Supporting information for

Graphene-based iron single-atom catalyst for electrocatalytic nitric oxide reduction: a first-principles study

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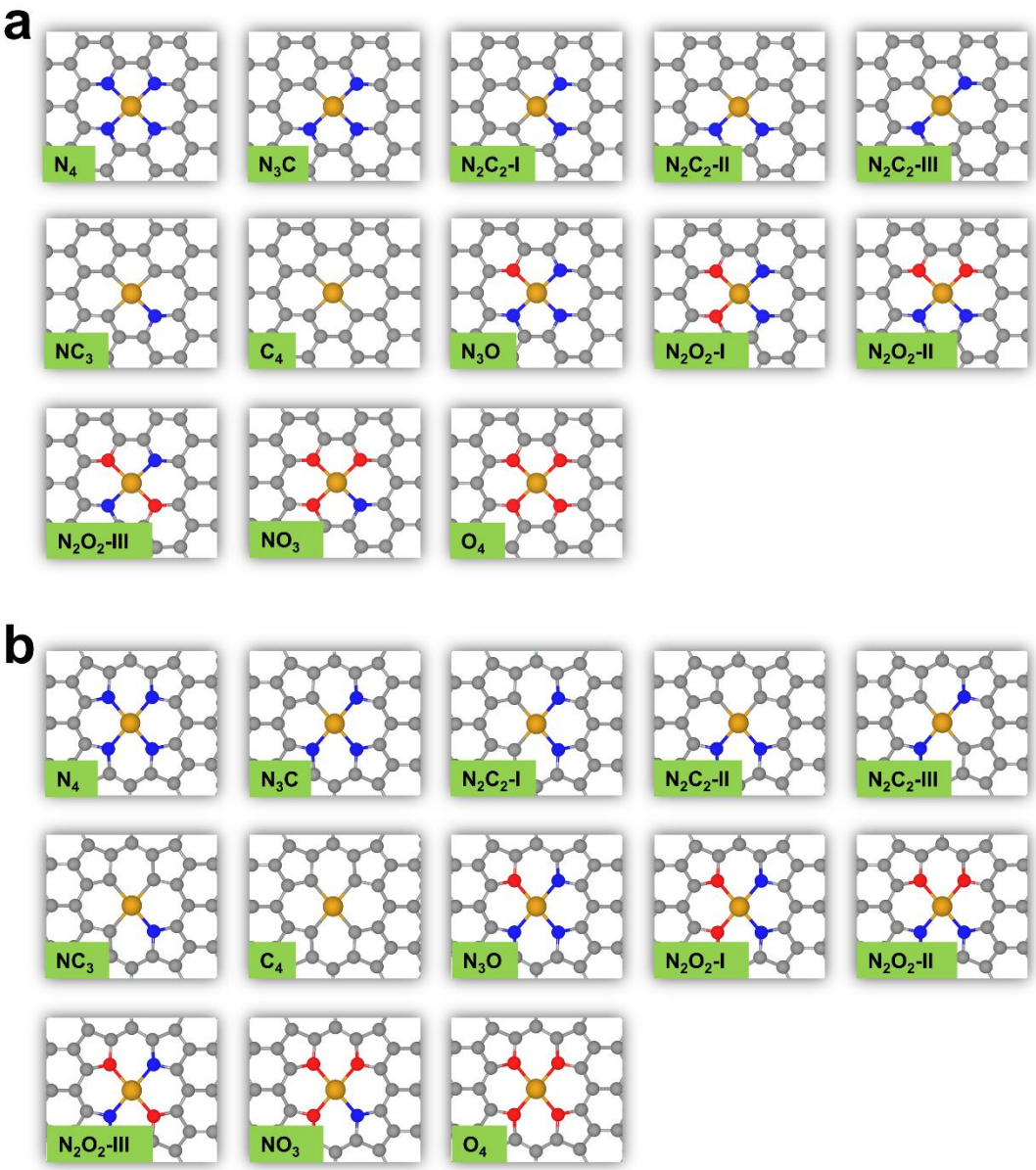


Fig. S1. Optimized atomic structures of the PD-Fe-SACs (a) and PR-Fe-SACs (b).

