Spin-Crossover-Mediated Potential-Dependent Selective NO Reduction Reaction on Iron-Polyphthalocyanine: A DFT Study

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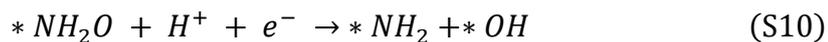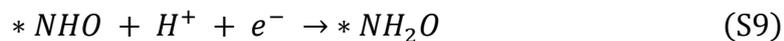
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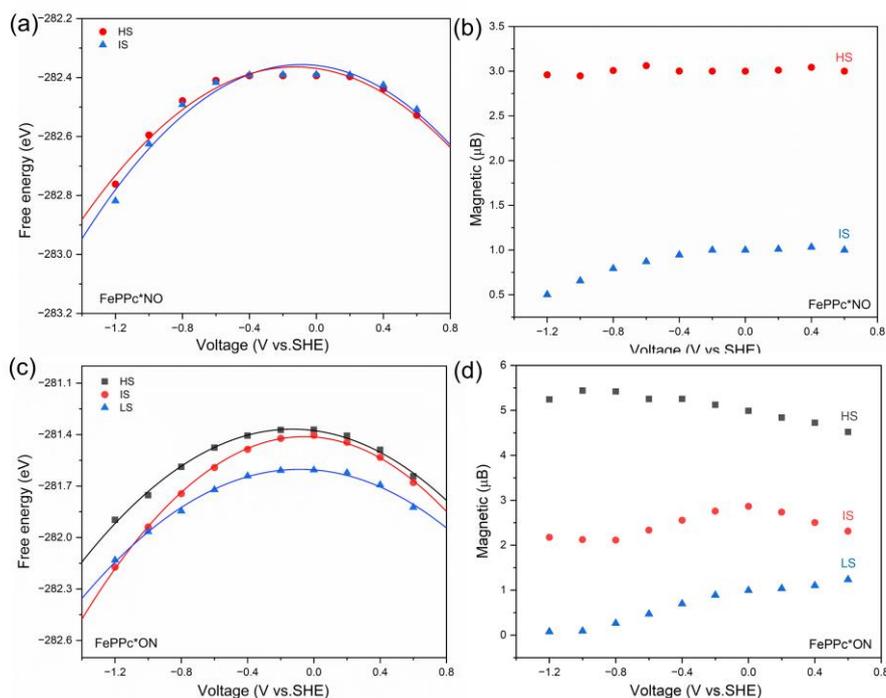**Gibbs free energy calculation at constant potential.**

The four-step proton-coupled electron transfer process in NORR is defined as follows:

$$* + NO \rightarrow *NO \tag{S3}$$

$$*NO + H^+ + e^- \rightarrow *NHO \tag{S4}$$

$$*NHO + H^+ + e^- \rightarrow *NH_2O \tag{S5}$$

$$*NH_2O + H^+ + e^- \rightarrow *NH_2OH \tag{S6}$$

The five-step proton-coupled electron transfer process in NORR is defined as follows:

$$* + NO \rightarrow *NO \tag{S7}$$

$$*NO + H^+ + e^- \rightarrow *NHO \tag{S8}$$

$$*NHO + H^+ + e^- \rightarrow *NH_2O \tag{S9}$$

$$*NH_2O + H^+ + e^- \rightarrow *NH_2 + *OH \tag{S10}$$

$$*NH_2 + *OH + H^+ + e^- \rightarrow *NH_3 + *OH \tag{S11}$$

Figure S1. FePPc*NO (a) Free energy of intermediate spin (HS) and low spin (IS) at different potential, (b) The spin moment for various spin states at different potential. FePPc*ON (c) Free energy of high spin(HS), intermediate spin (IS) and low spin (LS) at different potential, (d) The spin moment for various spin states at different potential.
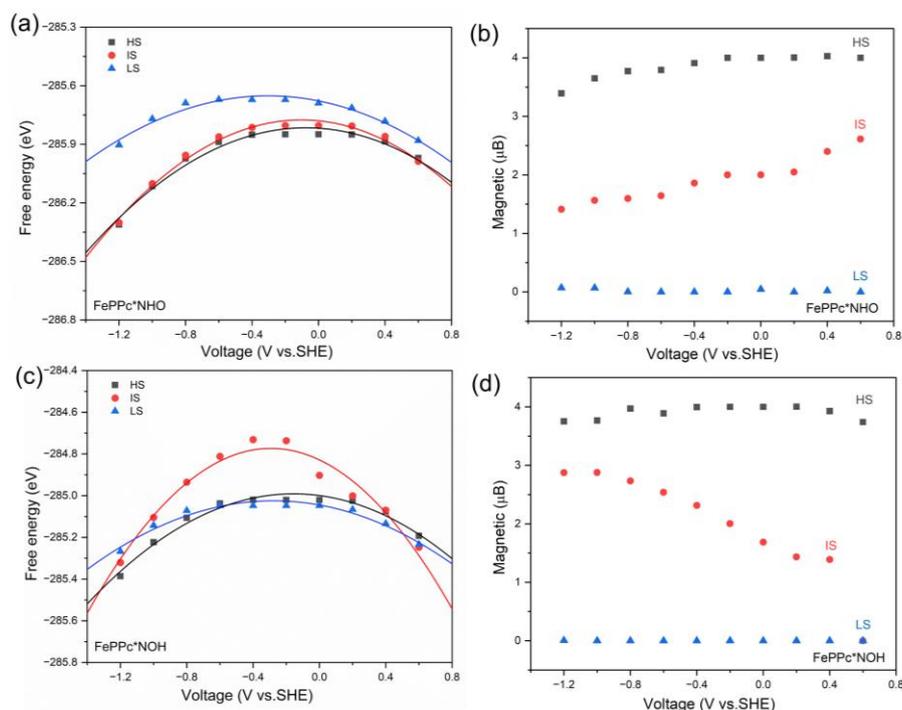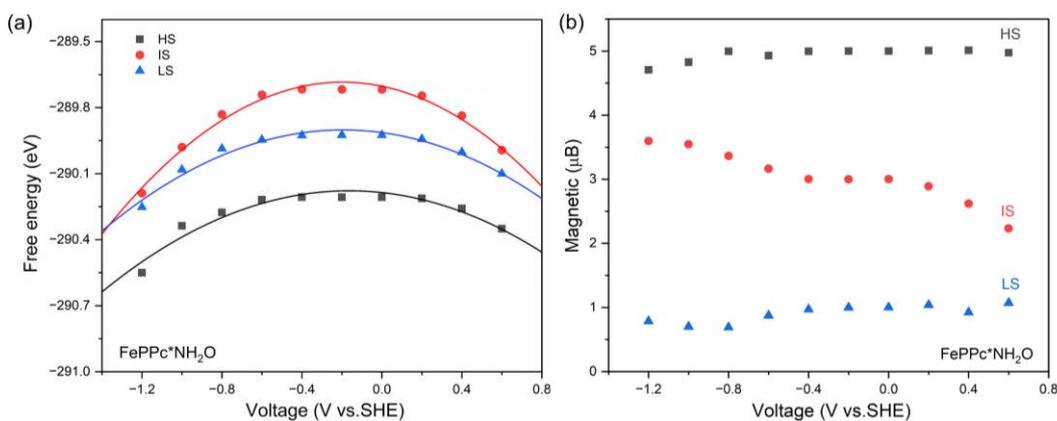

