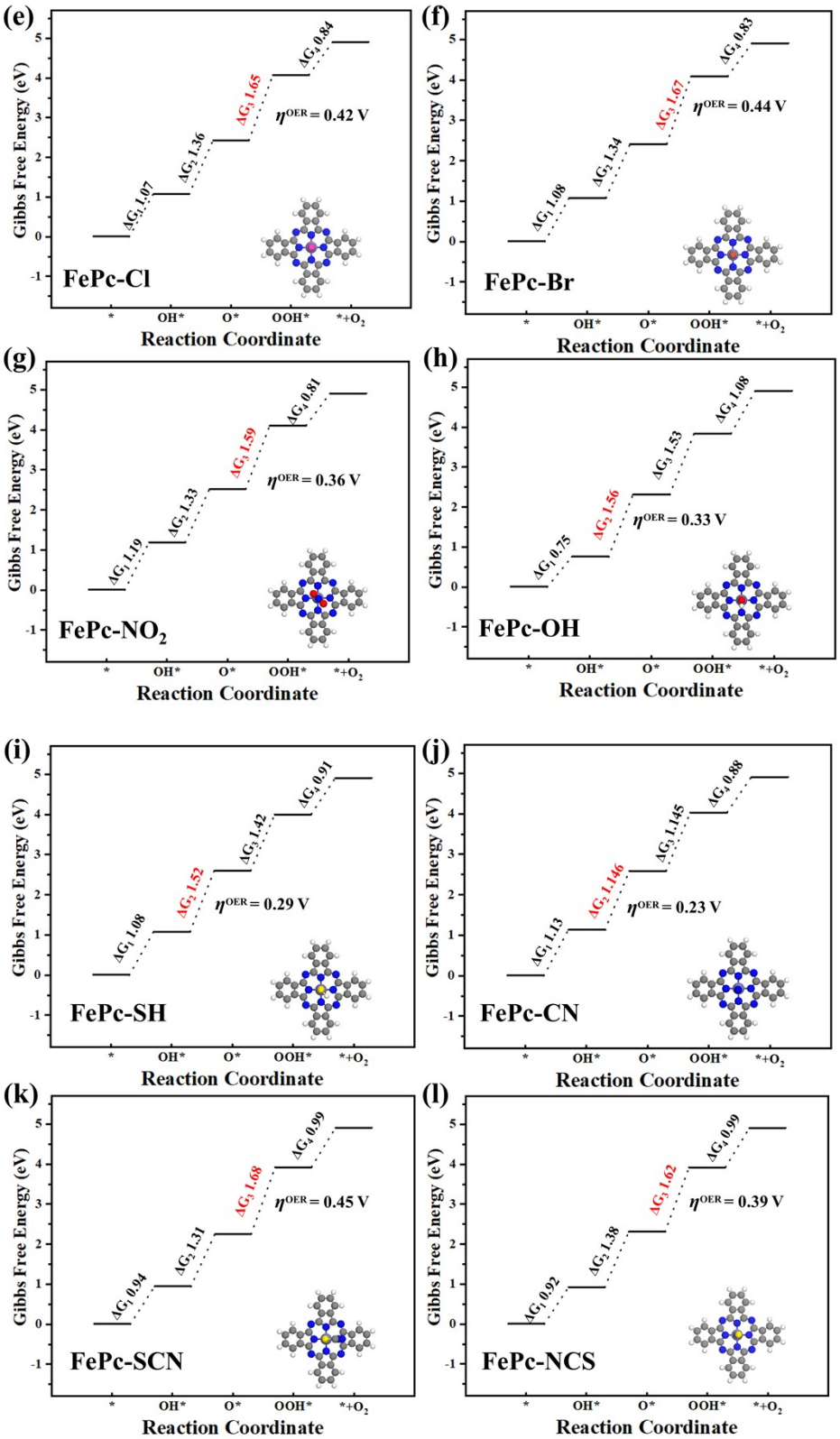


Figure S1. The energy variations and root-mean-square deviations (RMSD) of all selected models after the total time of 10 ps at T=300 K.




