Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Adsorption mechanism of the N_2 and NRR intermediates on oxygen modified MnN_4 – graphene layers - a single atom catalysis perspective

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Table S1. The average distances (d_{AV})between O/N and neighboring C atoms within each layer.

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	d_{AV} (Å)
MnN_4	N-C= 1.38
MnN_3O	N-C=1.39 O-C=1.43
MnN_2O_2 (hex)	N-C=1.38 O-C=1.43
MnN_2O_2 (pent)	N-C=1.39 O-C=1.43
MnN_2O_2 (opp)	N-C=1.39 O-C=1.43
$MnNO_3$	N-C=1.38 O-C=1.42

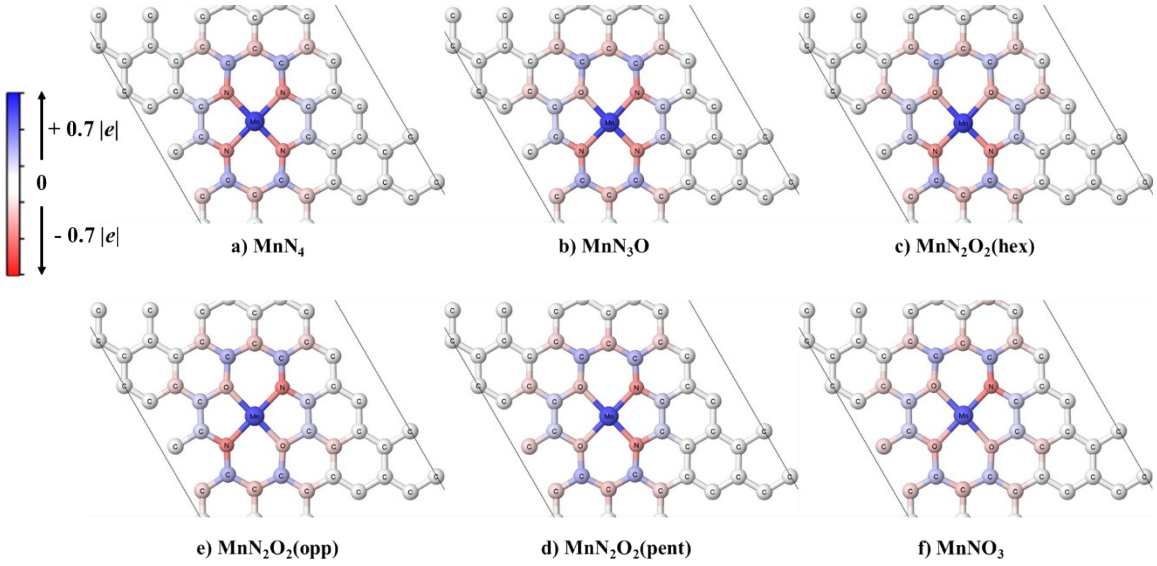

Figure S1. The excess electronic charges on each atom of the MnNxOy/G layers. The neutral charges are shown through white color, while the blue and red colors indicate the presence of a positive or negative charge on the atoms, respectively. The maximum positive and negative charges are changed between the range of +0.7 |*e*| and -0.7 |*e*| as seen in color bar.

Table S2. The Coulomb Forces (F) between Mn-O and Mn-N atoms in porphyrin units for bare layers using average values of atomic distances and atomic charges based on Bader and DDEC6 atomic charges. The "av" subscript shows the averaging of the relevant quantity.

	d (Å)	Average Bader Atomic Charges (|*e*|)	Average DDEC6 Atomic Charges(|*e*|)	Absolute Coulomb Forces based on Bader charges (nN)	Absolute Coulomb Forces based on DDEC6 charges (nN)
MnN_4	$(Mn\text{-}N)_{av}$=1.91	Mn=+1.38 N_{av}= -1.19	Mn=0.67 N=-0.32	$\|F_{Mn\text{-}N}\|$=10.36(10.32)	$\|F_{Mn\text{-}N}\|$=1.35(0.85)
MnN_3O	$(Mn\text{-}N)_{av}$=1.91 Mn-O=1.91	Mn= +1.34 N_{av}= -1.23 O = -1.11	Mn=0.65 N=-0.34 O=-0.15	$\|F_{Mn\text{-}N}\|$= 10.39 $\|F_{Mn\text{-}O}\|$= 9.38	$\|F_{Mn\text{-}N}\|$= 1.39 $\|F_{Mn\text{-}O}\|$= 0.61
MnN_2O_2 (hex)	$(Mn\text{-}N)_{av}$=1.86 $(Mn\text{-}O)_{av}$=1.98	Mn= +1.18 N_{av}= -1.18 O_{av}= -1.12	Mn=0.62 N=-0.34 O=-0.17	$\|F_{Mn\text{-}N}\|$= 9.26 $\|F_{Mn\text{-}O}\|$= 7.76	$\|F_{Mn\text{-}N}\|$= 1.40 $\|F_{Mn\text{-}O}\|$= 0.62
MnN_2O_2 (pent)	$(Mn\text{-}N)_{av}$=1.89 $Mn\text{-}O_{av}$=1.95	Mn= +1.20 N_{av}= -1.20 O_{av}= -1.10	Mn=0.57 N=-0.35 O=-0.15	$\|F_{Mn\text{-}N}\|$= 9.27(8.35) $\|F_{Mn\text{-}O}\|$= 7.99(6.22)	$\|F_{Mn\text{-}N}\|$= 1.28(0.79) $\|F_{Mn\text{-}O}\|$= 0.52(0.42)
MnN_2O_2 (opp)	$(Mn\text{-}N)_{av}$=1.90 $(Mn\text{-}O)_{av}$=1.93	Mn= +1.22 N_{av}= -1.23 O_{av}= -1.09	Mn=0.60 N=-0.38 O=-0.15	$\|F_{Mn\text{-}N}\|$= 9.56(7.97) $\|F_{Mn\text{-}O}\|$= 8.21(6.72)	$\|F_{Mn\text{-}N}\|$= 1.45(0.89) $\|F_{Mn\text{-}O}\|$= 0.56(0.44)
$MnNO_3$	$(Mn\text{-}O)_{av}$=2.00 Mn-N=1.90	Mn= +1.31 N= -1.28 O_{av}= -1.15	Mn=0.53 N=-0.36 O=-0.16	$F_{Mn\text{-}N}$= 10.69(8.21) $F_{Mn\text{-}O}$= 8.66(5.92)	$\|F_{Mn\text{-}N}\|$= 1.22(0.89) $\|F_{Mn\text{-}O}\|$= 0.49(0.44)

