Supplementary Information (SI) for Sustainable Energy & Fuels.

Functional Group Effects on the Electrocatalytic Activity of Iron Phthalocyanine for ORR, OER, and HER in Aqueous Medium: Insights from Density Functional Theory

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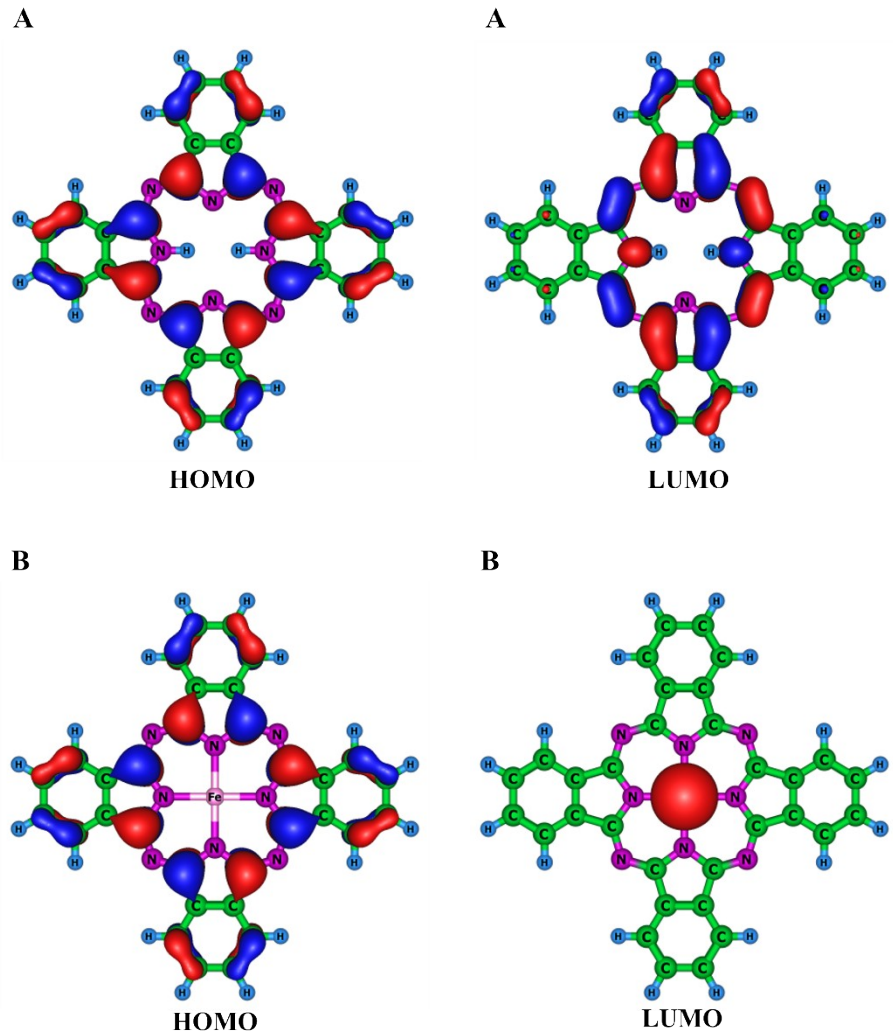

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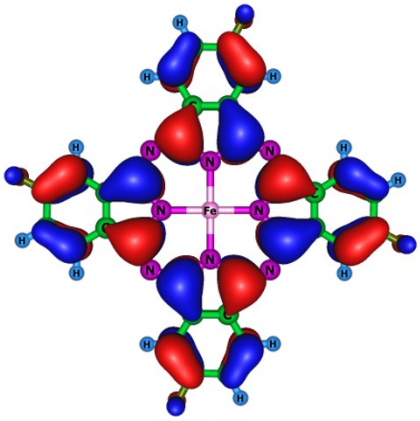

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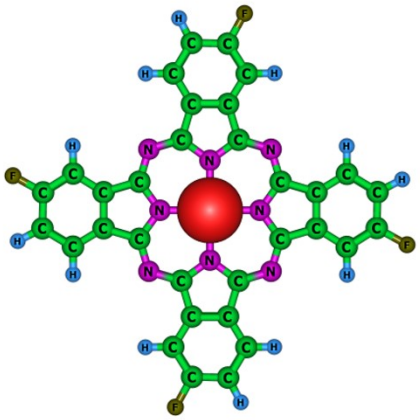

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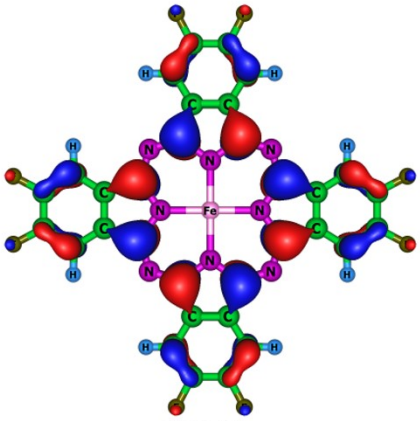

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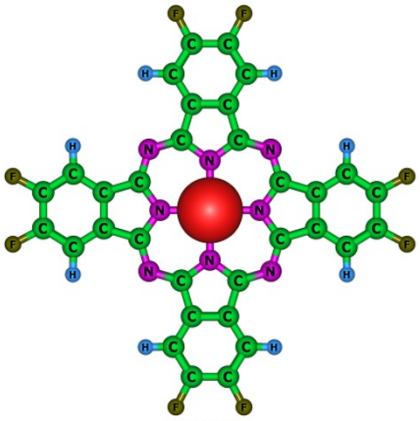

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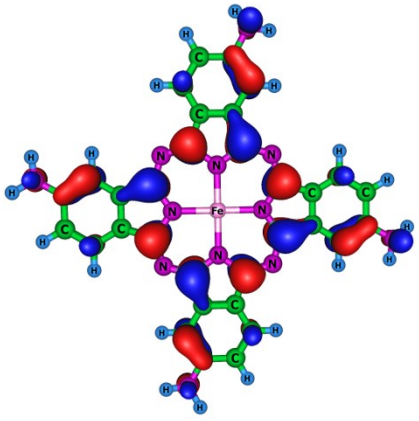

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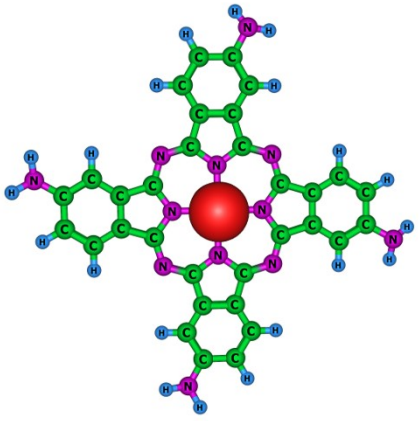