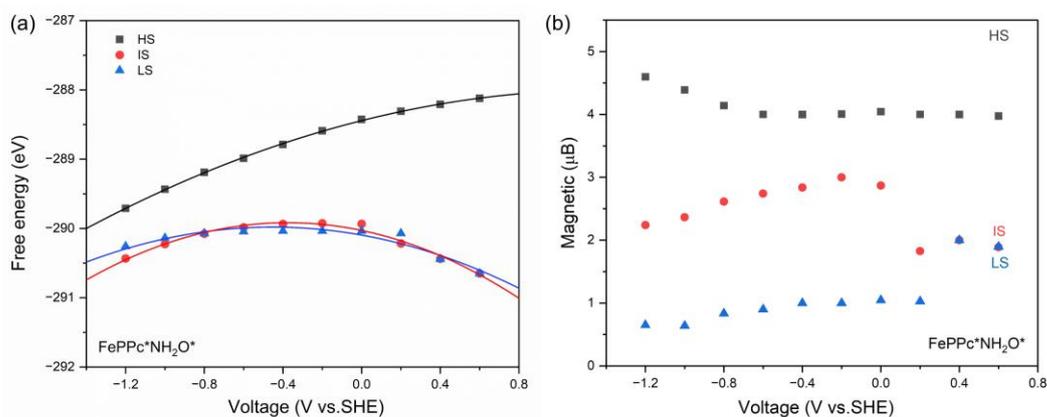**Figure S2.** FePPc*NHO (a) Free energy of HS, IS and LS at different potential, (b) The

spin moment for various spin states at different potential. FePPc*NOH (c) Free energy of HS, IS and LS at different potential, (d) The spin moment for various spin states at different potential.
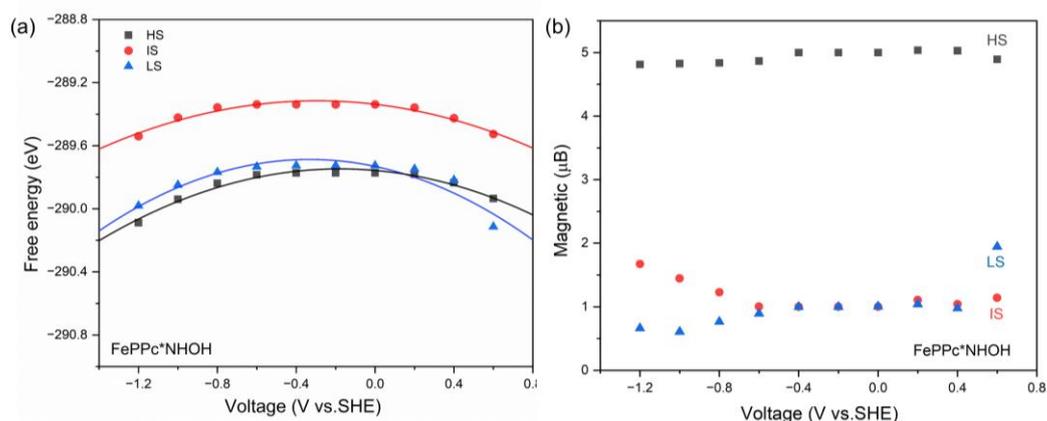

Figure S3. FePPc*NHOH (a) Free energy of HS, IS and LS at different potential, (b) The spin moment for various spin states at different potential.

Figure S4. FePPc*NH$_2$O (a) Free energy of HS, IS and LS at different potential, (b) The spin moment for various spin states at different potential.
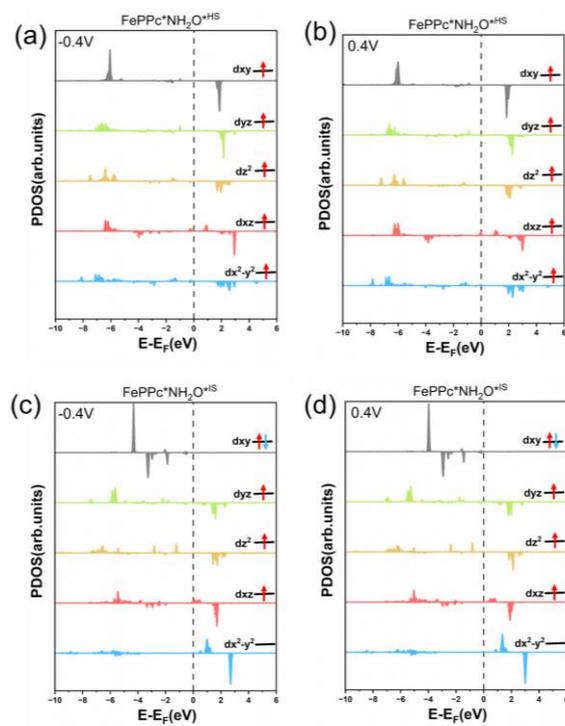