Table S3. The average DDEC6 charges and bond orders of the atoms and the selected bond on the layers, respectively.

Layers	Average DDEC6 Atomic Charges(|*e*|)	Average Atomic DDEC6 Bond Orders[1]	Average DDEC6 Bond Orders of the Selected Bonds
MnN_4	Mn=0.67 N=-0.32 C= 0.01	Mn=3.13 N=3.56 C=4.00	Mn-N=0.69 N-C=1.27
MnN_3O	Mn=0.65 N=-0.34 O=-0.15 C=0.01	Mn=3.02 N=3.60 O=2.74 C=4.00	Mn-N=0.72 Mn-O=0.49 N-C=1.27 O-C=1.00
MnN_2O_2 (hex)	Mn=0.62 N=-0.34 O=-0.17 C=-0.01	Mn=2.91 N=3.65 O=2.75 C=4.00	Mn-N=0.76 Mn-O=0.49 N-C=1.28 O-C=1.00
MnN_2O_2 (pent)	Mn=0.57 N=-0.35 O=-0.15 C=0.01	Mn=2.93 N=3.62 O=2.80 C=4.00	Mn-N=0.74 Mn-O=0.53 N-C=1.28 O-C=1.01
MnN_2O_2 (opp)	Mn=0.60 N=-0.38 O=-0.15 C=0.01	Mn=2.93 N=3.64 O=2.79 C=4.00	Mn-N=0.73 Mn-O=0.54 N-C=1.29 O-C=0.99
$MnNO_3$	Mn=0.53 N=-0.36 O=-0.16 C=-0.01	Mn=2.65 N=3.68 O=2.80 C=4.01	Mn-N=0.75 Mn-O=0.49 N-C=1.31 O-C=1.03

[1] Occasionally the DDEC6 average total bond orders may go beyond their chemically expected values. E.g. values of bond orders for the N atoms of 3.5, above the chemically expected value of 3.0. This is due to the large number of (small) interactions considered, as well as to potential integration limitations (density of FFT grid). As all these settings are common for all the bonds considered, the comparison between average total bond orders can be performed

1. Limas, N.G. and T.A. Manz, *Introducing DDEC6 atomic population analysis: part 4. Efficient parallel computation of net atomic charges, atomic spin moments, bond orders, and more.* RSC advances, 2018. **8**(5): p. 2678-2707, 2. Rohling, R.Y., et al., *Correlations between density-based bond orders and orbital-based bond energies for chemical bonding analysis.* The Journal of Physical Chemistry C, 2019. **123**(5): p. 2843-2854..