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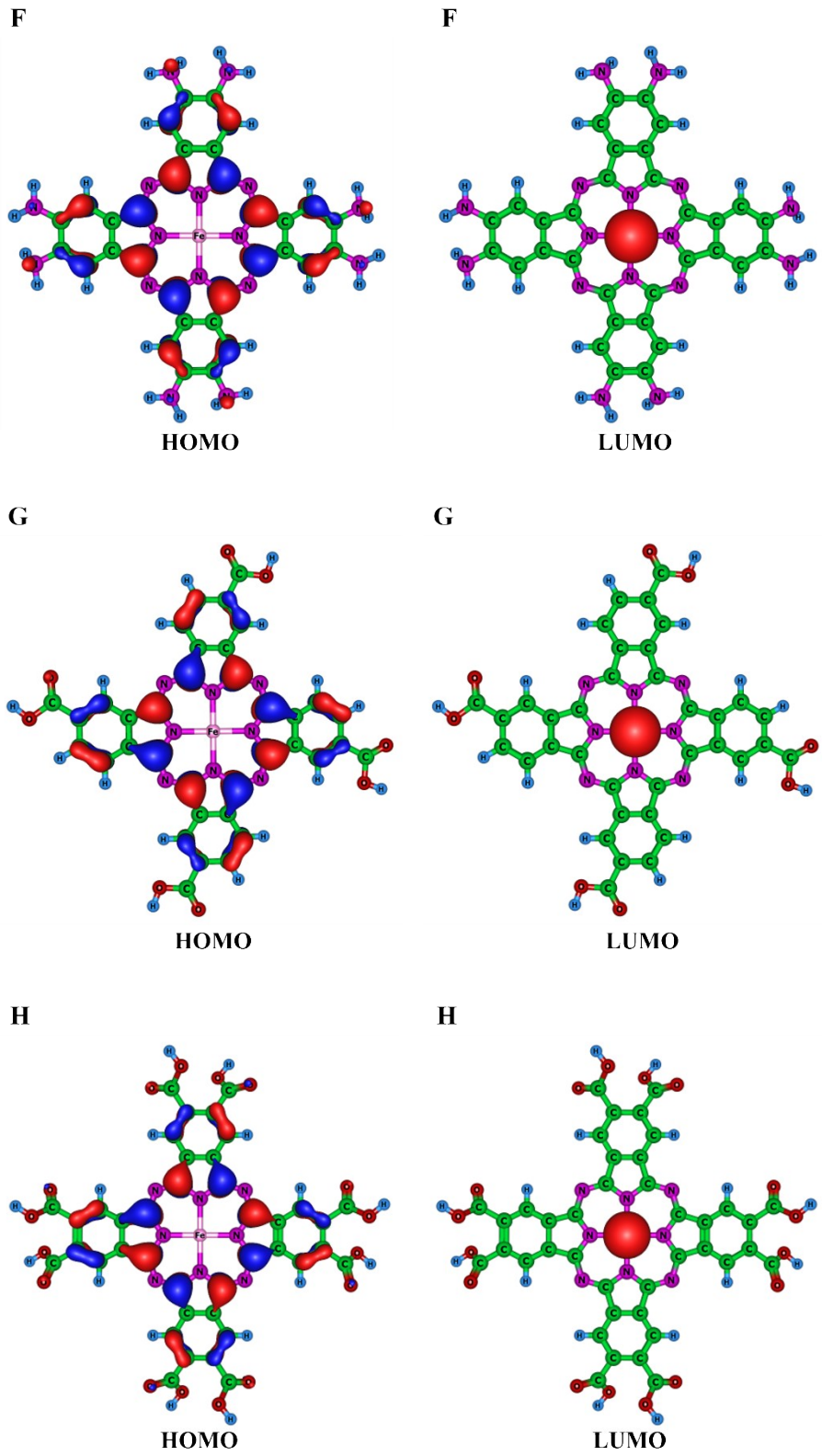
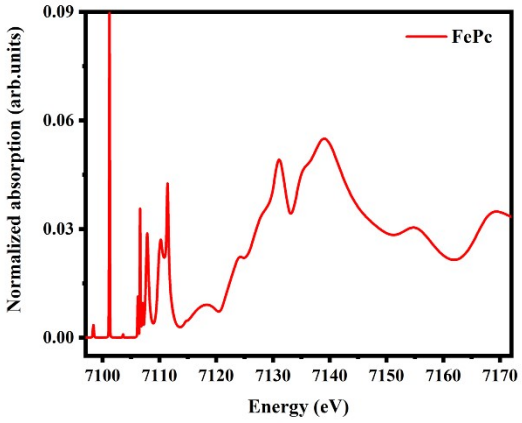


Fig. S1. HOMO-LUMO plots of **A)** Pp **B)** FePc **C)** $FePc(F)_4$ **D)** $FePc(F)_8$ **E)** $FePc(NH_2)_4$ **F)** $FePc(NH_2)_8$ **G)** $FePc(COOH)_4$ and **H)** $FePc(COOH)_8$.

Table S1. The formation energy (E_f), binding energy per atom (E_b), HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}), and $E_{HOMO-LUMO}$ gap of the catalytic surfaces / eV (in vacuum).

Structure	E_f	E_b	E_{HOMO}	E_{LUMO}	$E_{HOMO-LUMO}$ gap
Pc	-	-6.76	-4.98	-2.84	2.15
FePc	-5.97	-6.91	-4.93	-3.37	1.56
$FePc(F)_4$	-5.91	-6.95	-5.20	-3.63	1.57
$FePc(F)_8$	-5.84	-6.98	-5.46	-3.86	1.60
$FePc(NH_2)_4$	-9.30	-6.67	-4.32	-2.89	1.43
$FePc(NH_2)_8$	-9.23	-6.48	-4.25	-2.84	1.41
$FePc(COOH)_4$	-9.28	-7.09	-5.43	-3.85	1.59
$FePc(COOH)_8$	-8.98	-7.19	-5.73	-4.10	1.63

A



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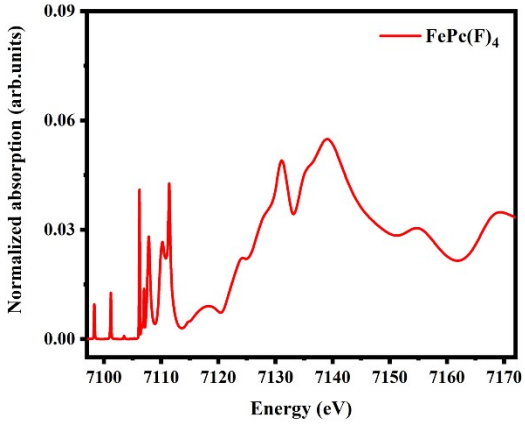