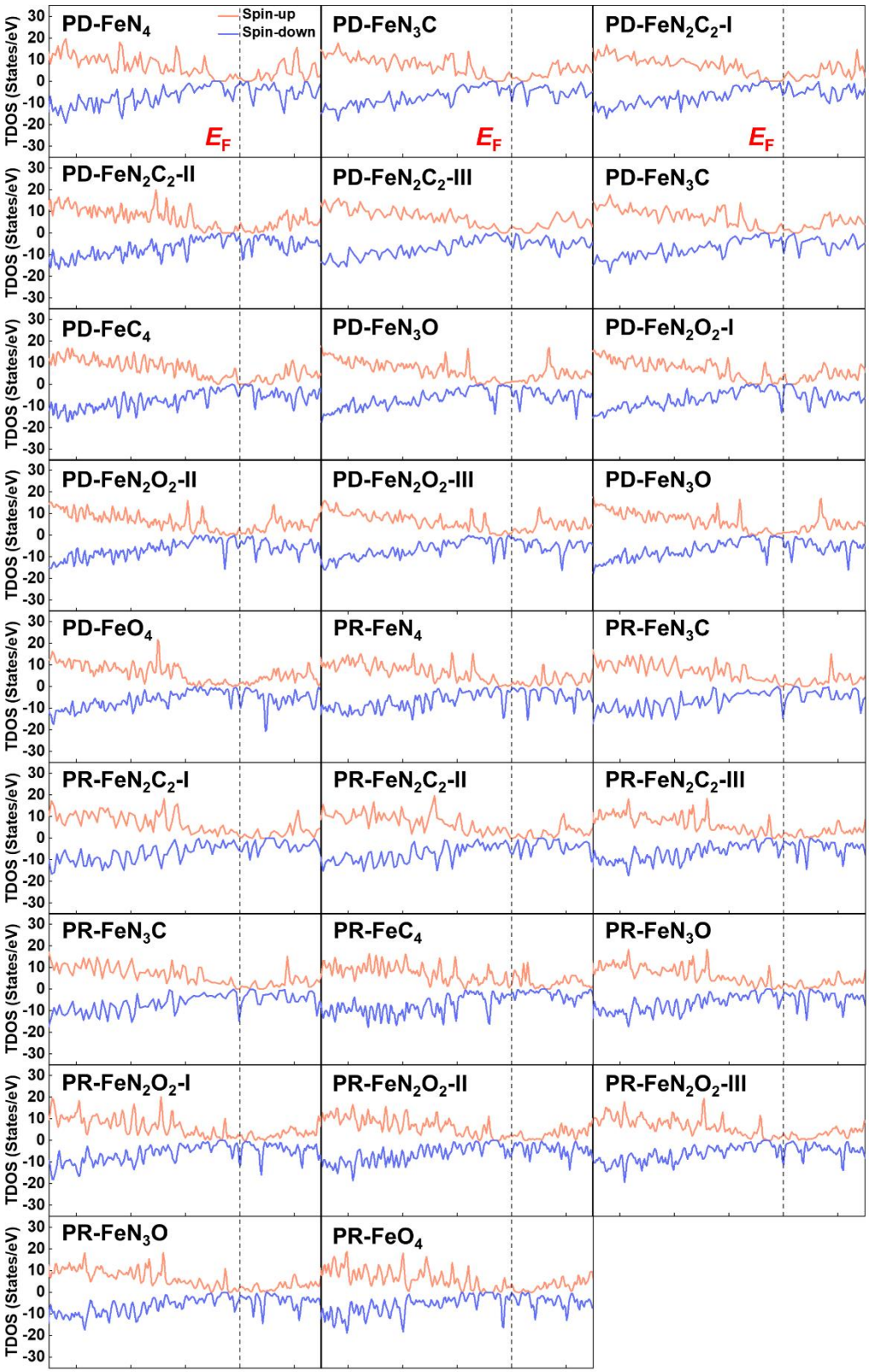


Fig. S2. Calculated total density of states (TDOS) of the PD-Fe-SACs and PR-Fe-SACs. The Fermi level (E_F) is set to 0 eV.