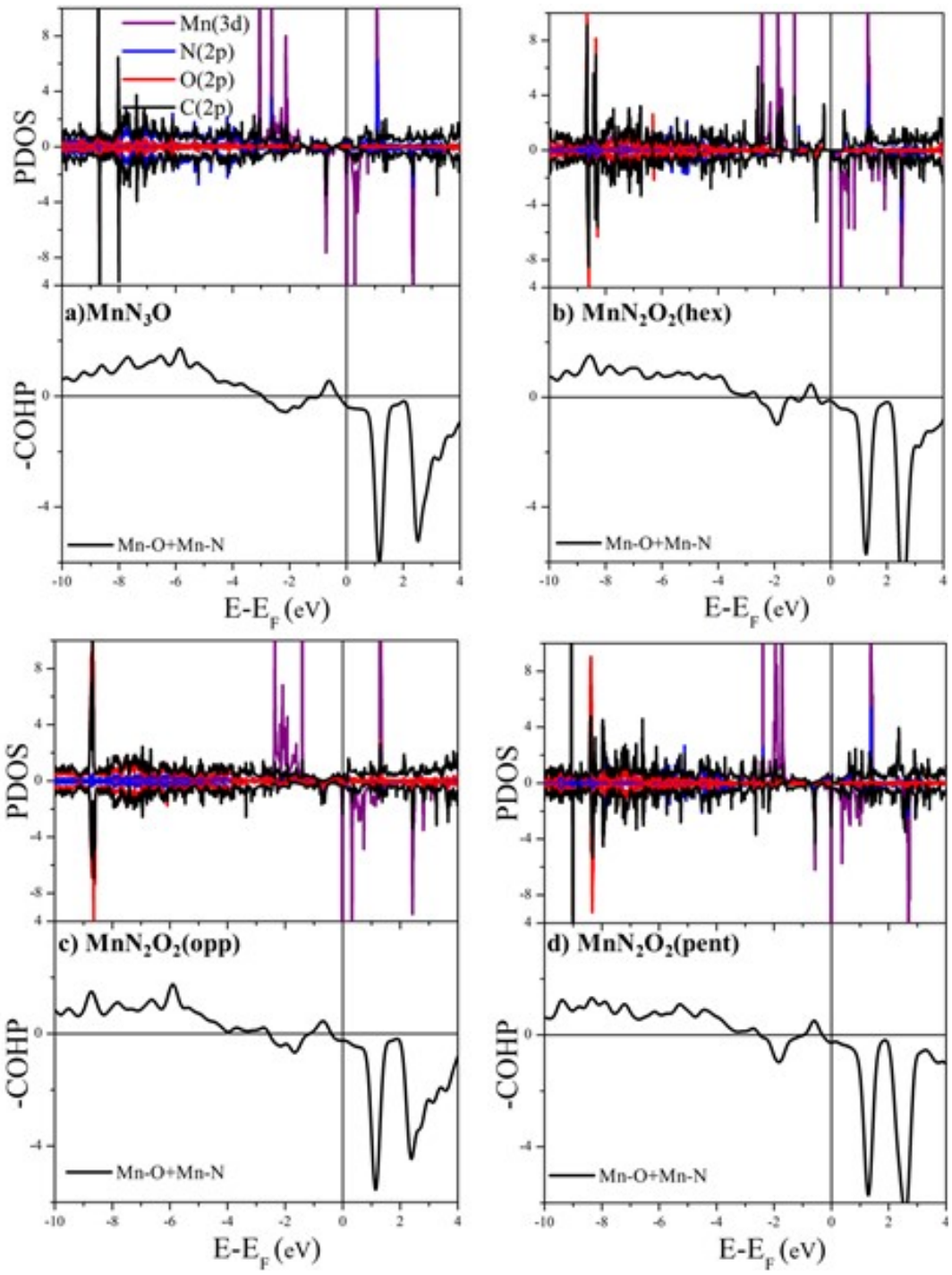

Figure-S2. Partial density of states (PDOS) and Crystal Orbital Hamiltonian Populations (COHP) plots for a) MnN_3O, b) MnN_2O_2(hex), c) MnN_2O_2(opp) and c)

MnN_2O_2(pent). The purple, blue, red and black lines in the PDOS represent the manganese 3d, nitrogen 2p, oxygen 2p and carbon 2p orbitals, respectively. In the COHP plot the black line corresponds to the sum of the Mn-N and Mn-O interactions from the porphyrin units.

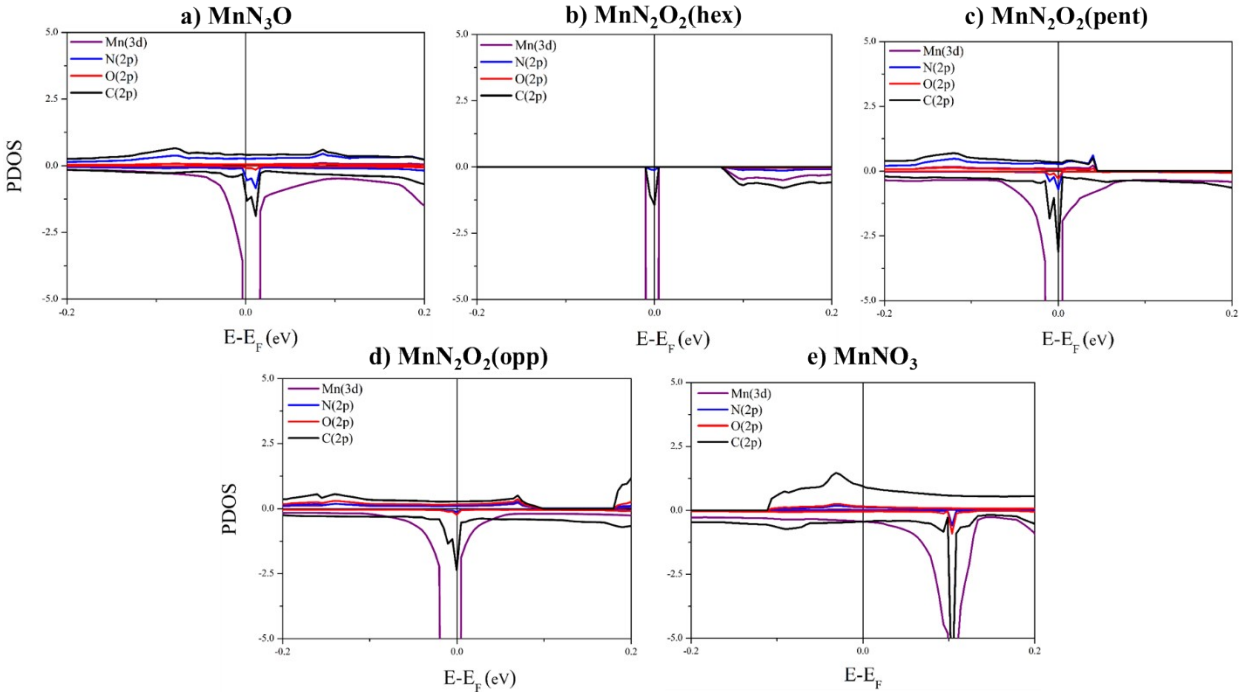

Figure S3. The PDOS for a) MnN_3O, b) MnN_2O_2(hex), c) MnN_2O_2(pent), d) MnN_2O_2(opp) and f) $MnNO_3$ layers within the range of -0.2- 0.2 eV.