(e)
FePc-Cl
ΔG1 1.07
ΔG2 1.36
ΔG3 1.65
ΔG4 0.84
η^OER = 0.42 V
(f)
FePc-Br
ΔG1 1.08
ΔG2 1.34
ΔG3 1.67
ΔG4 0.83
η^OER = 0.44 V
(g)
FePc-NO2
ΔG1 1.19
ΔG2 1.33
ΔG3 1.59
ΔG4 0.81
η^OER = 0.36 V
(h)
FePc-OH
ΔG1 0.75
ΔG2 1.56
ΔG3 1.53
ΔG4 1.08
η^OER = 0.33 V
(i)
FePc-SH
ΔG1 1.08
ΔG2 1.52
ΔG3 1.42
ΔG4 0.91
η^OER = 0.29 V
(j)
FePc-CN
ΔG1 1.13
ΔG2 1.146
ΔG3 1.145
ΔG4 0.88
η^OER = 0.23 V
(k)
FePc-SCN
ΔG1 0.94
ΔG2 1.31
ΔG3 1.68
ΔG4 0.99
η^OER = 0.45 V
(l)
FePc-NCS
ΔG1 0.92
ΔG2 1.38
ΔG3 1.62
ΔG4 0.99
η^OER = 0.39 V
Gibbs Free Energy (eV)
Reaction Coordinate
*
OH*
O*
OOH*
*+O2

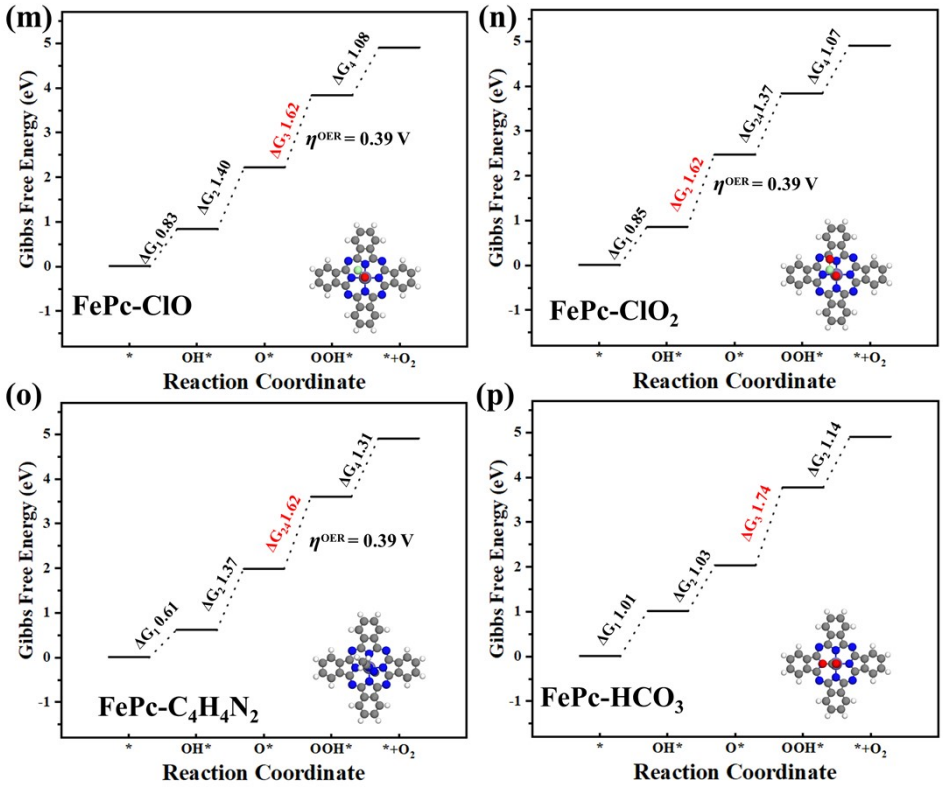


Figure S2. The free energy diagrams of OER on the pristine FePc and axially coordinated FePc-Xs.