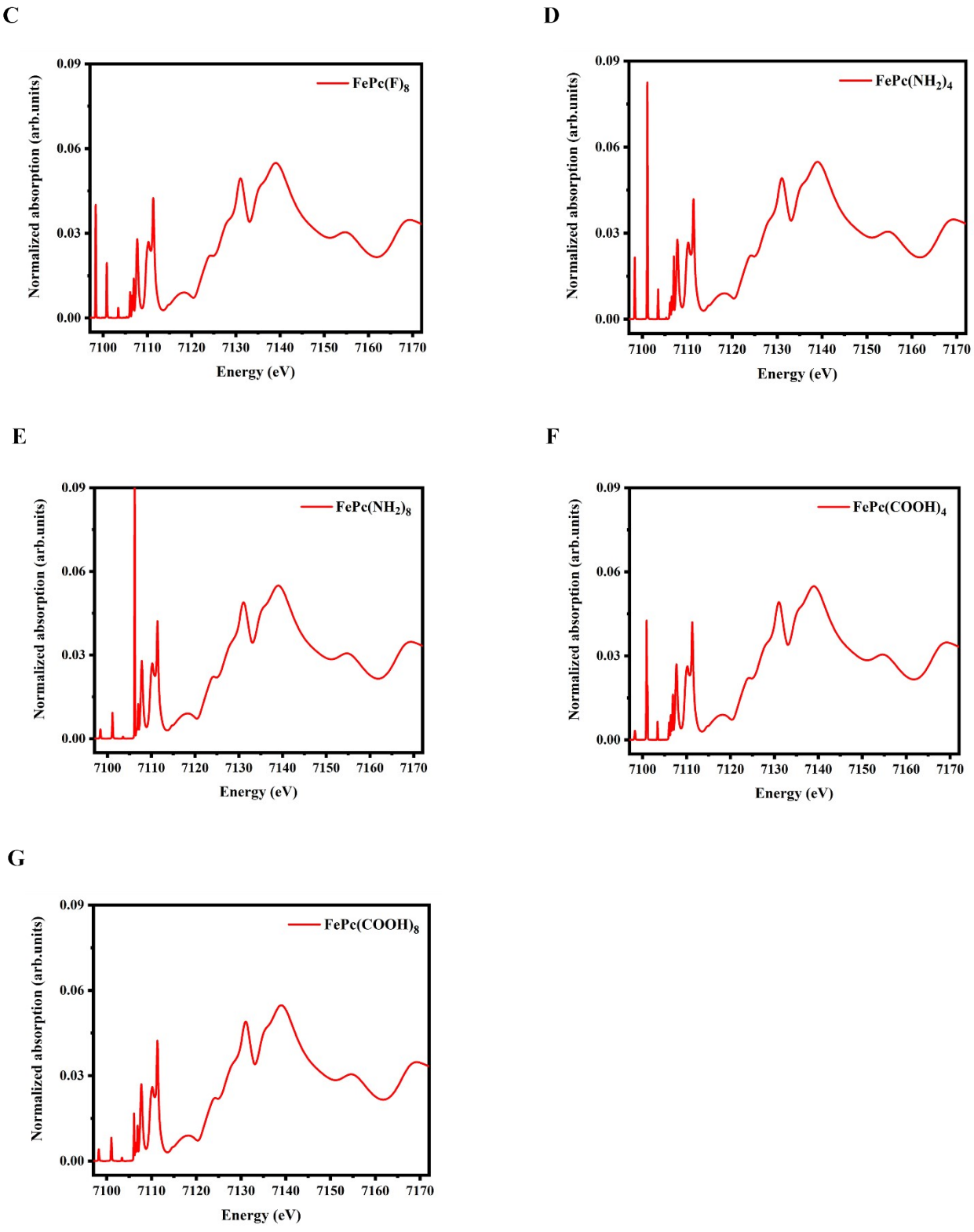

Fig. S2. Full range Fe K-edge XAS plots of **A)** FePc, **B)** $FePc(F)_4$, **C)** $FePc(F)_8$, **D)** $FePc(NH_2)_4$, **E)** $FePc(NH_2)_8$, **F)** $FePc(COOH)_4$, and **G)** $FePc(COOH)_8$ in vacuum.

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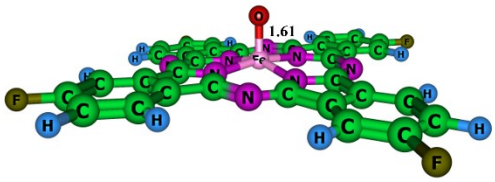

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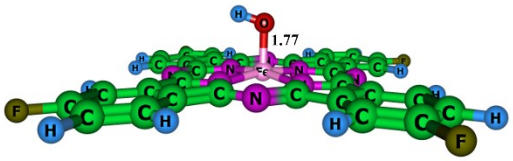

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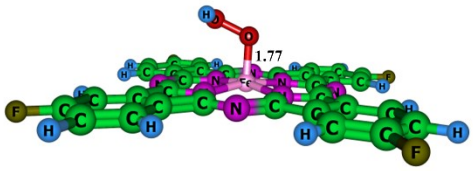

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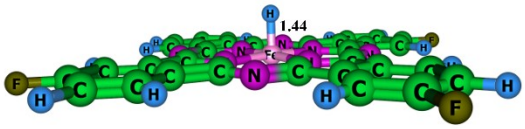

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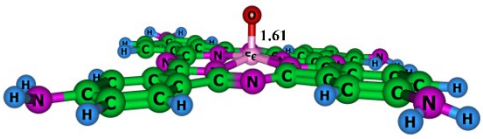

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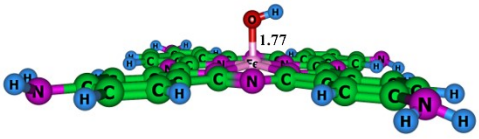

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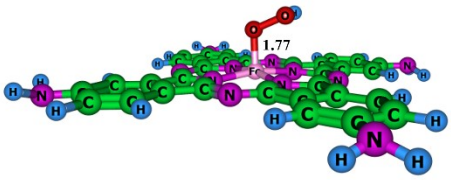

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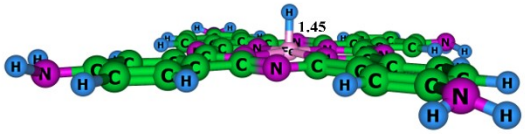

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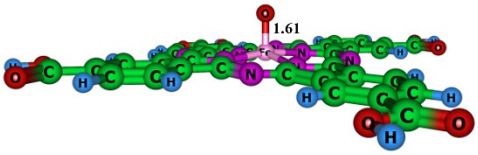

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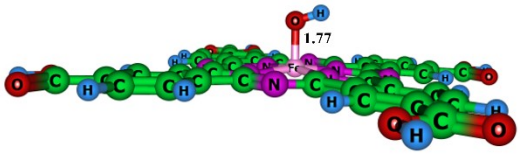

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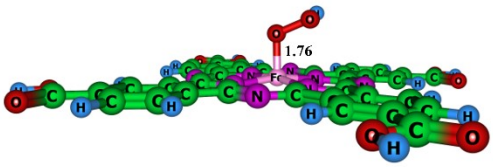

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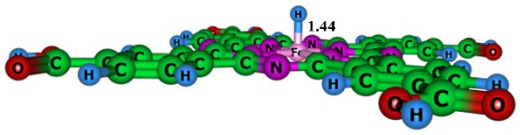


