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Regulating Molecular Structure of Phthalocyanine-based Catalysts for High-Efficiency Nitrogen Reduction: A DFT Study

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Table S1. Summary of calculated results for all Phthalocyanine-based Catalysts: the shortest distance from Fe to the coordinating N atom (d_s in Å), binding energy and formation energy of catalysts(E_b in eV), and d-band center energy of Fe relative to the Fermi level (ε_d in eV).

Substrate	d_s	ΔE_{b*}	E_{fermi}	ε_d
FePc	1.943	10.15	-4.624	-0.361
FePc-FePc	1.938	11.48	-4.705	-0.382
FePc-CoPc	1.939	11.05	-4.700	-0.452
FePc-Pc	1.940	10.86	-4.876	-0.324

* The ΔE_b is calculated as follows: $\Delta E_b = E_S + E_{Fe} - E_{S\text{-}Fe}$, where the E_S, E_{Fe}, and $E_{S\text{-}Fe}$ are the total energies of substrate, isolated Fe atom, and , respectively. It notes that more positive ΔE_b indicates high stability of catalysts.

Table S2.. Formal charge, calculated Bader and net charges of Fe in catalysts. For assigning the formal oxidation state of Fe, Bader and net charges of Fe on catalysts are shown

	formal charges	Bader charge	net charge*
FePc	+2	6.542	0.458
FePc-FePc	+2	6.789	0.211
FePc-CoPc	+2	6.347	0.653
FePc-Pc	+2	7.167	-0.167

* The net charge is obtained by the number of valence electrons in free Fe (7 e) minus the Bader charge.

Table S3. Free energy corrections. Computed zero-point energies (ZPE) and entropies multiplied by T (T = 298.15 k) (-TS) for adsorbed species.

Species	E_{ZPE} (eV)	TS (eV)	E_{ZPE} -TS (eV)
Distal			
*N_2	0.200	0.187	0.013
*N_2H	0.548	0.162	0.386
*N_2H_2	0.968	0.229	0.739
*N	0.091	0.052	0.040
*NH	0.291	0.159	0.132
*NH_2	0.607	0.198	0.409
*NH_3	0.976	0.236	0.740
Alternating			
*N_2	0.200	0.187	0.013
*N_2H	0.548	0.162	0.386
*NH-NH	0.891	0.214	0.677
*NH-NH_2	1.110	0.218	0.892
*NH_2-NH_2	1.472	0.216	1.256
*NH_2	0.607	0.198	0.409
*NH_3	0.976	0.236	0.740

Table S4. Free energy changes (in eV) of all elementary steps for distal mechanism catalyzed on various considered substrates. Numbers in red indicate the maximum free energy barrier among all elementary steps.

substrate	*→ *N-N	*N-N→ *N-NH	*N-NH→ *N-NH_2	*N-NH_2→ *N-NH_3	*N-NH_3→ *NH	*NH→ *NH_2	*NH_2→ *NH_3	*NH_3→ *
FePc	-0.538	1.57	-0.370	0.712	-0.859	-1.084	-1.159	0.732
FePc-FePc	-0.570	1.468	-0.139	0.558	-0.800	-0.210	-0.700	-0.202
FePc-CoPc	-0.599	1.56	-0.348	-1.239	-0.936	-0.876	-0.098	1.53
FePc-Pc	-0.465	0.794	-0.475	0.522	-1.005	-0.305	-0.618	0.557

Table S5. Free energy changes (in eV) of all elementary steps for the alternating mechanism catalyzed on various considered substrates. Numbers in red indicate the maximum free energy barrier among all elementary steps.

substrate	*→ *N-N	*N-N→ *N-NH	*N-NH→ *NH-NH	*NH-NH→ *NH-NH_2	*NH-NH_2→ *NH_2-NH_2	*NH_2-NH_2→ *NH_2	*NH_2→ *NH_3	*NH_3→ *
FePc	-0.538	1.571	-0.343	0.183	-0.540	-0.9007	-1.1587	0.7319
FePc-FePc	-0.570	1.468	0.357	-0.627	-0.473	-0.158	-0.7000	-0.202
FePc-CoPc	-0.0.599	1.56	-0.351	0.042	-0.052	-3.087	-0.098	1.53
FePc-Pc	-0.465	0.794	-0.423	0.130	-0.437	-0.533	-0.618	0.557