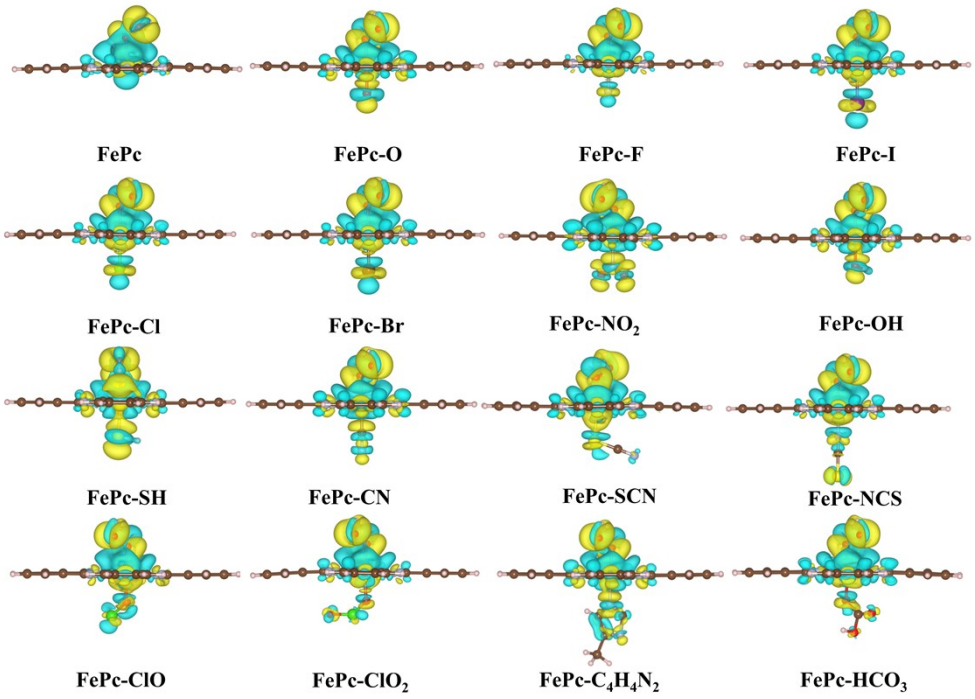
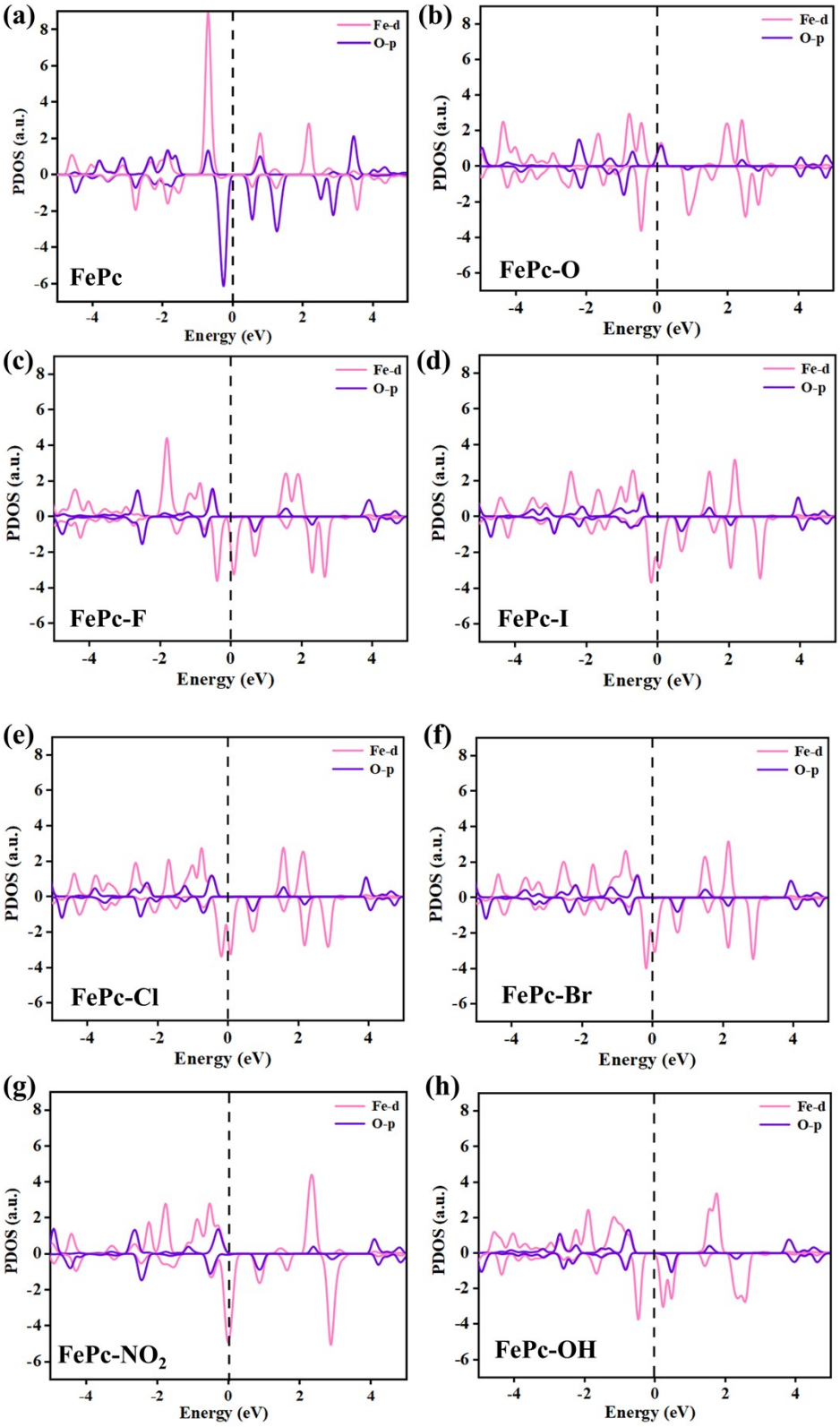