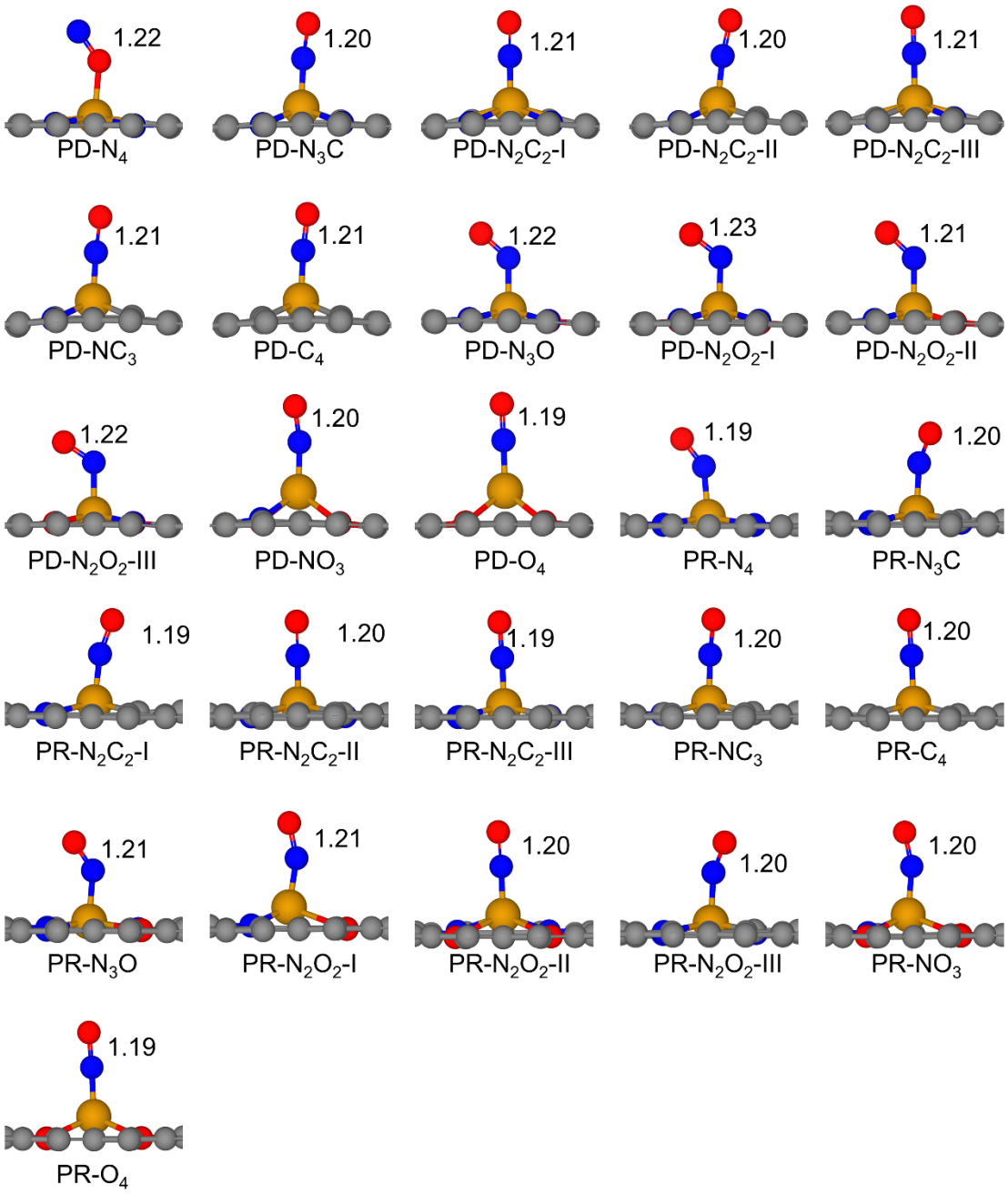