Figure S5. FePPc*NH$_2$O* (a) Free energy of HS, IS and LS at different potential, (b) The spin moment for various spin states at different potential.
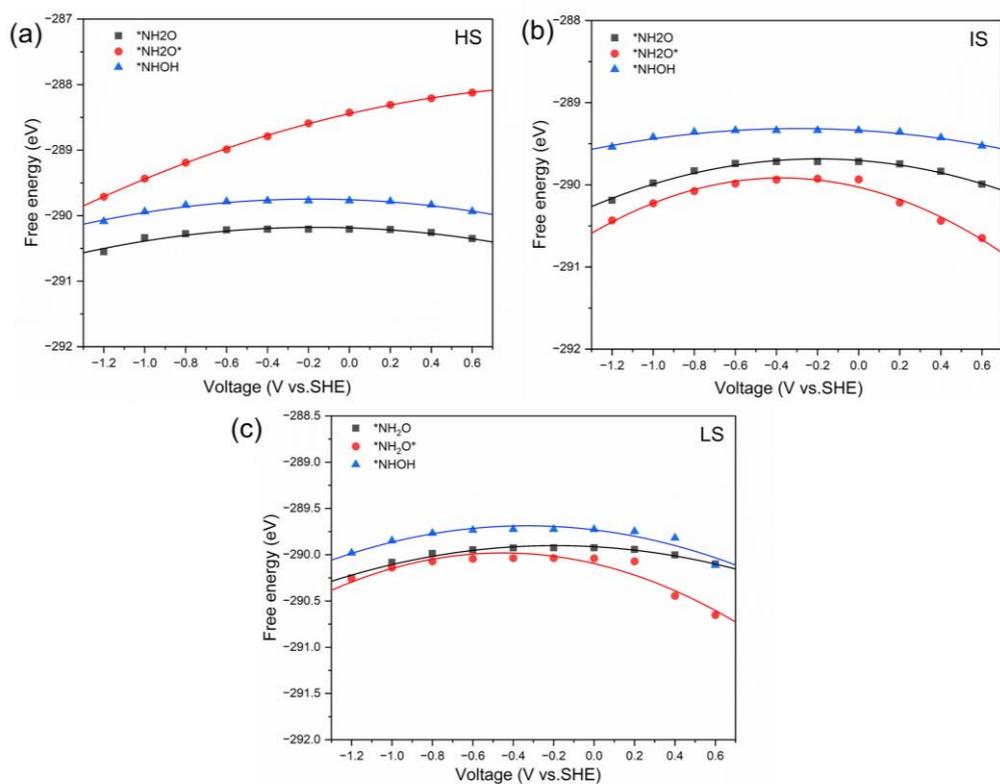
Figure S6. Free energy of FePPc*NH$_2$O/*NH$_2$O*/*NHOH (a) HS, (b) IS, (c)LS.

Figure S7. PDOS of FePPc^{HS}*NH$_2$O*(a)-0.4V, (b)0.4V; FePPc^{IS}*NH$_2$O*(c)-0.4V, (d)0.4V.

Figure S8. PDOS of FePPc^{LS}*NH$_2$O*(a)-0.8V, (b)-0.4V, (c)0.4V.

Figure S9. Spin density of FePPc^{LS}*NH$_2$O*(a)-0.8V, (b)-0.4V, (c)0.4V.
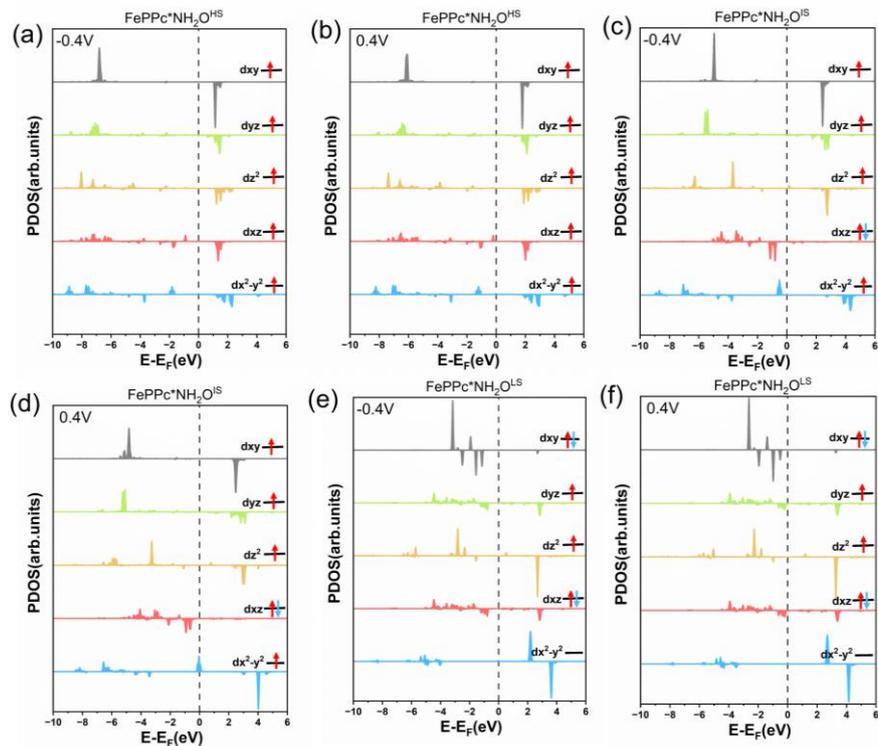
Figure S10. PDOS of FePPc^{HS}*NH$_2$O(a)-0.4V, (b)0.4V; FePPc^{IS}*NH$_2$O(c)-0.4V, (d)0.4V, FePPc^{LS}*NH$_2$O(e)-0.4V, (f)0.4V.
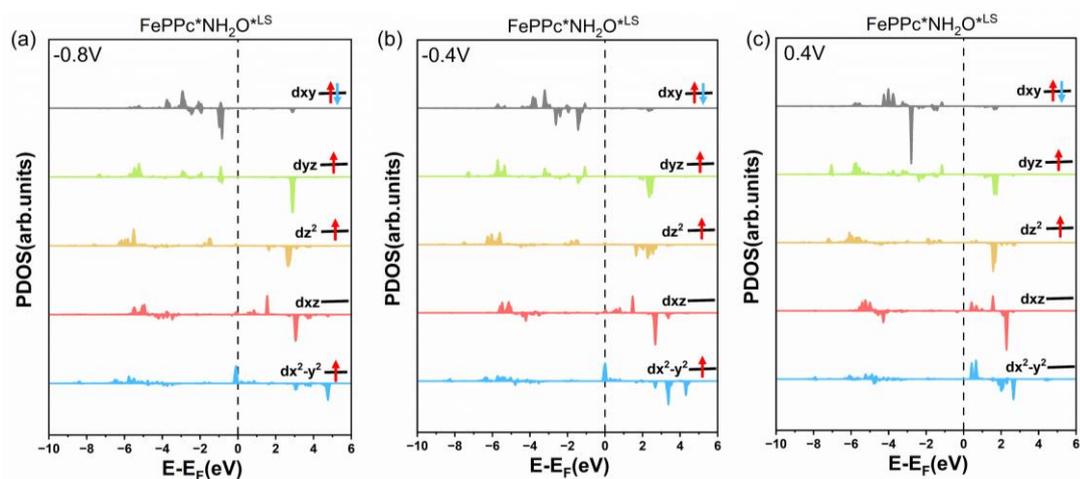