Figure S3. Charge density difference for the OOH* adsorption on the pristine FePc

and axially coordinated FePc-Xs, where the blue and yellow denote the electron depletion and electron accumulation, respectively.



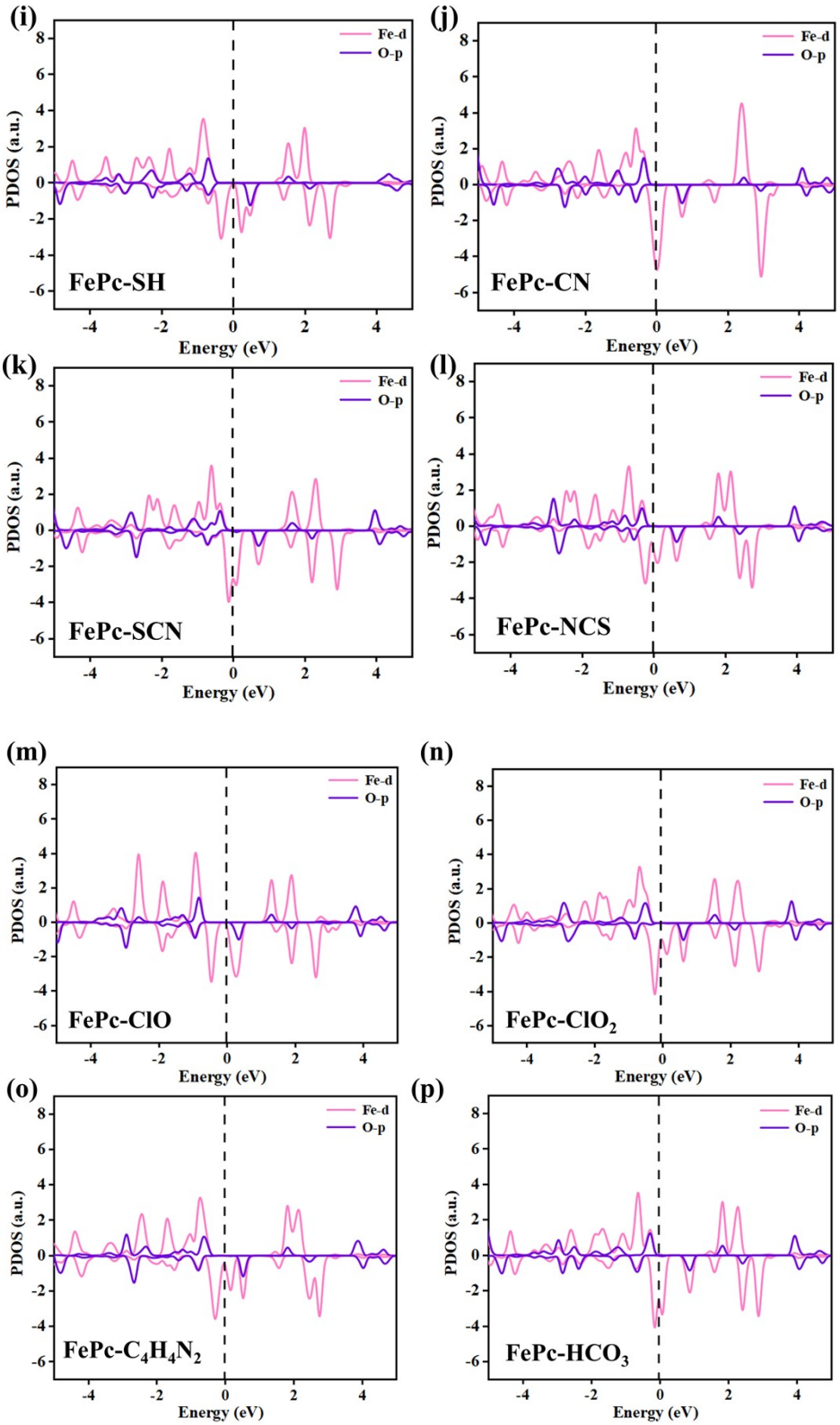


Figure S4. Partial density of states (PDOS) of Fe-3*d* orbitals and O-2*p* orbitals after OOH* bonded on FePc and FePc-Xs.

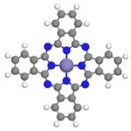
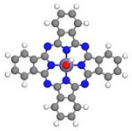
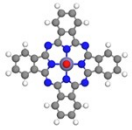
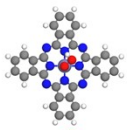
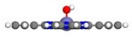
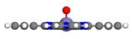
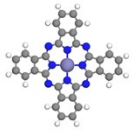
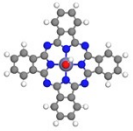
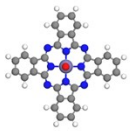
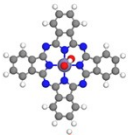
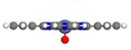
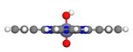
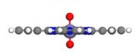
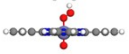
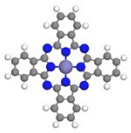
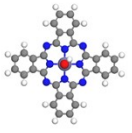