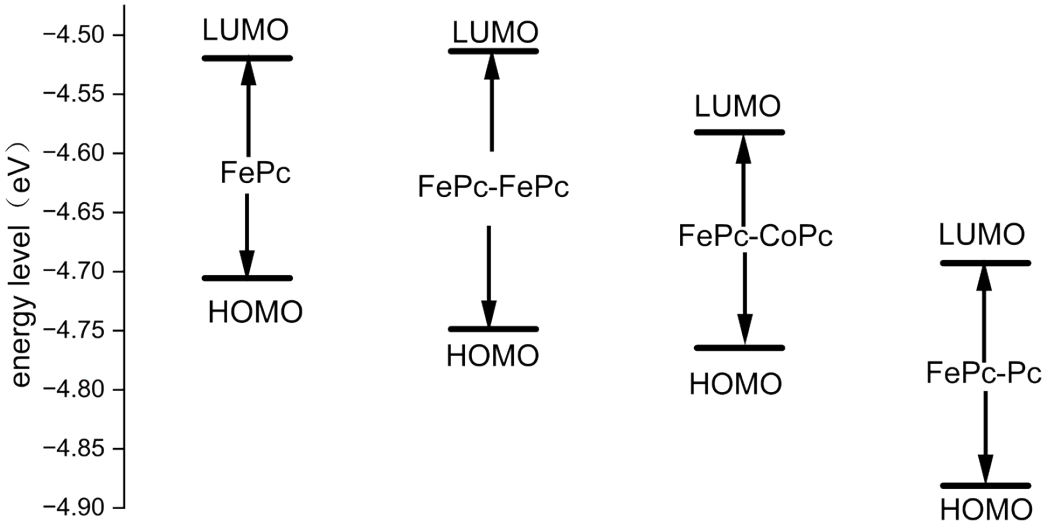

Figure S1. The calculated energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and HOMO–LUMO gaps for the studied catalyst.

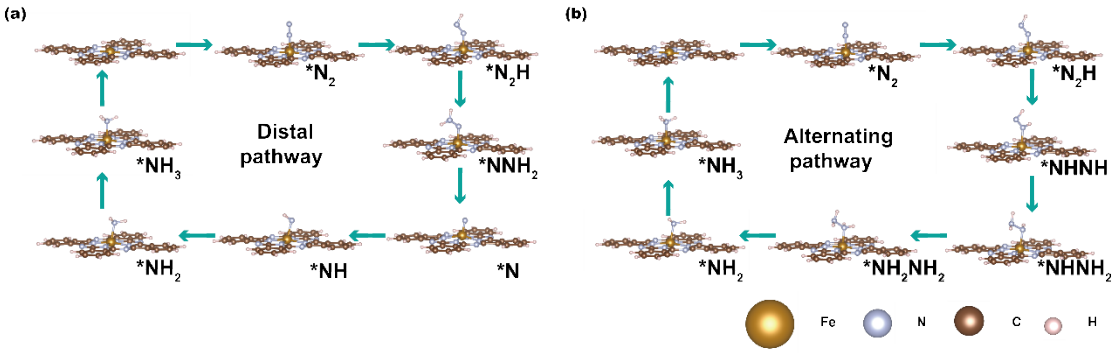

Figure S2. Configurations along the different reaction mechanisms of NRR on FePc.

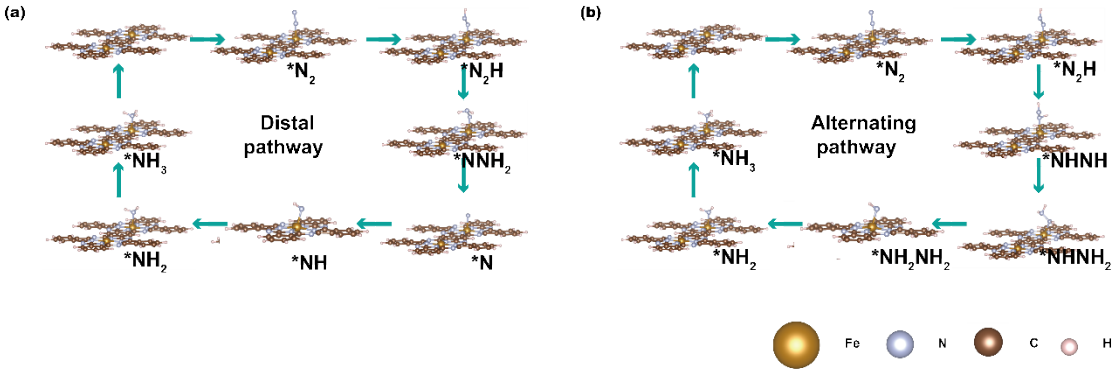

Figure S3. Configurations along the different reaction mechanisms of NRR on FePc-FePc.