Table S4. The distances between Mn-N, Mn-C, neighboring N-C and O-C atoms on N_2 adsorbed systems on all MnN_xO_y/G layers. The "av" subscript corresponds to the average distances between the mentioned atoms.

	d (Å)	
N_2 adsorbed systems	**Side-on**	**End-on**
MnN_4	Mn-N1=1.92 Mn-N2=1.92 Mn-N3=1.92 Mn-N4=1.92 (N-C)av=1.38	Mn-N1=1.93 Mn-N2=1.93 Mn-N3=1.93 Mn-N4=1.93 (N-C)av=1.39
MnN_3O		Mn-N1=1.91 Mn-N2=1.89 Mn-N3=1.95 Mn-O1=2.01 (N-C)av=1.38 (O-C)av=1.41
MnN_2O_2 (hex)		Mn-N1=1.89 Mn-N2=1.90 Mn-O1=2.09 Mn-O2=2.20 (N-C)av=1.39 (O-C)av=1.42
MnN_2O_2 (pent)	Mn-N1=2.09 Mn-N2=2.09 Mn-O1=2.30 Mn-O2=2.30 (N-C)av=1.37 (O-C)av=1.41	Mn-N1=1.91 Mn-N2=1.91 Mn-O1=1.99 Mn-O2=1.99 (N-C)av=1.38 (O-C)av=1.42
$MnNO_3$	Mn-N1=2.04 Mn-O1=2.29 Mn-O2=2.40 Mn-O3=2.26 (N-C)av=1.38 (O-C)av=1.41	Mn-N1=2.02 Mn-O1=2.24 Mn-O2=2.40 Mn-O3=2.30 (N-C)av=1.38 (O-C)av=1.41
MnN_2O_2 (opp)	Mn-N1=2.12 Mn-N2=2.12 Mn-O1=2.22 Mn-O2=2.22 (N-C)av=1.37 (O-C)av=1.40	Mn-N1=1.92 Mn-N2=1.93 Mn-O1=1.99 Mn-O2=2.00 (N-C)av=1.39 (O-C)av=1.42

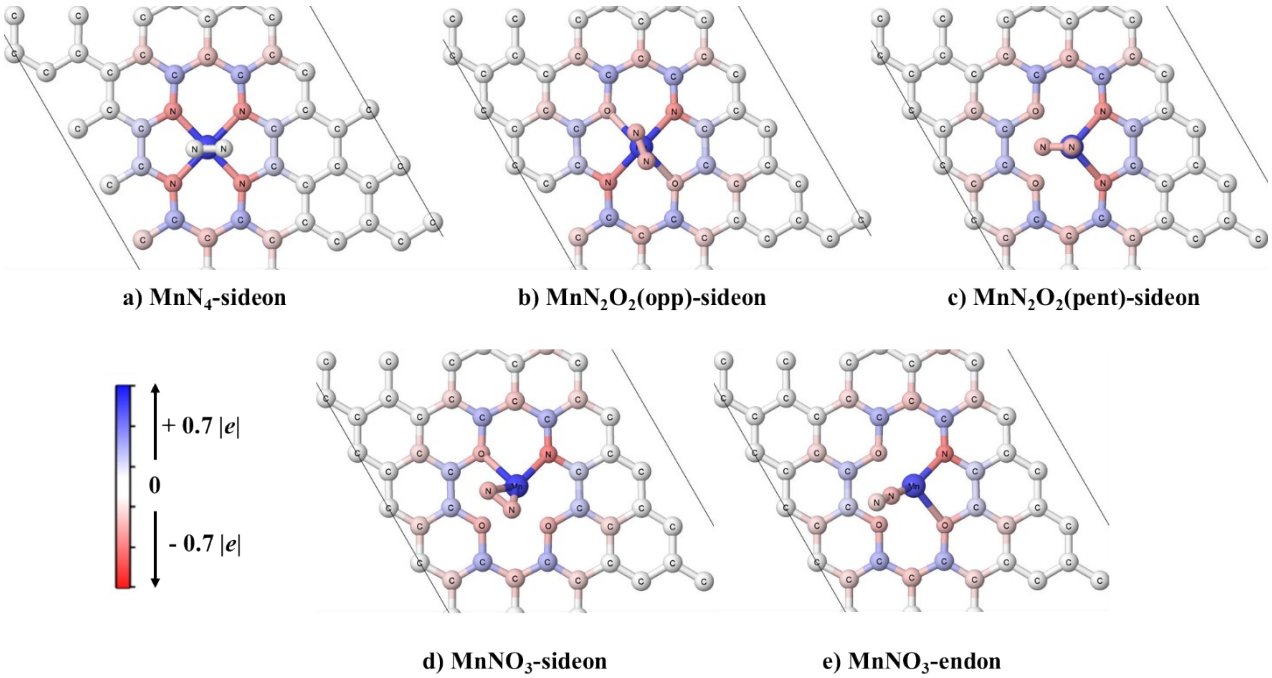

Figure S4. The excess electronic charges on each atom of the MnN_xO_y/G layers. The neutral atom are shown through white color, while blue and red colors indicate the positively and negatively charged atoms, respectively. The maximum positive and negative charges are changed between the range of +0.7 |*e*| and -0.7 |*e*| as seen in color bar.