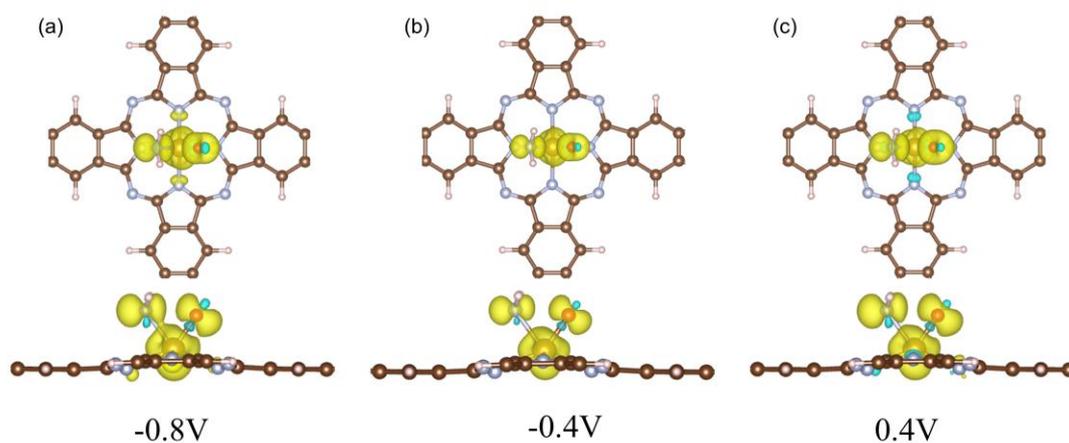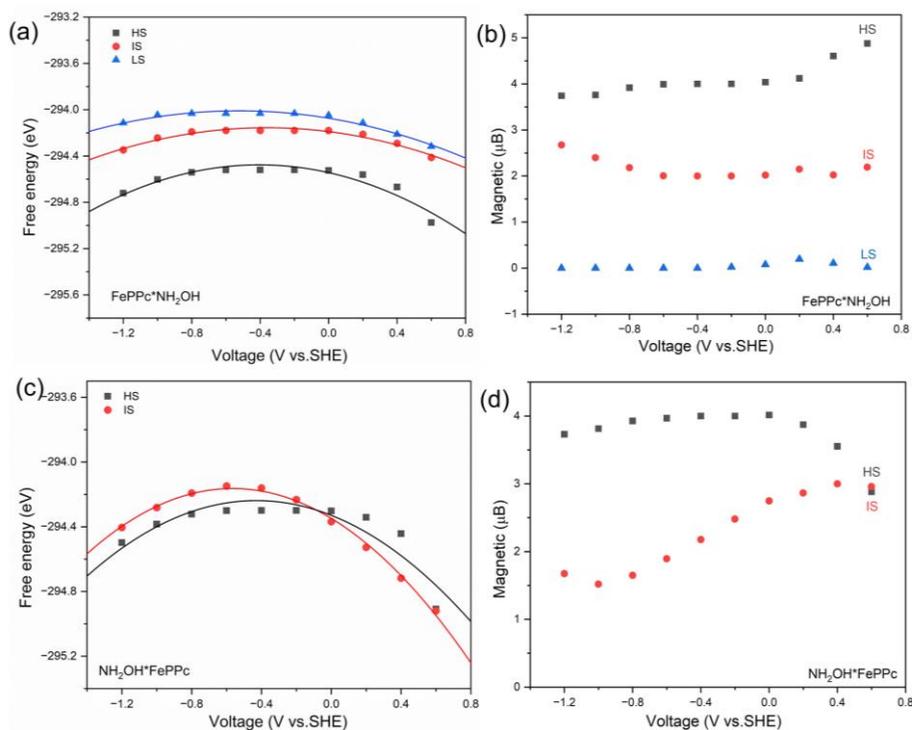**Figure S11.** FePPc*NH$_2$OH (a) Free energy of HS, IS and LS at different potential, (b) The spin moment for various spin states at different potential. NH$_2$OH*FePPc (c) Free energy of HS and IS at different potential, (d) The spin moment for various spin states at different potential.
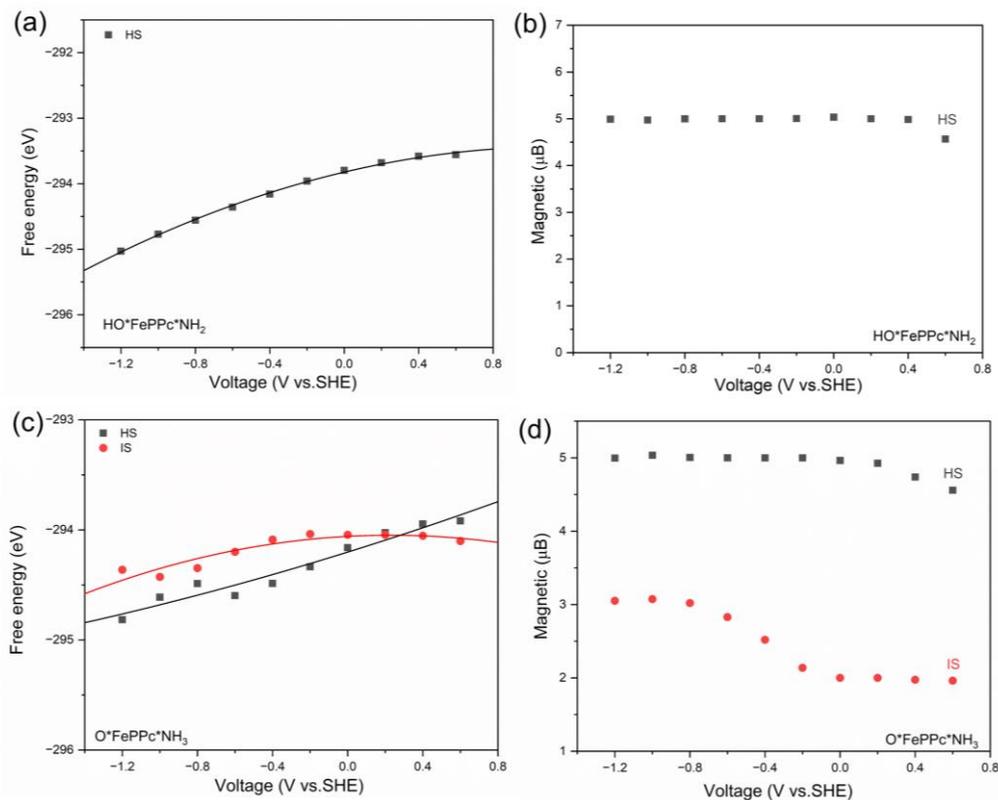