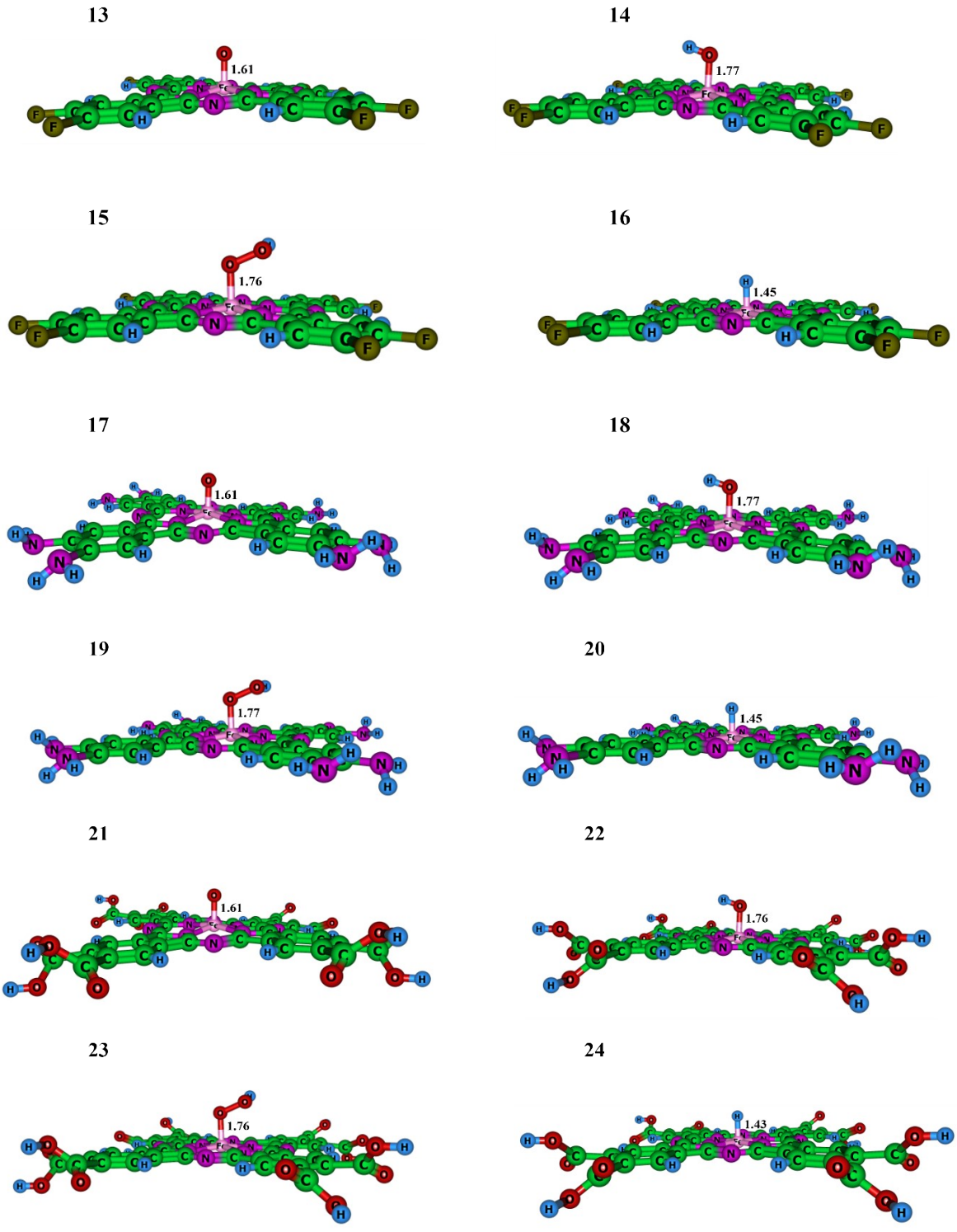
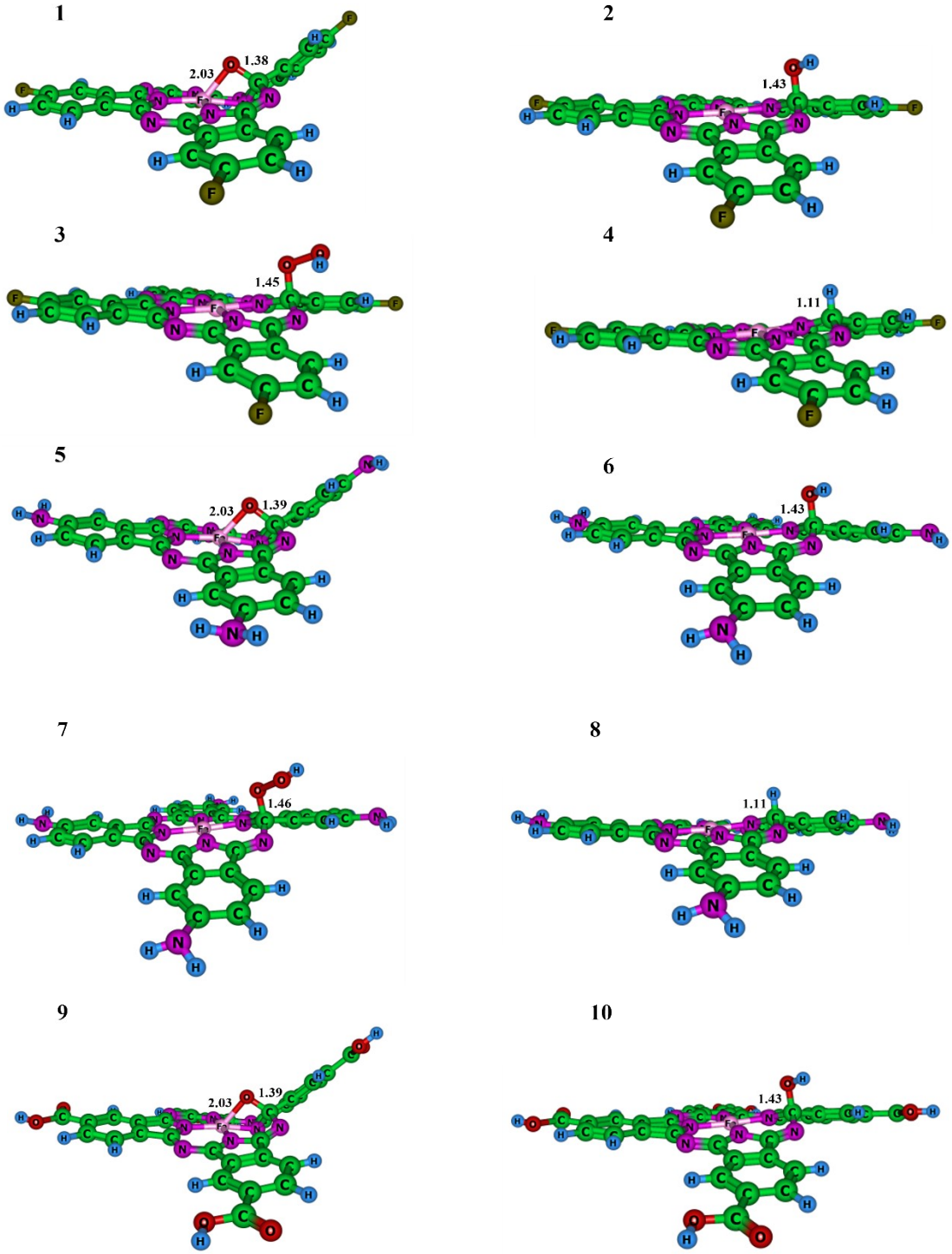