Table S5. The average DDEC6 charges and bond orders of the atoms and selected bonds of the considered layers-

N_2 adsorbed systems	**Average and total DDEC6 atomic charges**	**Average and total DDEC bond orders for selected bonds**
N_2 on MnN_4 sideon	$N(mol)_{tot}$ =0.01 Mn=0.65 $N(porp)_{avr}$=-0.21 C_{av}=0.01	$(N1\text{-}N2)_{mol}$=2.75 Mn-N1=0.0 Mn-N2=0.0 $(Mn\text{-}N_{porp})_{av}$=0.68 $(N_{porp}\text{-}C)_{av}$=1.26
N_2 on MnN_2O_2 (pent)-sideon	$N(mol)_{tot}$ =-0.35 Mn=0.6 $N(porp)_{avr}$ =-0.25 $O(porp)_{avr}$ =-0.16 C_{Av}=0.02	$(N1\text{-}N2)_{mol}$ =2.34 Mn-N1=0.52 Mn-N2=0.53 $(Mn\text{-}N_{porp})_{av}$ =0.49 $(Mn\text{-}O_{porp})_{av}$ =0.25 N_{porp}-C=1.33 O_{porp}-C=1.06
N_2 on MnN_2O_2 (opp)-sideon	$N(mol)_{tot}$ =-0.34 Mn=0.61 $N(porp)_{avr}$ =-0.25 $O(porp)_{avr}$ =-0.15 C_{Av}=0.02	$(N1\text{-}N2)_{mol}$ =2.34 Mn-N1=0.51 Mn-N2=0.51 $(Mn\text{-}N_{porp})_{av}$ =0.47 $(Mn\text{-}O_{porp})_{av}$ =0.29 $(N_{porp}\text{-}C)_{av}$ =1.32 $(O_{porp}\text{-}C)_{av}$ =1.06
N_2 on $MnNO_3$-sideon	$N(mol)_{tot}$ =-0.35 Mn=0.64 $N(porp)_{avr}$ =-0.24 $O(porp)_{avr}$ =-0.17 C_{Av}=0.01	$(N1\text{-}N2)_{mol}$=2.33 Mn-N1=0.52 Mn-N2=0.53 $(Mn\text{-}N_{porp})_{av}$ =0.55 $(Mn\text{-}O_{porp})_{av}$ =0.25 $(N_{porp}\text{-}C)_{av}$ =1.31 $(O_{porp}\text{-}C)_{av}$ =1.05
N_2 on $MnNO_3$-endon	$N(mol)_{tot}$ =-0.24 Mn=0.64 $N(porp)_{avr}$ =-0.24 $O(porp)_{avr}$ =-0.17 C_{Av}=0.01	$(N1\text{-}N2)_{mol}$=2.66 Mn-N1=0.95 Mn-N2=0.0 $(Mn\text{-}N_{porp})_{av}$ =0.59 $(Mn\text{-}O_{porp})_{av}$ =0.27 $(N_{porp}\text{-}C)_{av}$ =1.30 $(O_{porp}\text{-}C)_{av}$ =1.05

Table S6. The Coulomb Forces (F) between Mn-O and Mn-N atoms in porphyrin units for **N_2 adsorbed systems** using average values of atomic distances and atomic charges based on Bader and DDEC6 atomic charges. The "av" subscript shows the averaging of the relevant quantity.

	d (Å)	Average Bader Atomic Charges ($\|e\|$)	Average DDEC6 Atomic Charges($\|e\|$)	Coulomb Forces based on Bader charges (nN)	Coulomb Forces based on DDEC6 charges (nN)
N_2 on MnN_4 (sideon)	$(Mn\text{-}N)_{av}$= 1.92	Mn= 1.39 N_{av}= -1.19	Mn=0.65 N= -0.21	$\|F_{Mn\text{-}N}\|$= 10.32	$\|F_{Mn\text{-}N}\|$= 0.85
N_2 on MnN_2O_2 (pent) (sideon)	$(Mn\text{-}N)_{av}$= 2.09 $Mn\text{-}O_{av}$= 2.30	Mn= 1.30 N_{av}= -1.22 O_{av}= -1.10	Mn= 0.60 N= -0.25 O= -0.16	$\|F_{Mn\text{-}N}\|$= 8.35 $\|F_{Mn\text{-}O}\|$= 6.22	$F_{Mn\text{-}N}$= 0.79 $F_{Mn\text{-}O}$= 0.42
N_2 on MnN_2O_2 (opp) (sideon)	$(Mn\text{-}N)_{av}$= 2.12 $(Mn\text{-}O)_{av}$= 2.22	Mn= 1.32 N_{av}= -1.18 O_{av}= -1.09	Mn= 0.61 N= -0.25 O= -0.15	$\|F_{Mn\text{-}N}\|$= 7.97 $\|F_{Mn\text{-}O}\|$= 6.72	$\|F_{Mn\text{-}N}\|$= 0.78 $\|F_{Mn\text{-}O}\|$= 0.43
N_2 on $MnNO_3$ (sideon)	$(Mn\text{-}O)_{av}$= 2.32 Mn-N=2.04	Mn= 1.27 N= -1.17 O_{av}= 1.09	Mn= -0.67 N= -0.24 O= -0.17	$\|F_{Mn\text{-}N}\|$= 8.21 $\|F_{Mn\text{-}O}\|$= 5.92	$\|F_{Mn\text{-}N}\|$= 0.89 $\|F_{Mn\text{-}O}\|$= 0.44
N_2 on $MnNO_3$ (endon)	$(Mn\text{-}O)_{av}$=2.32 Mn-N= 2.02	Mn= 1.22 N= 1.22 O_{av}= -1.11	Mn= 0.64 N= -0.24 O= -0.17	$\|F_{Mn\text{-}N}\|$= 8.39 $\|F_{Mn\text{-}O}\|$= 5.79	$\|F_{Mn\text{-}N}\|$= 0.85 $\|F_{Mn\text{-}O}\|$= 0.47