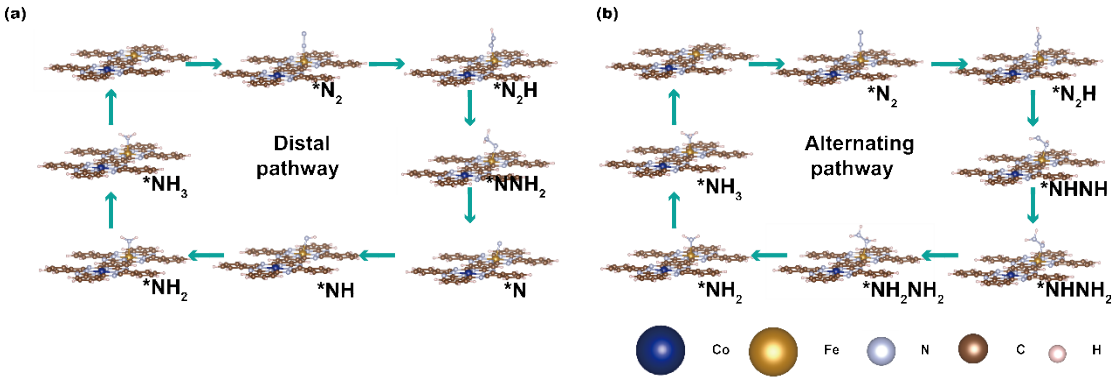

Figure S4. Configurations along the different reaction mechanisms of NRR on FePc CoPc.

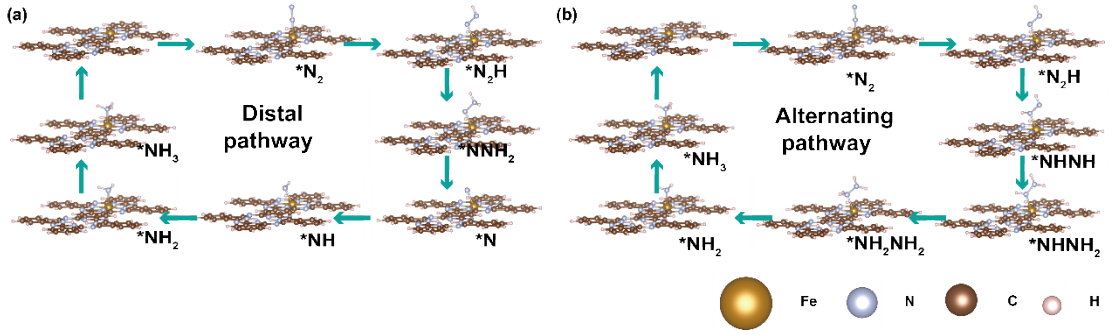

Figure S5. Configurations along the different reaction mechanisms of NRR on FePc - Pc.

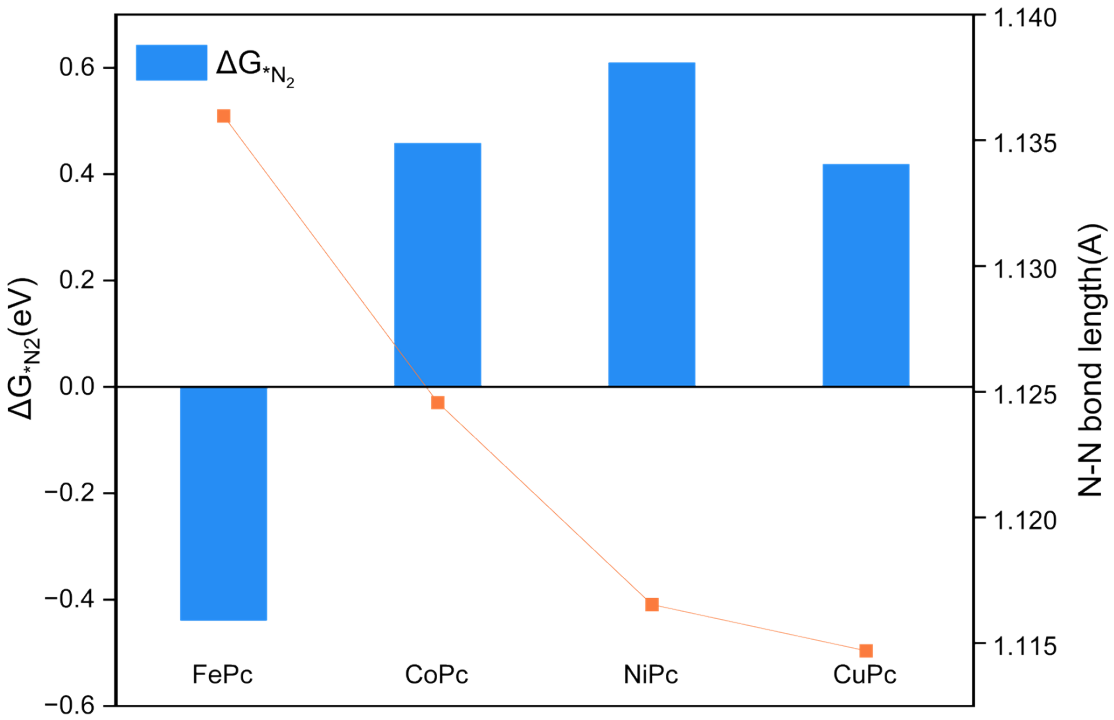

Figure S6. The Gibbs adsorption energy of N_2 on common metal phthalocyanine molecular catalysts and the bond length of N_2 molecules adsorbed on metal phthalocyanine.