Fig. S3. Optimized geometries of adsorption intermediates on M-sites **1)** O-FePc$(F)_4$ **2)** OH-FePc$(F)_4$ **3)** OOH-FePc$(F)_4$ **4)** H-FePc$(F)_4$ **5)** O-FePc$(NH_2)_4$ **6)** OH-FePc$(NH_2)_4$ **7)** OOH-FePc$(NH_2)_4$ **8)** H-FePc$(NH_2)_4$ **9)** O-FePc$(COOH)_4$ **10)** OH-FePc$(COOH)_4$ **11)** OOH-

$FePc(COOH)_4$ **12)** H-$FePc(COOH)_4$ **13)** O-$FePc(F)_8$ **14)** OH-$FePc(F)_8$ **15)** OOH-$FePc(F)_8$ **16)** H-$FePc(F)_8$ **17)** O-$FePc(NH_2)_8$ **18)** OH-$FePc(NH_2)_8$ **19)** OOH-$FePc(NH_2)_8$ **20)** H-$FePc(NH_2)_8$ **21)** O-$FePc(COOH)_8$ **22)** OH-$FePc(COOH)_8$ **23)** OOH-$FePc(COOH)_8$ **24)** H-$FePc(COOH)_8$.



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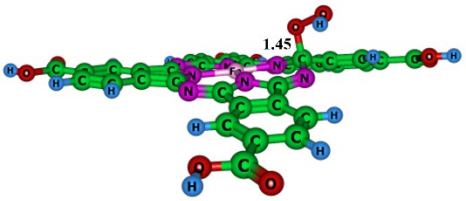

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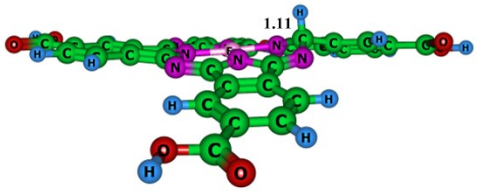

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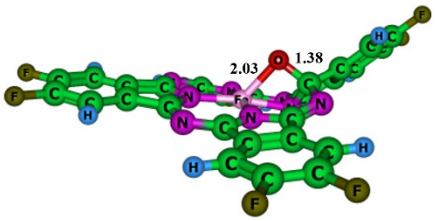

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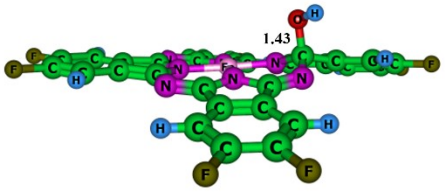

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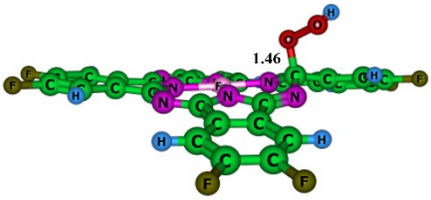

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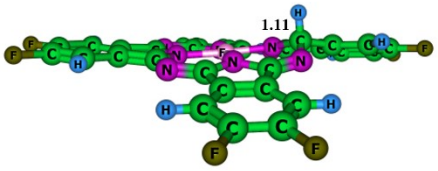

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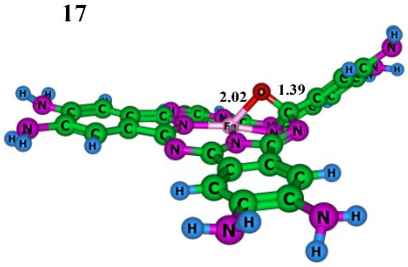

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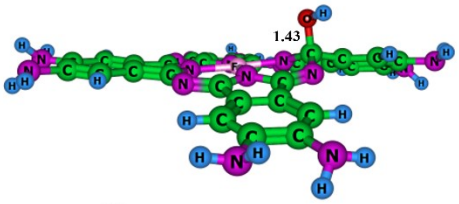

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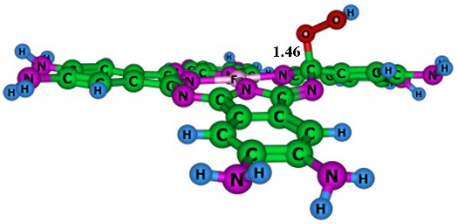

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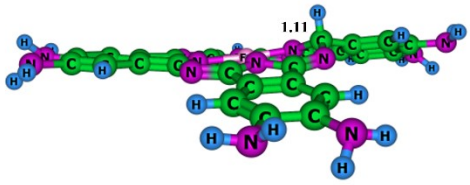

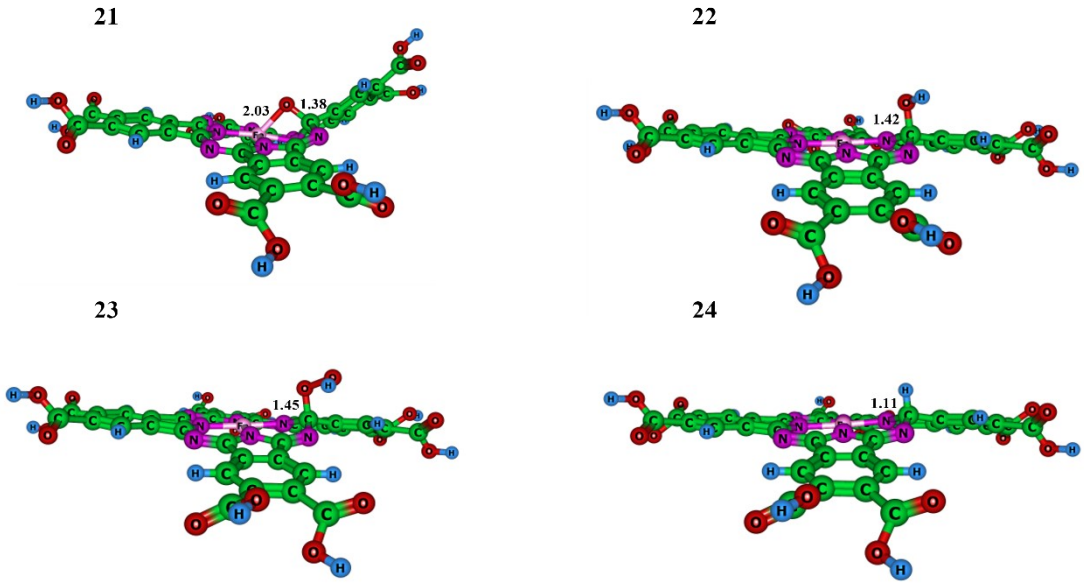

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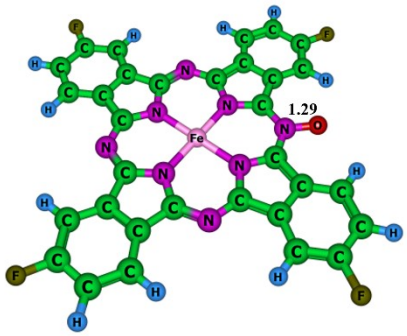

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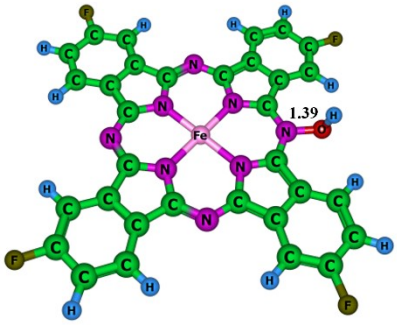