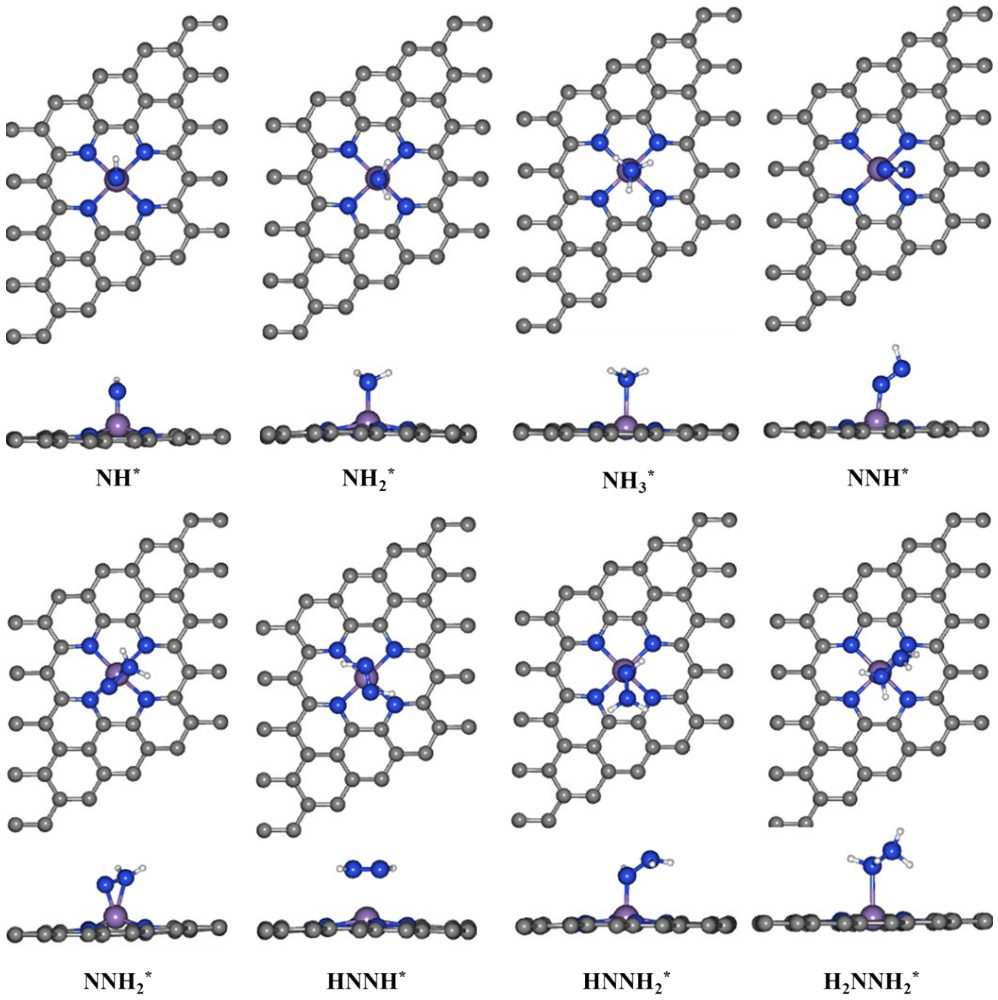

Figure S5. Adsorption configurations of all N_2 fixation reaction intermediates on MnN4 layer. The asteriks (*) mean adsorbed states.