Figure S12. FePPc*NH₂+*OH (a) Free energy of HS, IS and LS at different potential, (b) The spin moment for HS at different potential. FePPc*NH₃+*O (c) Free energy of HS and IS at different potential, (d) The spin moment for various spin states at different potential.
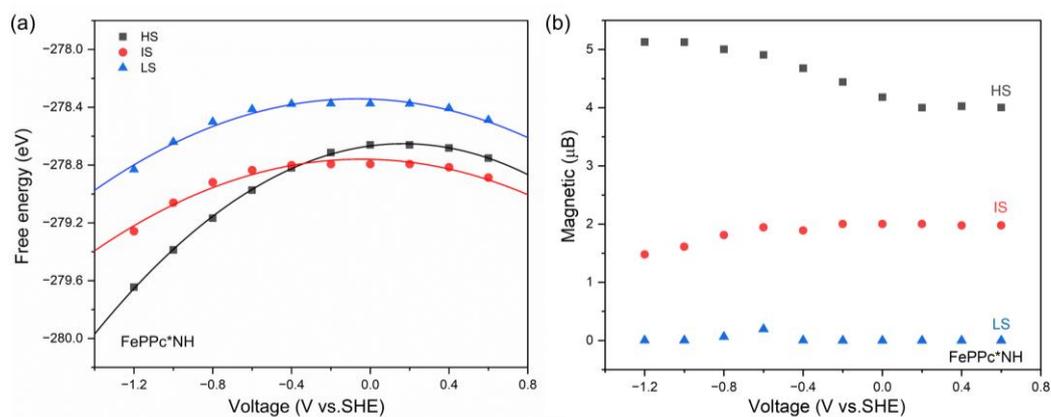
Figure S13. FePPc*NH (a) Free energy of HS, IS and LS at different potential, (b) The spin moment for various spin states at different potential.