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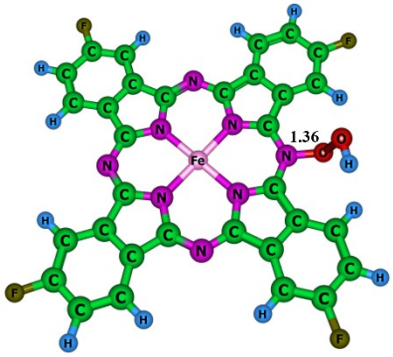

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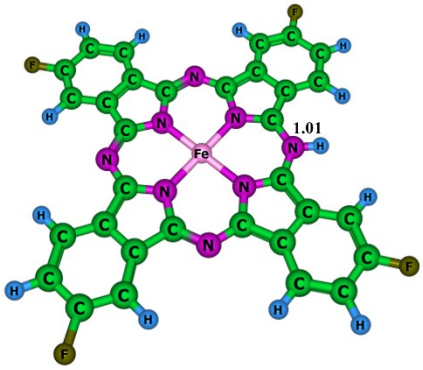

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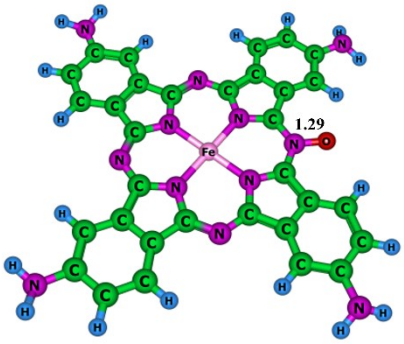

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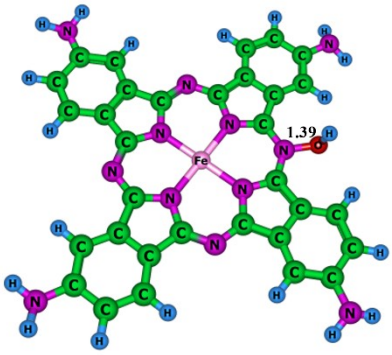

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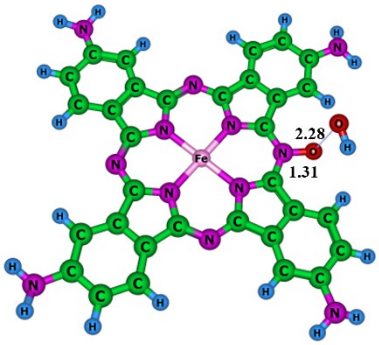

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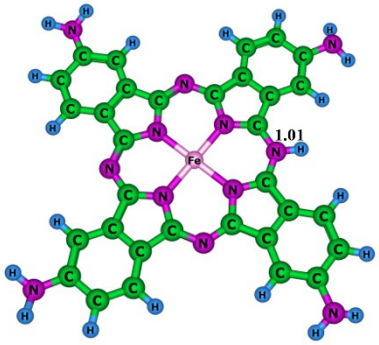

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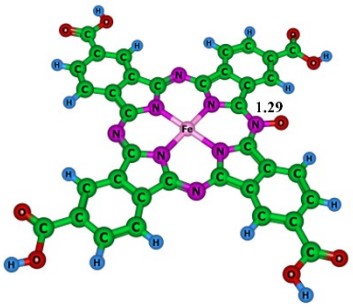

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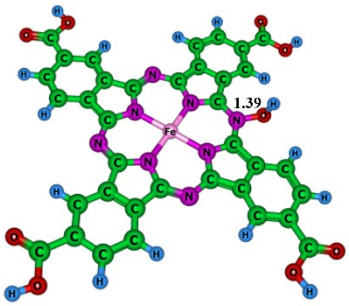

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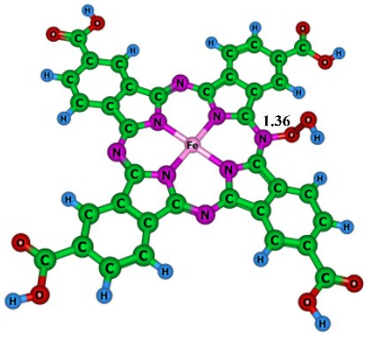

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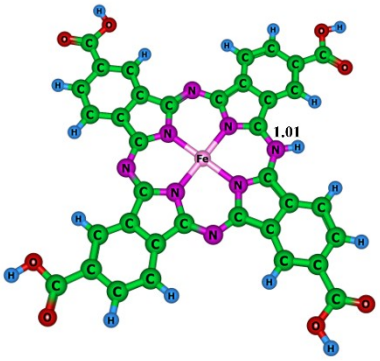

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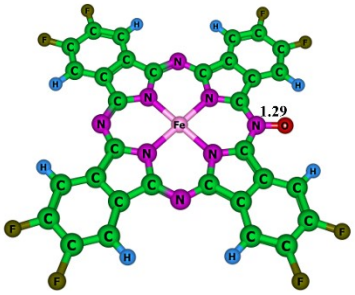

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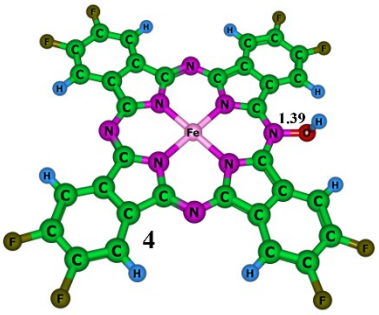

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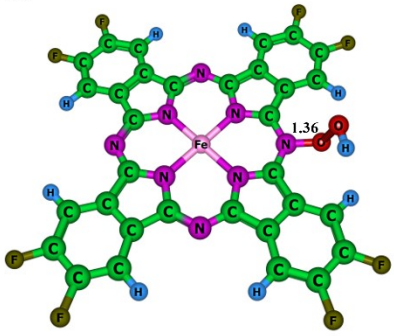
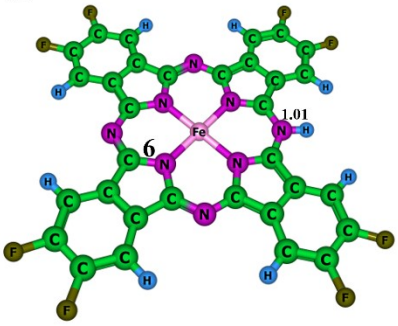