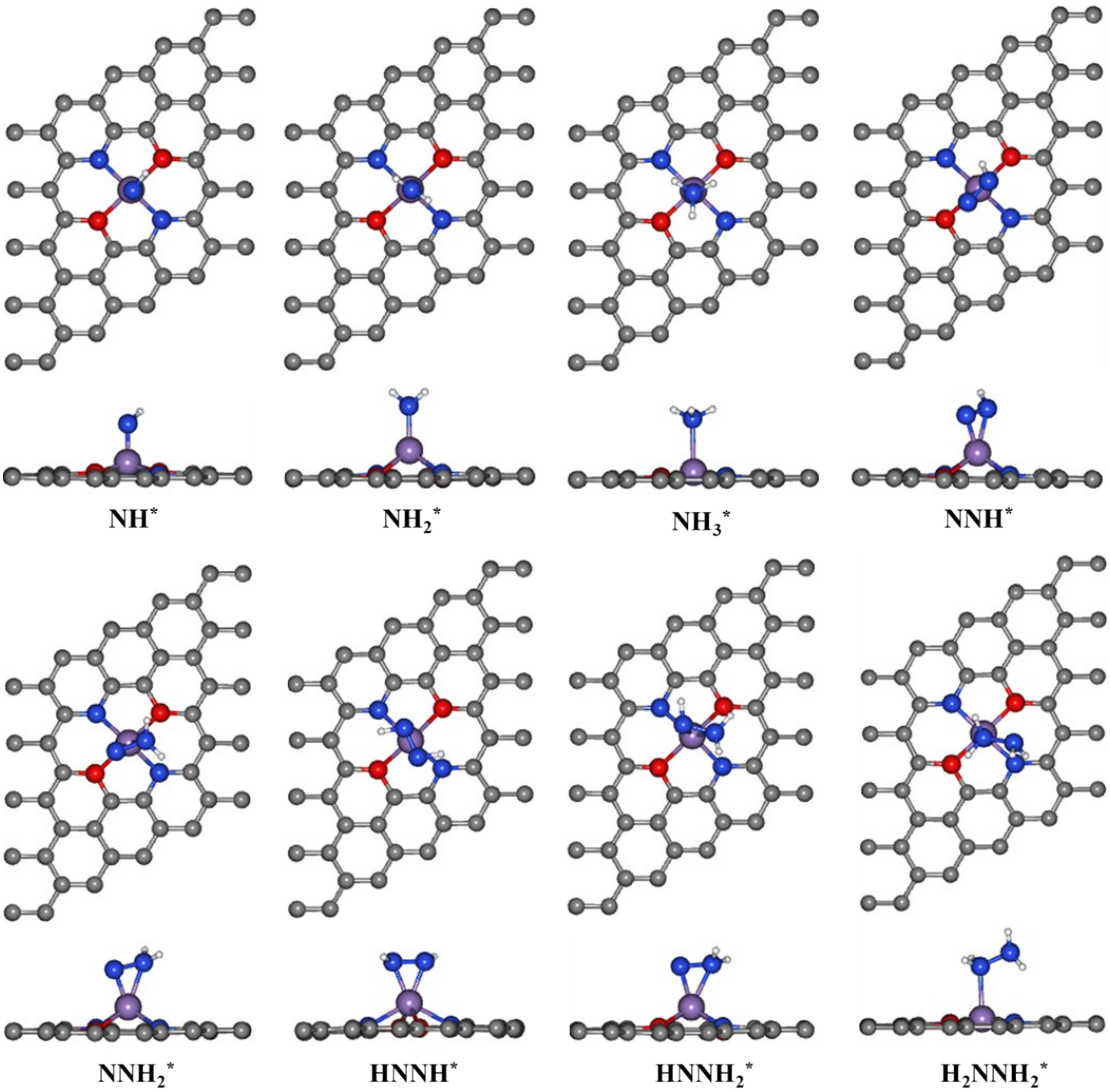

Figure S6. Adsorption configurations of all N_2 fixation reaction intermediates on MnN_2O_2(opp) layer. The asteriks (*) mean adsorbed states.