Figure S14. FePPc*NH$_2$ (a) Free energy of HS, IS and LS at different potential, (b) The spin moment for various spin states at different potential. HO*FePPc*NH$_3$ (a) Free energy of HS at different potential, (b) The spin moment for HS at different potential.

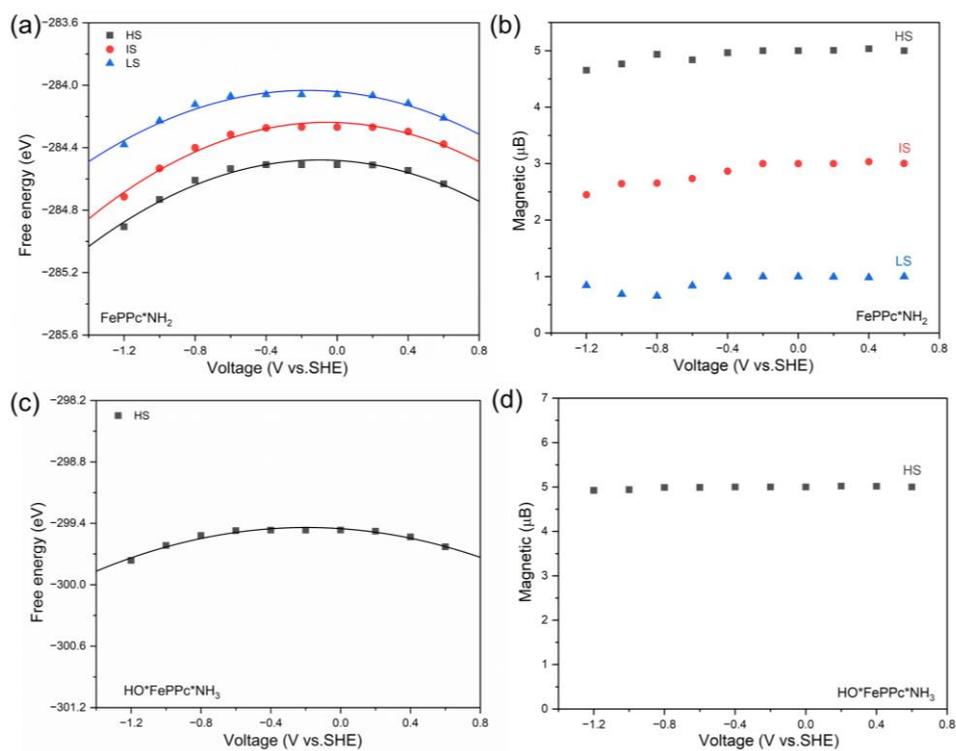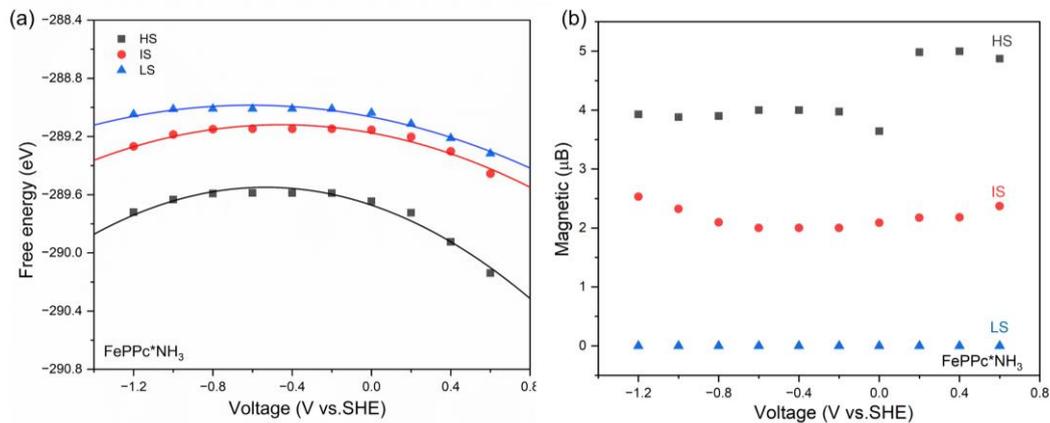**Figure S15.** FePPc*NH$_3$ (a) Free energy of HS, IS and LS at different potential, (b) The spin moment for various spin states at different potential.
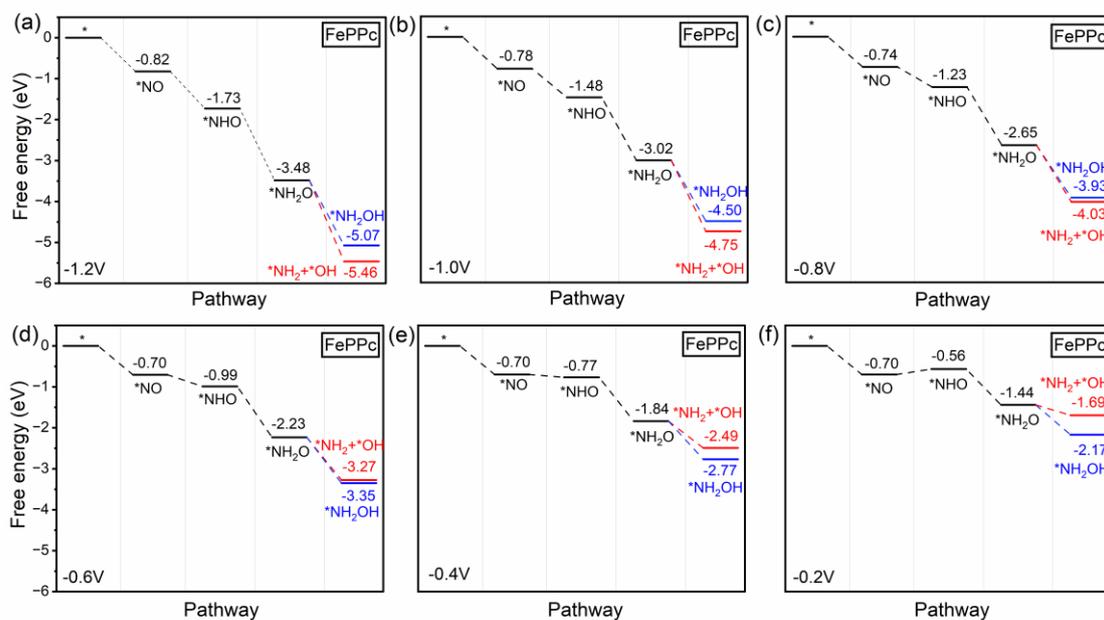