16



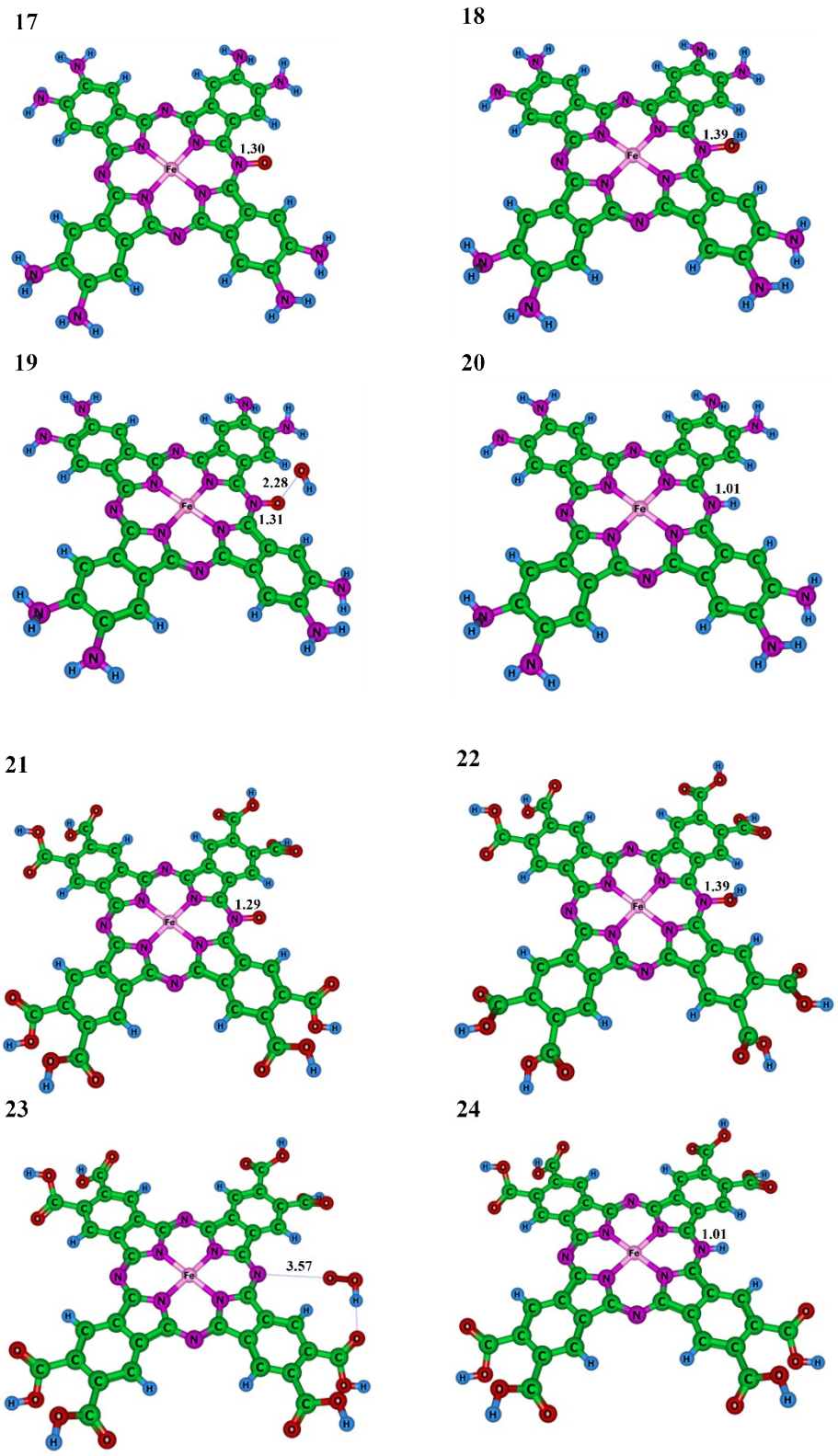


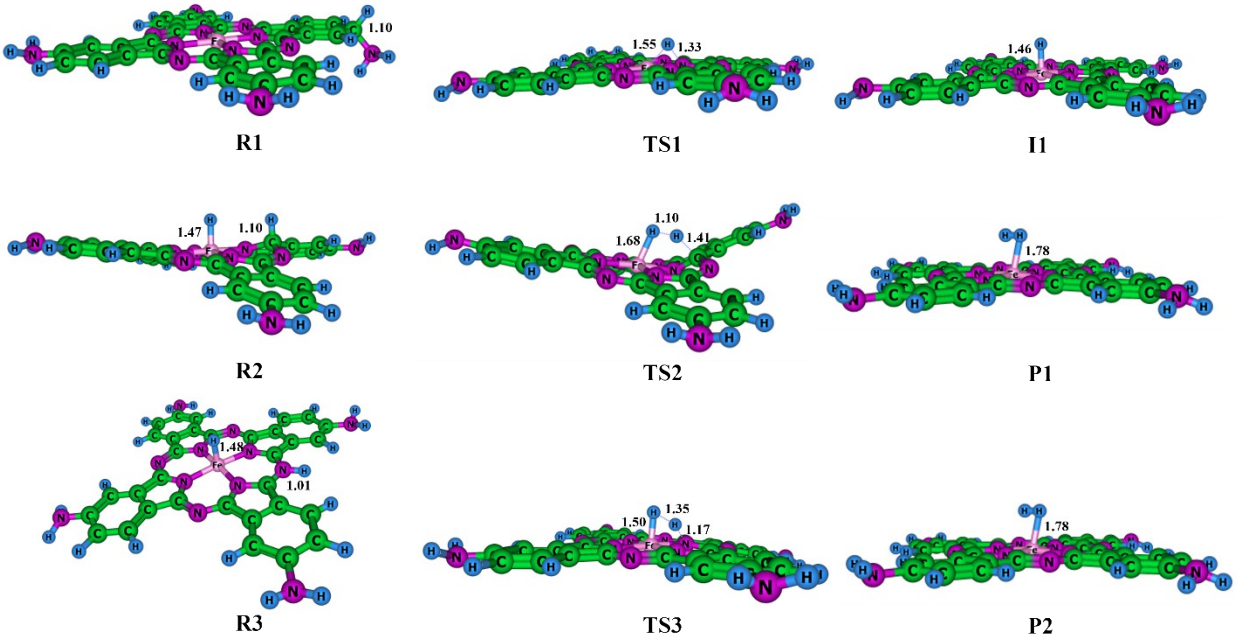
Fig. S5. Optimized geometries of adsorption intermediates on N-sites **1)** O-FePc$(F)_4$ **2)** OH-FePc$(F)_4$ **3)** OOH-FePc$(F)_4$ **4)** H-FePc$(F)_4$ **5)** O-FePc$(NH_2)_4$ **6)** OH-FePc$(NH_2)_4$ **7)** OOH-

$FePc(NH_2)_4$ **8)** H-$FePc(NH_2)_4$ **9)** O-$FePc(COOH)_4$ **10)** OH-$FePc(COOH)_4$ **11)** OOH-$FePc(COOH)_4$ **12)** H-$FePc(COOH)_4$ **13)** O-$FePc(F)_8$ **14)** OH-$FePc(F)_8$ **15)** OOH-$FePc(F)_8$ **16)** H-$FePc(F)_8$ **17)** O-$FePc(NH_2)_8$ **18)** OH-$FePc(NH_2)_8$ **19)** OOH-$FePc(NH_2)_8$ **20)** H-$FePc(NH_2)_8$ **21)** O-$FePc(COOH)_8$ **22)** OH-$FePc(COOH)_8$ **23)** OOH-$FePc(COOH)_8$ **24)** H-$FePc(COOH)_8$.