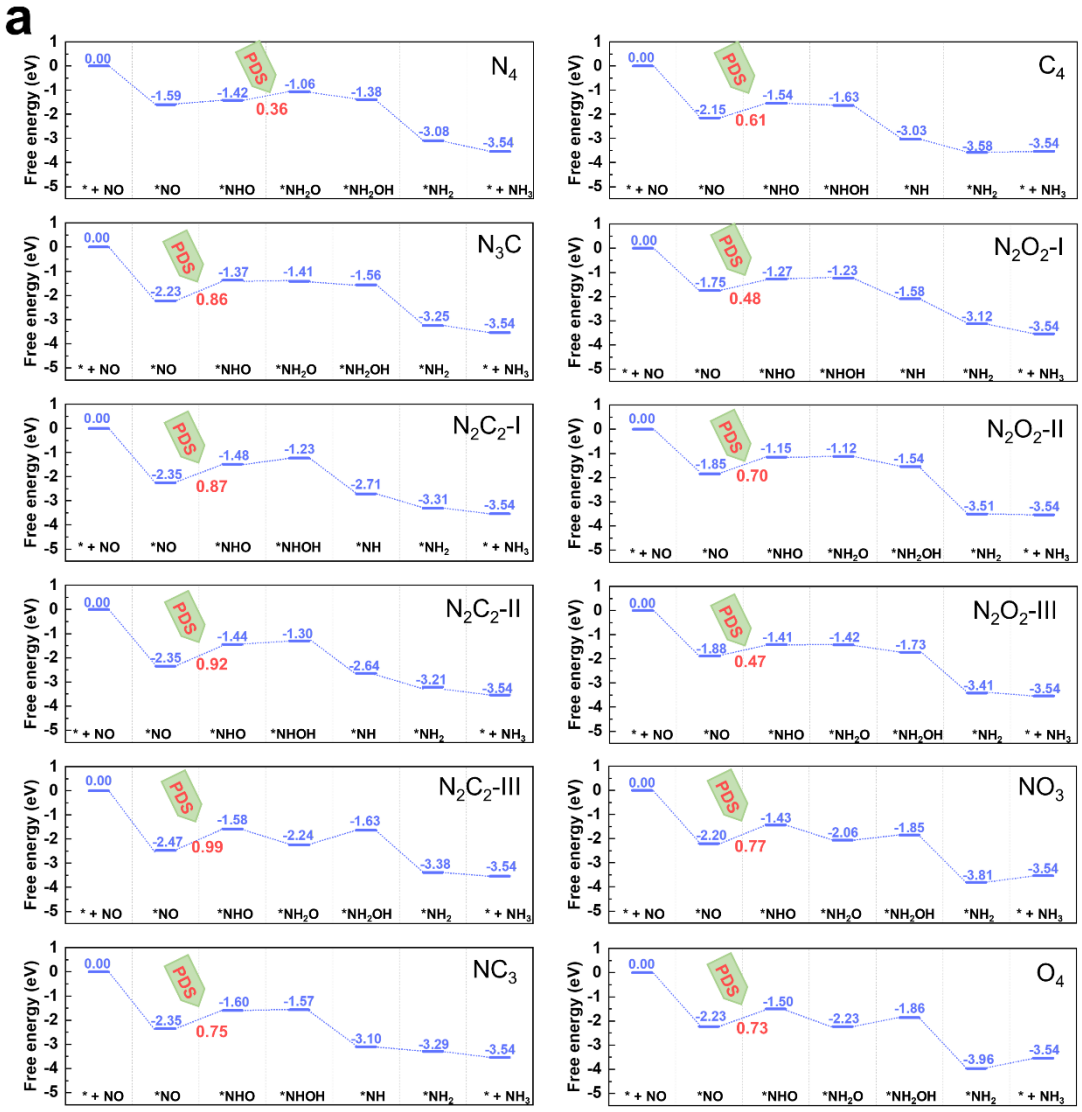