Figure S16. Free energy diagram of the NORR (a) -1.2V, (b) -1.0V, (c) -0.8V, (d) -0.6V, (e) -0.4V, (f)-0.2V.
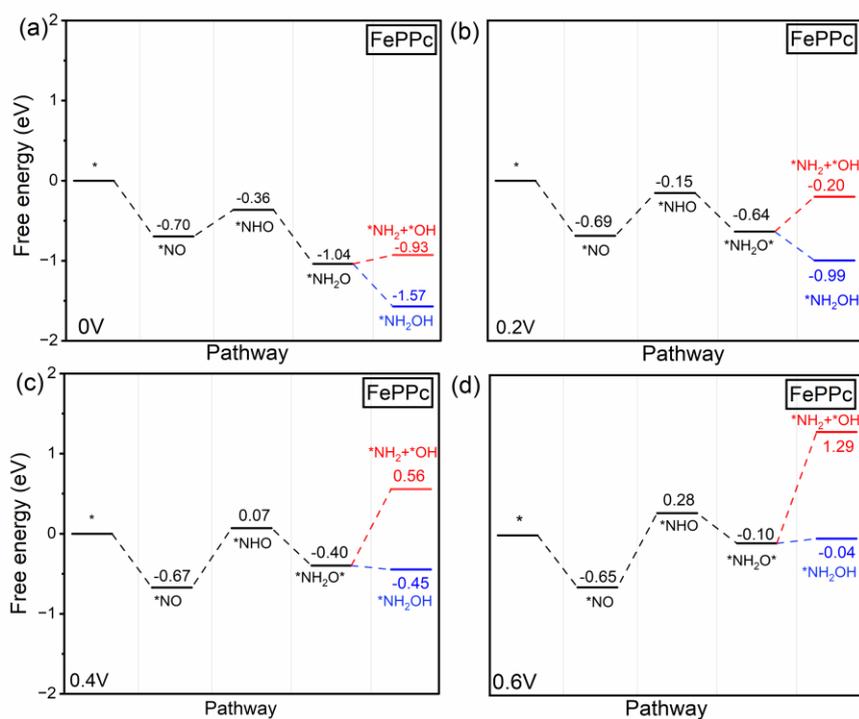
Figure S17. Free energy diagram of the NORR (a) 0V, (b) 0.2V, (c) 0.4V, (d) 0.6V.
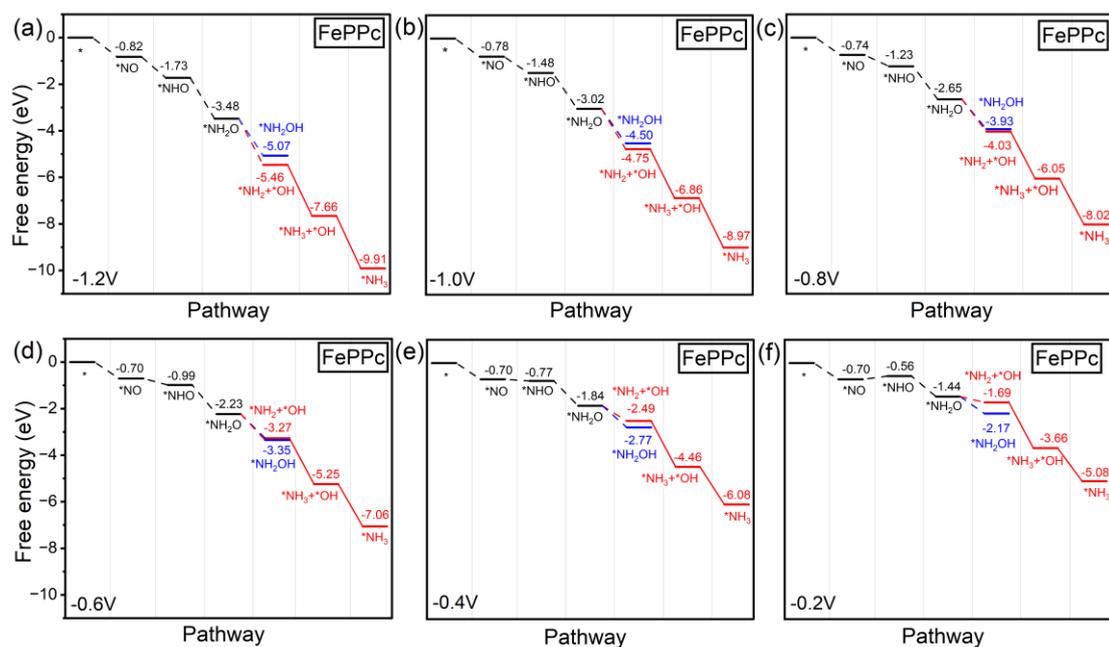
Figure S18. Free energy diagram of the NORR (a) -1.2V, (b) -1.0V, (c) -0.8V, (d) -0.6V, (e) -0.4V, (f)-0.2V.
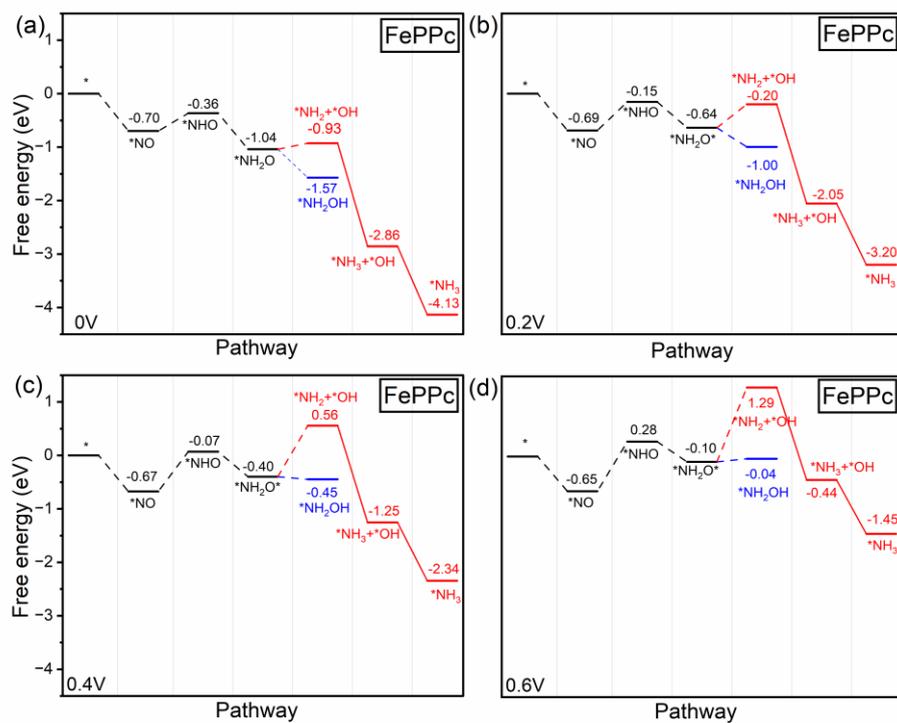
Figure S19. Free energy diagram of the NORR (a) 0V, (b) 0.2V, (c) 0.4V, (d) 0.6V.