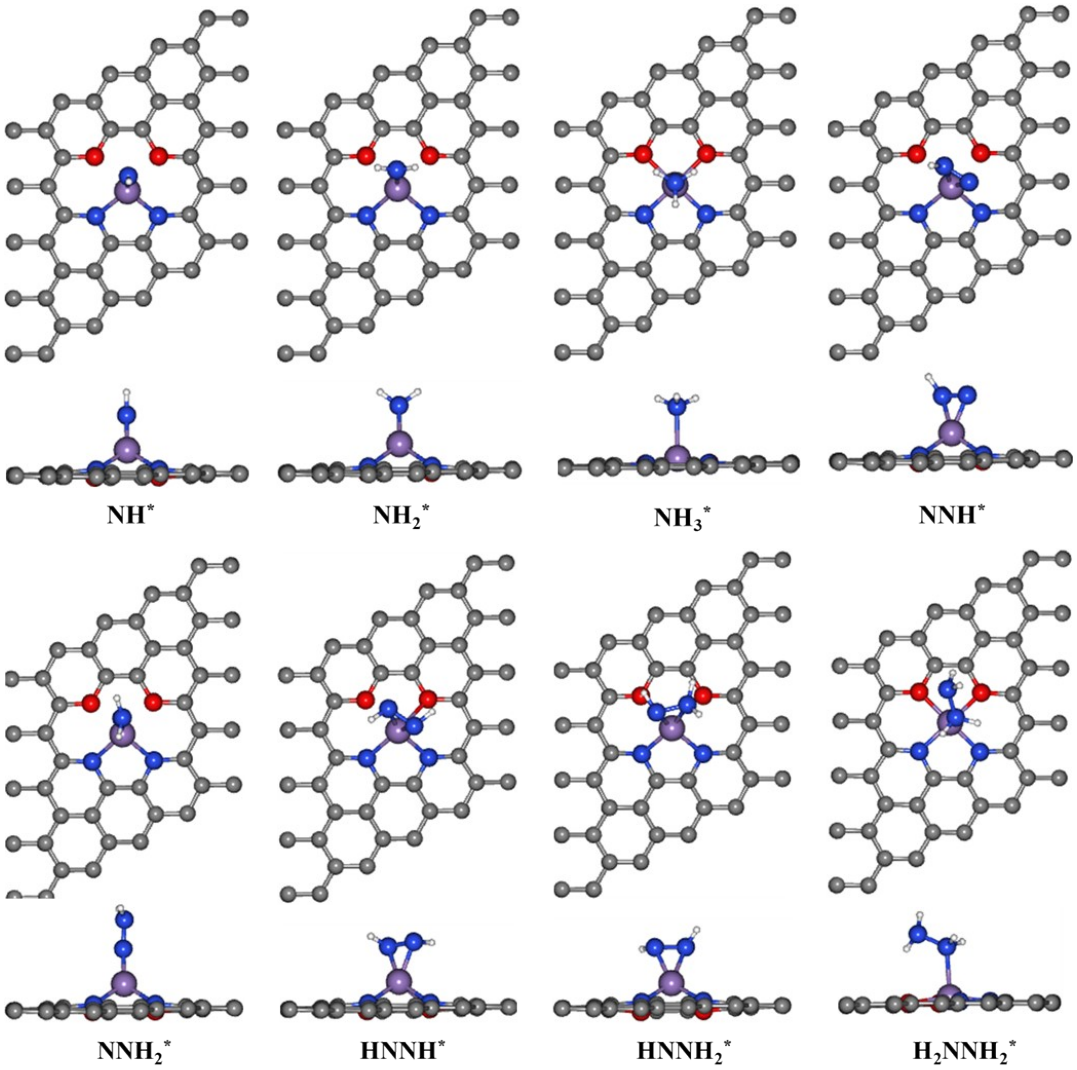

Figure S7. Adsorption configurations of all N_2 fixation reaction intermediates on MnN_2O_2(pent) layer. The asteriks (*) mean adsorbed states.

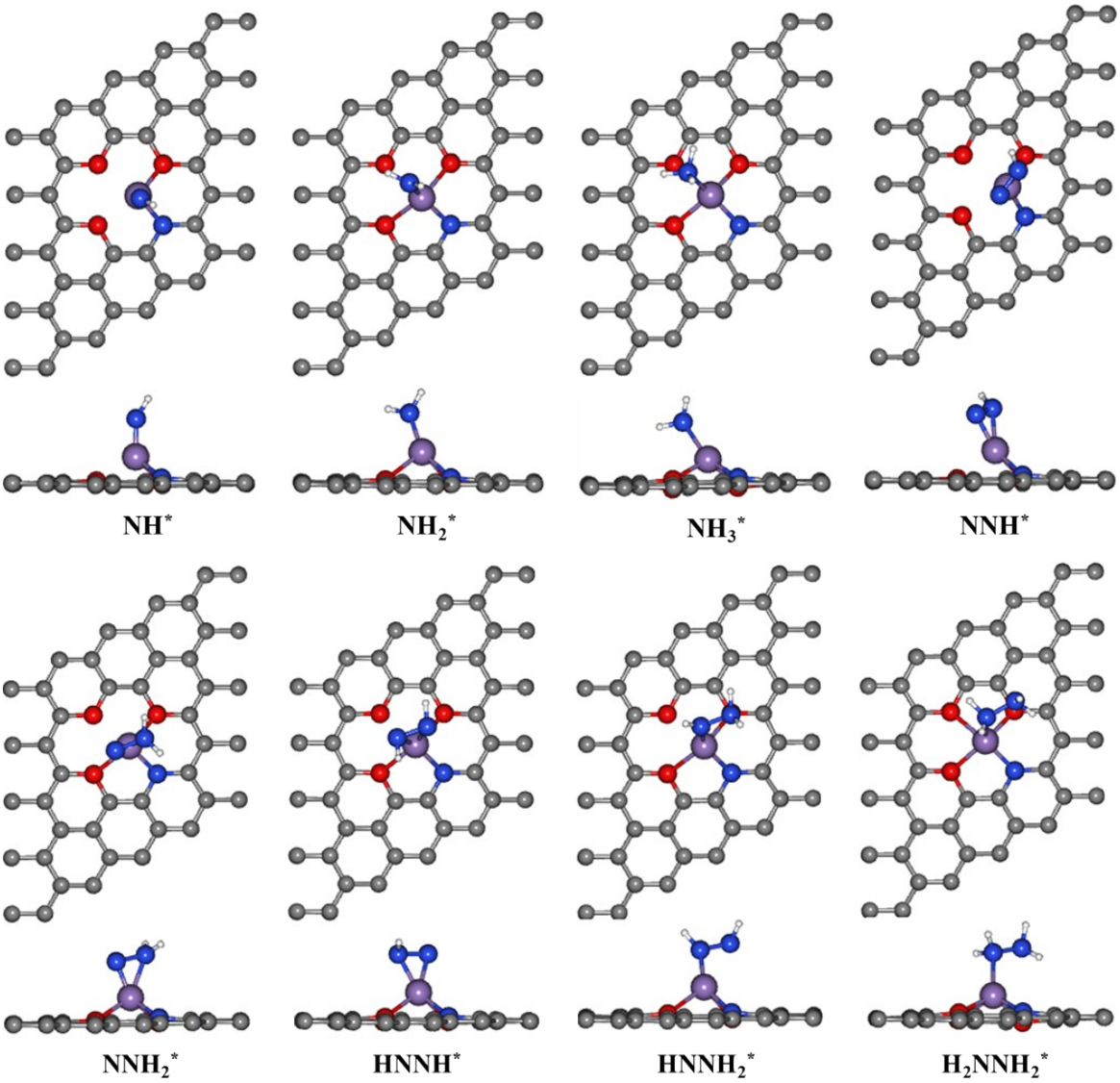

Figure S8. Adsorption configurations of all N_2 fixation reaction intermediates on $MnNO_3$ layer. The asteriks (*) mean adsorbed states.

References

1. Limas, N.G. and T.A. Manz, *Introducing DDEC6 atomic population analysis: part 4. Efficient parallel computation of net atomic charges, atomic spin moments, bond orders, and more.* RSC advances, 2018. **8**(5): p. 2678-2707.
2. Rohling, R.Y., et al., *Correlations between density-based bond orders and orbital-based bond energies for chemical bonding analysis.* The Journal of Physical Chemistry C, 2019. **123**(5): p. 2843-2854.