Fig. S3. The most stable configurations and corresponding bond length (in Å) of NO adsorption on the PD-Fe-SACs and PR-Fe-SACs.


a
N4
0.00
-1.59
-1.42
-1.06
-1.38
-3.08
-3.54
PDS
0.36
C4
0.00
-2.15
-1.54
-1.63
-3.03
-3.58
-3.54
PDS
0.61
N3C
0.00
-2.23
-1.37
-1.41
-1.56
-3.25
-3.54
PDS
0.86
N2O2-I
0.00
-1.75
-1.27
-1.23
-1.58
-3.12
-3.54
PDS
0.48
N2C2-I
0.00
-2.35
-1.48
-1.23
-2.71
-3.31
-3.54
PDS
0.87
N2O2-II
0.00
-1.85
-1.15
-1.12
-1.54
-3.51
-3.54
PDS
0.70
N2C2-II
0.00
-2.35
-1.44
-1.30
-2.64
-3.21
-3.54
PDS
0.92
N2O2-III
0.00
-1.88
-1.41
-1.42
-1.73
-3.41
-3.54
PDS
0.47
N2C2-III
0.00
-2.47
-1.58
-2.24
-1.63
-3.38
-3.54
PDS
0.99
NO3
0.00
-2.20
-1.43
-2.06
-1.85
-3.81
-3.54
PDS
0.77
NC3
0.00
-2.35
-1.60
-1.57
-3.10
-3.29
-3.54
PDS
0.75
O4
0.00
-2.23
-1.50
-2.23
-1.86
-3.96
-3.54
PDS
0.73
Free energy (eV)
1 0 -1 -2 -3 -4 -5
* + NO
*NO
*NHO
*NHOH
*NH
*NH2
*NH2OH
*NH2O
* + NH3