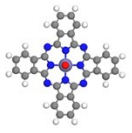
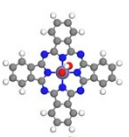
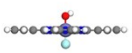
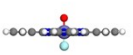
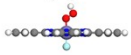
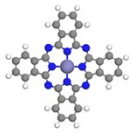
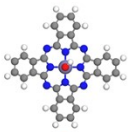
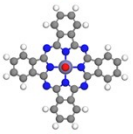
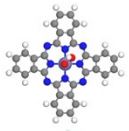
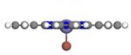
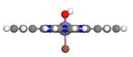
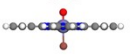
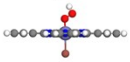
Table S1. The calculated total energies (E) and thermodynamic quantities for the gasphase H_2 species (T = 298.15 K, P = 1 bar), and free H_2O at the 298.15 K, 0.035 bar.

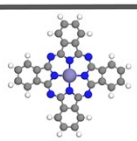
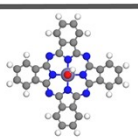
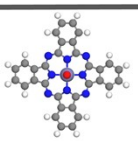
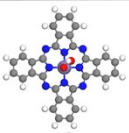
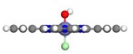
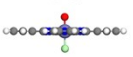
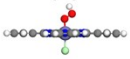
Species	E (eV)	ZPE-TS (eV)	G (eV)
H_2(g)	-6.76	-0.05	-6.80
H_2O(g)	14.22	-0.00	14.22