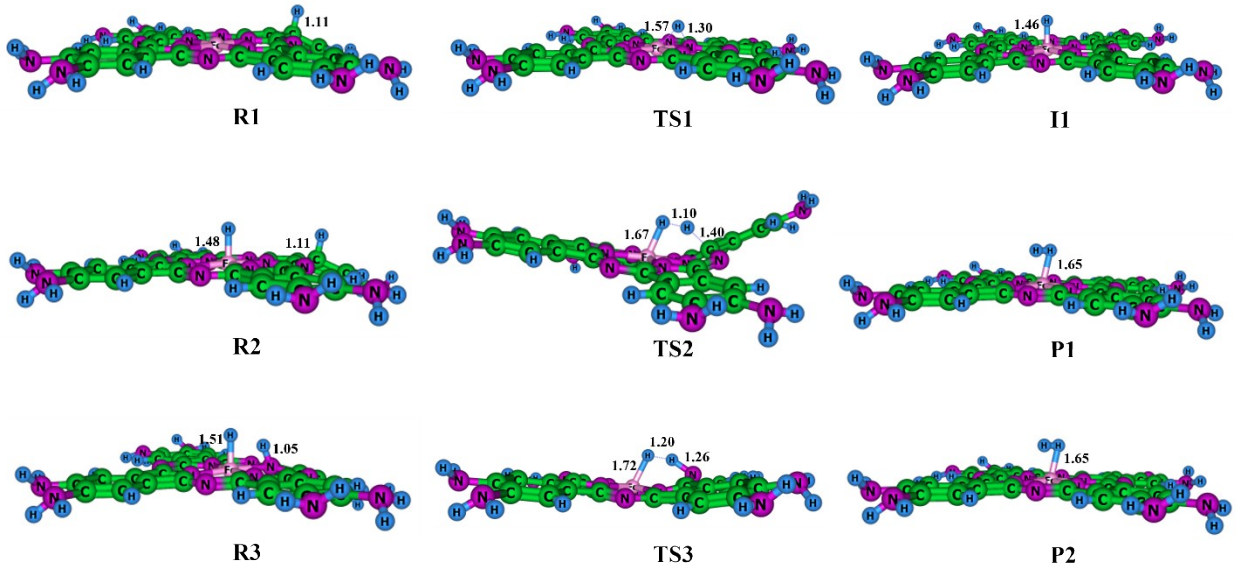
Table S2. The calculated adsorbed species (*O, *OH, *OOH and *H) free energy changes (ΔG_{OOH*}, ΔG_{O*}, ΔG_{OH*}, ΔG_{H*}), and ORR/OER/HER overpotentials (η) at C and N-sites (in vacuum).

Medium	Structures	ΔG_{OOH*} (eV)	ΔG_{O*} (eV)	ΔG_{OH*} (eV)	ΔG_{H*} (eV)	η^{ORR} (V)	η^{OER} (V)	η^{HER} (V)
C-site	**$FePc(F)_4$**	2.71	2.20	-0.24	-0.58	1.47	1.21	-0.58
	$FePc(F)_8$	2.75	2.22	-0.23	-0.56	1.46	1.22	-0.56
	$FePc(NH_2)_4$	1.00	0.41	-1.97	-0.63	3.20	2.69	-0.63
	$FePc(NH_2)_8$	2.71	2.12	-0.24	-0.61	1.47	1.13	-0.61
	$FePc(COOH)_4$	2.80	7.79	-0.16	-0.55	6.22	6.72	-0.55
	$FePc(COOH)_8$	2.82	2.35	-0.16	-0.53	1.39	1.28	-0.53
N-site	**$FePc(F)_4$**	3.94	2.33	1.24	-0.87	0.25	0.38	-0.87
	$FePc(F)_8$	3.95	2.32	1.21	-0.86	0.26	0.41	-0.86
	$FePc(NH_2)_4$	1.58	0.62	-0.41	-0.83	1.64	2.11	-0.83
	$FePc(NH_2)_8$	3.27	2.29	1.31	-0.81	0.26	0.42	-0.81
	$FePc(COOH)_4$	3.96	2.39	1.26	-0.93	0.27	0.34	-0.93
	$FePc(COOH)_8$	2.66	2.41	1.19	-0.99	0.99	1.03	-0.99

A


1.10
R1
1.55
1.33
TS1
1.46
I1
1.47
1.10
R2
1.10
1.68
1.41
TS2
1.78
P1
1.48
1.01
R3
1.35
1.50
1.17
TS3
1.78
P2

B


1.11
R1
1.57
1.30
TS1
1.46
I1
1.48
1.11
R2
1.10
1.67
1.40
TS2
1.65
P1
1.51
1.05
R3
1.20
1.72
1.26
TS3
1.65
P2

C

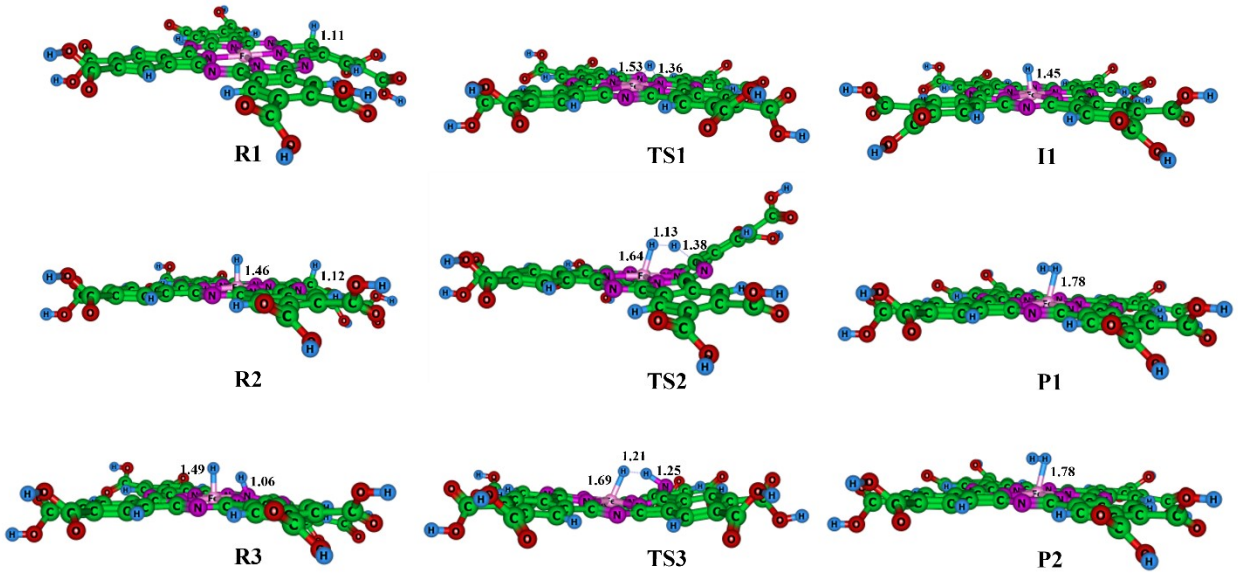


Fig. S6. Optimized geometries of reactants (R), intermediates (I), transition states (TS), and final product (P) for **A)** $FePc(NH_2)_4$ **B)** $FePc(NH_2)_8$ and **C)** $FePc(COOH)_8$ in the HER mechanism in solvent.