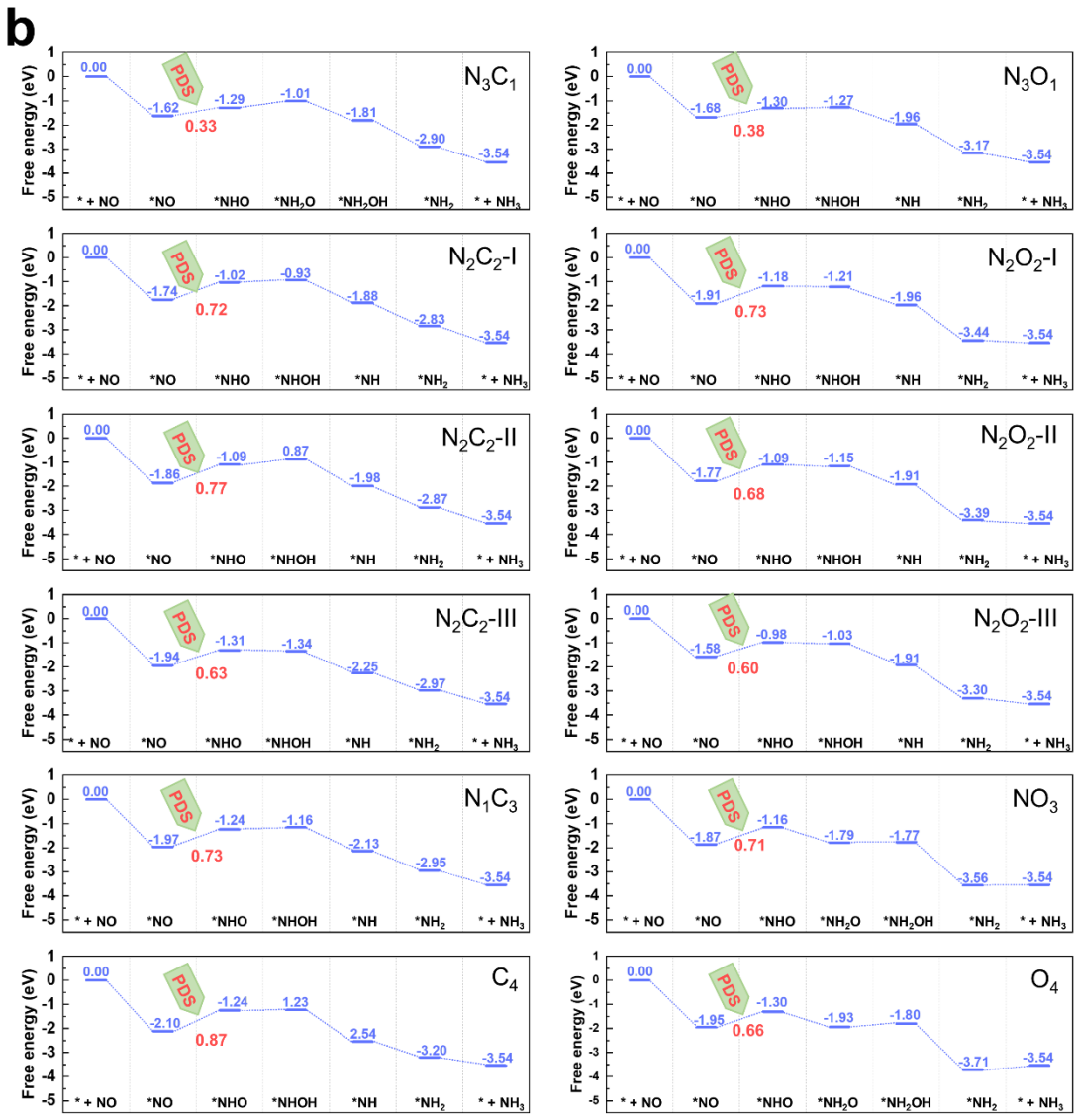


Fig. S4. NORR free energy diagram through the most favorable pathway for PD-Fe-SACs (a) and PR-Fe-SACs (b).

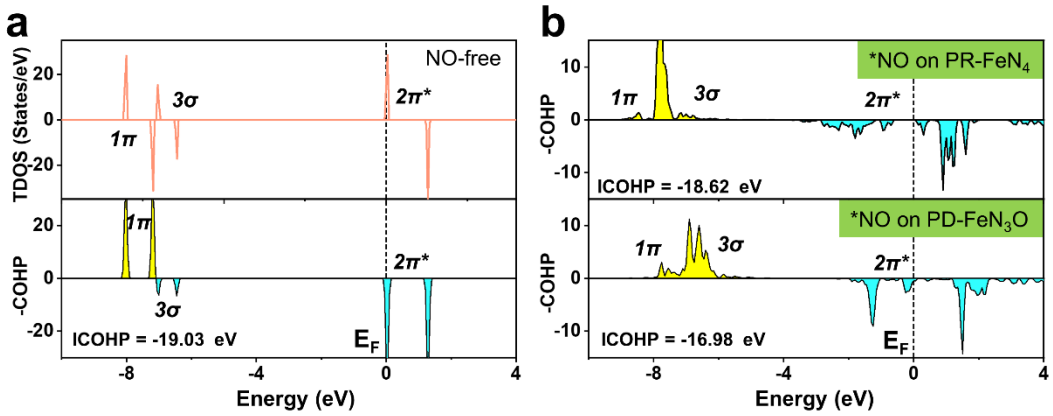


Fig. S5. (a) TDOS and corresponding COHP of free NO molecule. (b) COHP of *NO on PR-FeN_4 (up) and PD-FeN_3O (down) SACs. The Fermi level (E_F) is set to 0 eV.

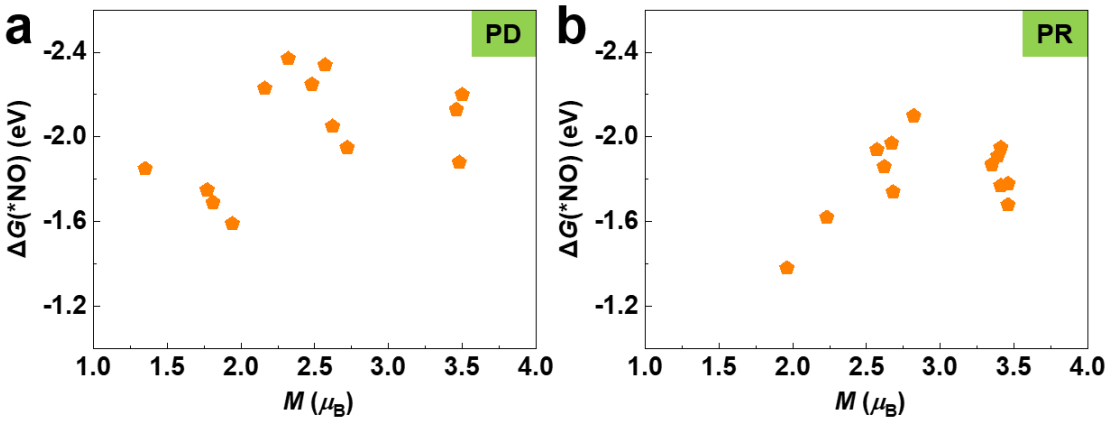


Fig. S6. The correlation between NO adsorption free energy (Δ*G*(*NO)) and magnetic moment (*M*) of the Fe active center for the PD-Fe-SACs (a) and PR-Fe-SACs (b).