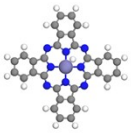
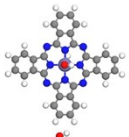
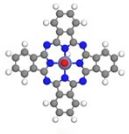
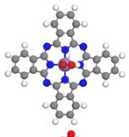
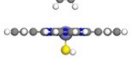
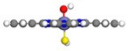
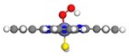
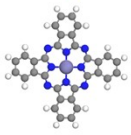
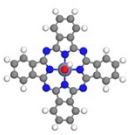
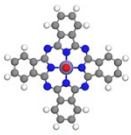
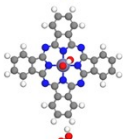
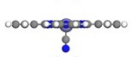
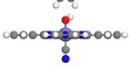
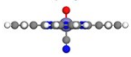
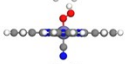
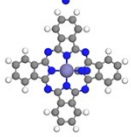
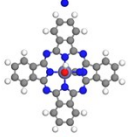
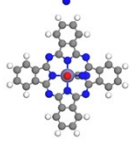
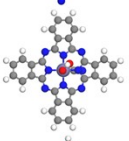
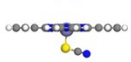
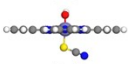
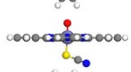
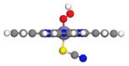
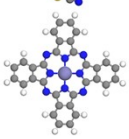
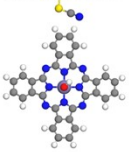
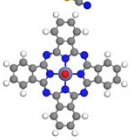
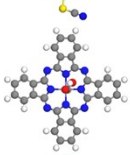
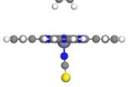
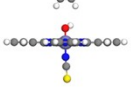
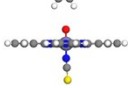
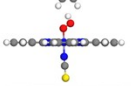
Table S2. Calculated results of the binding length of Fe-N/X (d_{Fe-N} and d_{Fe-X}, in units of Å), and optimized distance between Fe atom and catalyst plane (h, in units of Å) of optimized catalysts.

Structure	d_{Fe-N}	d_{Fe-X}	h
FePc	1.93	---	0.00
FePc-O	1.95	1.64	-0.29
FePc-F	1.96	1.84	-0.31
FePc-Cl	1.96	2.24	-0.30
FePc-Br	1.96	2.40	-0.28
FePc-I	1.93	2.49	-0.15
FePc-OH	1.94	1.79	-0.20
FePc-SH	1.94	2.13	-0.19
FePc-CN	1.93	1.83	-0.13
FePc-SCN	1.94	2.38	-0.23
FePc-NCS	1.96	1.92	-0.27
FePc-ClO	1.96	1.92	-0.23
FePc-ClO_2	1.95	2.00	-0.27
FePc-HCO_3	1.96	1.91	-0.25
FePc-NO_2	1.95	1.88	-0.18
FePc-$C_4H_4N_2$	1.96	2.00	-0.23

Table S3. Optimized modes of pristine FePc and axially coordinated FePc-Xs configurations (*) and their corresponding OH*, O* and OOH* adsorption configurations.

Structure		*	OH*	O*	OOH*
FePc	Top				
	Side				
FePc-O	Top				
	Side				
FePc-F	Top				
	Side				
FePc-I	Top				
	Side				

Structure		*	OH*	O*	OOH*
FePc-Cl	Top				
	Side				
FePc-Br	Top				
	Side				
FePc-NO_2	Top				
	Side				
FePc-OH	Top				
	Side				

Structure		*	OH*	O*	OOH*
FePc-SH	Top				
	Side				
FePc-CN	Top				
	Side				
FePc-SCN	Top				
	Side				
FePc-NCS	Top				
	Side				

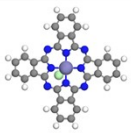
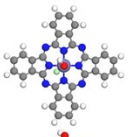
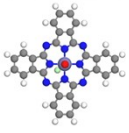
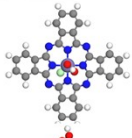
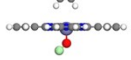
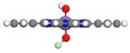
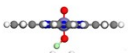
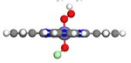
Structure		*	OH*	O*	OOH*
FePc-ClO	Top				
	Side				
$FePc-ClO_2$	Top				
	Side				
$FePc-NO_2$	Top				
	Side				
$FePc-HCO_3$	Top				
	Side				

Table S4. The calculated Gibbs free energy variations (ΔG_1, ΔG_2, ΔG_3, and ΔG_4) and overpotentials of the pristine FePc and axially coordinated FePc-Xs.