Table S1. Free energy at different voltages of FePPc*NO and FePPc*NHO.

model U(V vs SHE)	*NO^{HS} E(eV)	*NO^{IS} E(eV)	*NHO^{HS} E(eV)	*NHO^{IS} E(eV)	*NHO^{LS} E(eV)
-1.2	-282.761509	-282.8184	-286.311482	-286.301046	-285.903634
-1	-282.595138	-282.625492	-286.114293	-286.101518	-285.769581
-0.8	-282.478908	-282.491694	-285.972912	-285.956537	-285.688453
-0.6	-282.409606	-282.416822	-285.888617	-285.861733	-285.670821
-0.4	-282.393701	-282.391357	-285.850916	-285.813892	-285.671665
-0.2	-282.393707	-282.389873	-285.849105	-285.803982	-285.671671
0	-282.393726	-282.389933	-285.849154	-285.803967	-285.689204
0.2	-282.396463	-282.391307	-285.85042	-285.806153	-285.713758
0.4	-282.438371	-282.425479	-285.884942	-285.859787	-285.782408
0.6	-282.527627	-282.508225	-285.970699	-285.987264	-285.881389

Table S2. Free energy at different voltages of FePPc*NH$_2$O.

| model U(V vs SHE)	*NH$_2$O^{HS} E(eV)	*NH$_2$O^{IS} E(eV)	*NH$_2$O^{LS} E(eV)
-1.2	-290.550348	-290.188325	-290.252278
-1	-290.337297	-289.979598	-290.081915
-0.8	-290.276369	-289.83068	-289.986622
-0.6	-290.218625	-289.741366	-289.946383
-0.4	-290.20724	-289.717123	-289.926635
-0.2	-290.207377	-289.717393	-289.925427
0	290.207413	-289.717549	-289.925396
0.2	-290.212555	-289.745487	-289.942994
0.4	-290.258478	-289.836713	-290.002937
0.6	-290.350521	-289.993185	-290.10052

Table S3. Free energy at different voltages of FePPc*NHOH.

model U(V vs SHE)	*NHOH^{HS} E(eV)	*NHOH^{IS} E(eV)	*NHOH^{LS} E(eV)
-1.2	-290.088639	-289.539631	-289.980669
-1	-289.939777	-289.421323	-289.848368
-0.8	-289.838764	-289.356997	-289.767421
-0.6	-289.784462	-289.338185	-289.734019
-0.4	-289.772695	-289.338165	-289.725812

U(V vs SHE)	E(eV)	E(eV)	E(eV)
-0.2	-289.772652	-289.338175	-289.725664
0	-289.772718	-289.338078	-289.726058
0.2	-289.781347	-289.357708	-289.748035
0.4	-289.834233	-289.425397	-289.818171
0.6	-289.934973	-289.526256	-290.113667

Table S4. Free energy at different voltages of FePPc*NH$_2$O*.

model	*NH$_2$O*^{HS}	*NH$_2$O*^{IS}	*NH$_2$O*^{LS}
U(V vs SHE)	E(eV)	E(eV)	E(eV)
-1.2	-289.710558	-290.433359	-290.258266
-1	-289.433694	-290.225231	-290.138031
-0.8	-289.190746	-290.07604	-290.071617
-0.6	-288.989081	-289.984234	-290.044181
-0.4	-288.789165	-289.935723	-290.036735
-0.2	-288.591259	-289.925692	-290.036914
0	-288.426179	-289.933264	-290.039135
0.2	-288.309078	-290.21729	-290.070764
0.4	-288.209428	-290.437249	-290.443378
0.6	-288.122433	-290.648549	-290.651921

Table S5. Free energy at different voltages of FePPc*NH$_2$OH.

model	*NH$_2$OH^{HS}	*NH$_2$OH^{IS}	*NH$_2$OH^{LS}
U(V vs SHE)	E(eV)	E(eV)	E(eV)
-1.2	-294.721241	-294.347189	-294.114206
-1	-294.603688	-294.243511	-294.045983
-0.8	-294.540813	-294.190288	-294.032044
-0.6	-294.520742	-294.179573	-294.032054
-0.4	-294.520525	-294.179523	-294.032259
-0.2	-294.520374	-294.179336	-294.032286
0	-294.524441	-294.180446	-294.048467
0.2	-294.561782	-294.212014	-294.113907
0.4	-294.668463	-294.290854	-294.212752
0.6	-294.974674	-294.412651	-294.316829

Table S6. Free energy at different voltages of FePPc*NH$_3$+*O and FePPc*NH$_3$+*OH.

model U(V vs SHE)	*NH$_3$+*O HS E(eV)	*NH$_3$+*O IS E(eV)	*NH$_3$+*OH E(eV)
-1.2	-294.816231	-294.362066	-299.763153
-1	-294.611837	-294.426738	-299.616559
-0.8	-294.487398	-294.34664	-299.519777
-0.6	-294.597551	-294.199146	-299.471894
-0.4	-294.486835	-294.088028	-299.466662
-0.2	-294.33529	-294.037943	-299.466519
0	-294.161684	-294.04433	-299.466463
0.2	-294.026177	-294.044709	-299.477017
0.4	-293.946994	-294.052834	-299.53298
0.6	-293.918476	-294.101506	-299.628892

Table S7. Free energy at different voltages of FePPc*NH$_3$.

model U(V vs SHE)	*NH$_3$ HS E(eV)	*NH$_3$ IS E(eV)	*NH$_3$ LS E(eV)
-1.2	-289.720067	-289.267398	-289.047395
-1	-289.633877	-289.186169	-289.011791
-0.8	-289.592362	-289.149491	-289.009158
-0.6	-289.588187	-289.146799	-289.009306
-0.4	-289.588482	-289.14686	-289.009063
-0.2	-289.589654	-289.146727	-289.009684
0	-289.645196	-289.154321	-289.037149
0.2	-289.723846	-289.201928	-289.112468
0.4	-289.924063	-289.301672	-289.212103
0.6	-290.138807	-289.455083	-289.317428