Table S1. Calculated zero-point energy (E_{ZPE}, in eV) and the product of temperature (T = 298.15 K) and entropy (S) (TS, in eV) of various species involved in the reaction pathways for NORR, where * represents the adsorption site.

Species	E_{ZPE}	TS
*NO	0.19	0.09
*NHO	0.49	0.15
*NOH	0.48	0.14
*NH_2O	0.81	0.19
*NHOH	0.79	0.17
*NH_2OH	1.12	0.22
*NH	0.34	0.07
*NH_2	0.67	0.11
*NH_3	1.04	0.14
*N_2O_2	0.38	0.24
*N_2O_2H	0.68	0.27
*N_2O	0.31	0.21
*NO	0.19	0.09
*NHO	0.49	0.15
*NOH	0.48	0.14
*NH_2O	0.81	0.19
N_2O	0.29	0.68
NH_3	0.89	0.60
N_2	0.15	0.59
H_2	0.27	0.40
H_2O	0.56	0.67

Table S2. Key parameters of the studied Fe-SACs, including spin magnetic moment (M, in μ_B), net charge (Q, in e), the positive value means the electrons are transferred from the Fe atom to supports, and the d-band center (ε_d, in eV) of the Fe atom.

Systems	M	Q	ε_d
PD-N_4	1.94	1.40	-1.39
PD-N_3C	2.16	1.38	-1.08
PD-N_2C_2-I	2.48	1.32	-1.06
PD-N_2C_2-II	2.57	1.37	-0.95
PD-N_2C_2-III	2.32	1.35	-0.90
PD-NC_3	2.62	1.31	-1.24
PD-C_4	2.72	1.29	-1.29
PD-N_3O	1.81	1.42	-1.32
PD-N_2O_2-I	1.77	1.53	-1.30
PD-N_2O_2-II	1.35	1.33	-1.12
PD-N_2O_2-III	3.48	1.18	-1.28
PD-NO_3	3.50	1.17	-1.19
PD-O_4	3.46	1.38	-1.14
PR-N_4	1.96	1.34	-1.46
PR-N_3C	2.23	1.25	-1.36
PR-N_2C_2-I	2.68	1.19	-1.21
PR-N_2C_2-II	2.62	1.45	-1.13
PR-N_2C_2-III	2.57	1.38	-1.26
PR-NC_3	2.67	1.35	-1.13
PR-C_4	2.82	1.44	-1.06
PR-N_3O	3.46	1.42	-1.36
PR-N_2O_2-I	3.39	1.35	-1.16
PR-N_2O_2-III	3.41	1.40	-1.20
PR-N_2O_2-III	3.46	1.35	-1.24
PR-NO_3	3.35	1.39	-1.11
PR-O_4	3.41	1.44	-1.28

Table S3. N-O bond length of *NO (d_{N-O}, in Å) and the number of electrons transferred from the SACs to *NO on the studied Fe-SACs (ΔQ(*NO), in *e*).

Systems	d_{N-O}	ΔQ(*NO)
PD-N_4	1.22	0.53
PD-N_3C	1.20	0.62
PD-N_2C_2-I	1.21	0.64
PD-N_2C_2-II	1.20	0.63
PD-N_2C_2-III	1.21	0.65
PD-NC_3	1.21	0.61
PD-C_4	1.21	0.56
PD-N_3O	1.22	0.54
PD-N_2O_2-I	1.23	0.56
PD-N_2O_2-II	1.21	0.57
PD-N_2O_2-III	1.22	0.57
PD-NO_3	1.20	0.64
PD-O_4	1.19	0.63
PR-N_4	1.19	0.29
PR-N_3C	1.20	0.37
PR-N_2C_2-I	1.19	0.35
PR-N_2C_2-II	1.20	0.41
PR-N_2C_2-III	1.19	0.54
PR-NC_3	1.20	0.53
PR-C_4	1.20	0.57
PR-N_3O	1.21	0.36
PR-N_2O_2-I	1.21	0.53
PR-N_2O_2-III	1.20	0.39
PR-N_2O_2-III	1.20	0.36
PR-NO_3	1.20	0.45
PR-O_4	1.19	0.46