Structure	ΔG_1	ΔG_2	ΔG_3	ΔG_4	η^{OER}
FePc	**0.72**	**0.74**	**2.12**	**1.34**	**0.89**
FePc-O	**1.59**	**1.60**	**1.25**	**0.48**	**0.37**
FePc-F	**0.87**	**1.48**	**1.66**	**0.91**	**0.43**
FePc-Cl	**1.07**	**1.36**	**1.65**	**0.84**	**0.42**
FePc-Br	**1.08**	**1.34**	**1.67**	**0.83**	**0.44**
FePc-I	**0.89**	**1.33**	**1.66**	**1.04**	**0.43**
FePc-OH	**0.75**	**1.56**	**1.53**	**1.08**	**0.33**
FePc-SH	**1.08**	**1.52**	**1.41**	**0.91**	**0.29**
FePc-CN	**1.13**	**1.46**	**1.45**	**0.88**	**0.23**
FePc-SCN	**0.94**	**1.31**	**1.68**	**0.99**	**0.45**
FePc-NCS	**0.92**	**1.39**	**1.62**	**0.99**	**0.39**
FePc-ClO	**0.83**	**1.39**	**1.62**	**1.08**	**0.39**
FePc-ClO_2	**0.85**	**1.62**	**1.38**	**1.07**	**0.39**
FePc-HCO_3	**1.01**	**1.03**	**1.74**	**1.14**	**0.51**
FePc-NO_2	**1.19**	**1.33**	**1.59**	**0.81**	**0.36**
FePc-$C_4H_4N_2$	**0.61**	**1.38**	**1.62**	**1.31**	**0.39**

Table S5. The calculated Bader charge and *d*-band center of optimized models of FePc and FePc-Xs with bonding of OOH.

Structure	Bader Charge (|e|)			*d*-band center (eV)
	Q_{Fe}	Q_X	$\|Q_{Fe}\|-\|Q_X\|$	
FePc	1.26	/	1.26	-0.64
FePc-O	1.44	-0.54	0.90	-0.71
FePc-F	1.51	-0.59	0.92	-0.85
FePc-Cl	1.35	-0.42	0.93	-0.83
FePc-Br	1.35	-0.39	0.96	-0.85
FePc-I	1.30	-0.28	1.02	-0.92
FePc-OH	1.46	-0.40	1.06	-1.00
FePc-SH	1.29	-0.19	1.10	-0.99
FePc-CN	1.28	-0.47	0.81	-0.77
FePc-SCN	1.30	-0.40	0.90	-0.84
FePc-NCS	1.44	-0.48	0.96	-0.91
FePc-ClO	1.41	-0.36	1.05	-1.12
FePc-ClO_2	1.43	-0.37	1.06	-0.82
FePc-HCO_3	1.36	-0.61	0.75	-0.79
FePc-NO_2	1.39	-0.53	0.86	-0.75
FePc-$C_4H_4N_2$	1.42	-0.30	1.12	-0.93

Table S6. The calculated ICOHP of Fe-O bonds during binding with OH, O and OOH and bonding lengths of Fe and OOH for both pristine FePc and FePc-Xs.

Structure	ICOHP (eV)			
	OH*	O*	OOH*	Fe-OOH*(Å)
FePc	-1.70	-2.86	-2.00	1.75
FePc-O	-1.27	-2.63	-1.19	1.94
FePc-F	-1.61	-2.95	-1.60	1.84
FePc-Cl	-1.52	-2.85	-1.53	1.85
FePc-Br	-1.50	-2.82	-1.50	1.85
FePc-I	-1.01	-2.21	-0.98	1.86
FePc-OH	-1.54	-2.83	-1.50	1.86
FePc-SH	-1.42	-2.70	-1.34	1.89
FePc-CN	-1.43	-2.47	-1.36	1.88
FePc-SCN	-1.51	-2.78	-1.51	1.85
FePc-NCS	-1.57	-2.88	-1.63	1.84
FePc-ClO	-1.55	-2.85	-1.55	1.85
FePc-ClO_2	-1.59	-2.88	-1.69	1.82
FePc-HCO_3	-1.58	-2.93	-1.68	1.83
FePc-NO_2	-1.48	-2.65	-1.42	1.87
FePc-$C_4H_4N_2$	-1.59	-2.77	-1.59	1.84