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Supporting Information

Axial ligand engineering for highly efficient oxygen reduction catalyst in transition metal-N_4 doped graphene

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Table S1. The total energies (eV) for convergence test with respect to the k-grid sampling size for CrN_4-Gra, FeN_4-Gra/ben/NO_2, RuN_4-Gra/ben/NO_2 and FeN_4-Gra/benzene.

k-grid	CrN_4-Gra	FeN_4-Gra/ben/NO_2	RuN_4-Gra/ben/NO_2	FeN_4-Gra/benzene
5x5x1	-450.625	-537.264	-537.133	-521.731
6x6x1	-450.626	-537.225	-537.146	-521.731
7x7x1	-450.658	-537.225	-537.188	-521.733
8x8x1	-450.625	-537.264	-537.146	-521.731
10x10x1	-450.625	-537.264	-537.145	-521.732

Table S2. The charge (e^-) of Cr atom in all the catalysts before (Q1) and after (Q2) the oxygen-containing intermediates are adsorbed.

Model	**Q_1**	**Q2**			
		***O_2**	***OOH**	***O**	***OH**
CrN_4-Gra	1.23	1.54	1.47	1.53	1.51
CrN_4-Gra/O	1.47	1.48	1.61	1.59	1.64
CrN_4-Gra/OH	1.54	1.64	1.63	1.61	1.57
CrN_4-Gra/OOH	1.51	1.60	1.57	1.58	1.63
CrN_4-Gra/ CH	1.34	1.30	1.36	1.32	1.44
CrN_4-Gra/CH_2	1.33	1.47	1.48	1.60	1.52
CrN_4-Gra/CH_3	1.35	1.52	1.48	1.58	1.53
CrN_4-Gra/NH	1.44	1.49	1.58	1.56	1.60
CrN_4-Gra/NH_2	1.45	1.57	1.55	1.60	1.54
CrN_4-Gra/NH_3	1.39	1.56	1.55	1.50	1.58
CrN_4-Gra/ben	1.35	1.53	1.47	1.40	1.51
CrN_4-Gra/ben/NH_2	1.38	1.54	1.50	1.59	1.52
CrN_4-Gra/ben/NO_2	1.35	1.51	1.46	1.39	1.47

Table S3. The Cr−O (d_{Cr-O}) bond distances between Cr and O in absored O_2, and the adsorption energies ΔE_{ads} (eV) for the most stable ORR intermediates for the studied catalysts.

	d_{Cr-O}(Å)	*O_2	*O	*OH	*OOH	*H	*H_2O	*HOOH
CrN_4-Gra	1.85	-2.13	-5.90	-3.68	-2.30	-1.57	-0.30	O+H_2O
CrN_4-Gra/O	3.11	-0.20	-3.08	-2.01	-0.65	-1.41	-0.17	-0.20
CrN_4-Gra/OH	1.91	-0.89	-4.33	-2.84	-1.52	-1.46	-0.35	-0.39
CrN_4-Gra/OOH	1.90	-0.92	-4.45	-2.94	-1.56	-1.49	-0.30	-0.39
CrN_4-Gra/CH	2.89	-0.25	-3.02	-1.93	-0.67	-1.37	-0.18	-0.26
CrN_4-Gra/CH_2	1.94	-0.45	-3.34	-2.28	-0.97	-1.50	-0.22	-0.31
CrN_4-Gra/CH_3	1.91	-0.96	-4.06	-3.59	-1.32	-1.51	-0.30	-0.36
CrN_4-Gra/NH	3.20	-0.22	-3.08	-2.25	-0.90	-1.37	-0.19	-0.22
CrN_4-Gra/NH_2	1.90	-0.82	-4.21	-2.86	-1.56	-1.43	-0.30	-0.37
CrN_4-Gra/NH_3	1.87	-1.77	-5.41	-3.70	-2.31	-1.54	-0.52	O+H_2O
CrN_4-Gra/ben	1.91	-0.83	-3.91	-2.57	-1.25	-1.49	-0.30	-0.35
CrN_4-Gra/ben/NH_2	1.91	-0.79	-3.89	-2.57	-1.27	-1.48	-0.28	-0.35
CrN_4-Gra/ben/NO_2	1.91	-0.76	-3.90	-2.57	-1.34	-1.50	-0.32	-0.33

Table S4. Adsorption energies ΔE_{ads} (eV) for the most stable ORR intermediates and Gibbs adsorption free energies of the oxygenated intermediates (ΔG_{*OOH}, ΔG_{*O}, and ΔG_{*OH}) and overpotentials (η) for MN_4-Gra/CH_3 catalysts.

	E_{ads} (eV)			ΔG (eV)			η(V)
	*O	*OH	*OOH	*OOH	*O	*OH	
ScN_4-Gra/CH_3[a]	-3.06	-1.10	-		-		
TiN_4-Gra/CH_3[b]	-	-	-1.23		-		
VN_4-Gra/CH_3[c]	-	-2.90	-1.47		-		
CrN_4-Gra/CH_3	-4.06	-3.59	-1.32	4.02	1.76	0.86	0.37
MnN_4-Gra/CH_3	-3.63	-2.58	-1.34	3.99	2.22	0.96	0.30
FeN_4-Gra/CH_3	-3.46	-4.05	-2.63	4.01	2.37	1.06	0.32
CoN_4-Gra/CH_3	-2.87	-2.12	-0.94	4.38	3.04	1.40	0.69
NiN_4-Gra/CH_3	-2.91	-2.19	-0.99	4.31	2.99	1.34	0.62
CuN_4-Gra/CH_3	-2.77	-1.69	-0.51	4.83	3.13	1.84	1.14
ZnN_4-Gra/CH_3[d]	-	-0.75	-			-	
RuN_4-Gra/CH_3	-3.76	-2.77	-1.62	3.73	2.08	0.79	0.44
RhN_4-Gra/CH_3	-3.02	-2.28	-1.14	4.16	2.88	1.23	0.47
PdN_4-Gra/CH_3	-3.12	-2.62	-1.38	3.94	2.78	0.88	0.35
IrN_4-Gra/CH_3	-2.91	-2.53	-0.98	4.32	2.91	0.95	0.63
PtN_4-Gra/CH_3	-2.81	-2.95	-1.27	4.00	3.06	0.57	0.66

[a]*OOH was not adsorbed on the ScN_4-Gra/CH_3.

[b]The ligand CH_3 falls off when *O and *OH were adsorbed on the TiN_4-Gra/CH_3, respectively.

[c]The ligand CH_3 falls off when *O was adsorbed on the VN_4-Gra/CH_3.

[d]*O and *OOH were not adsorbed on the ZnN_4-Gra/CH_3.

Table S5. Adsorption energies ΔE_{ads} (eV) for the most stable ORR intermediates and Gibbs adsorption free energies of the oxygenated intermediates (ΔG_{*OOH}, ΔG_{*O}, and ΔG_{*OH}) and overpotentials (η) for MN_4-Gra/ben/NO_2 catalysts.

	E_{ads} (eV)			ΔG (eV)			η(V)
	*O	*OH	*OOH	*OOH	*O	*OH	
ScN_4-Gra/ben/NO_2[a]	-3.02	-1.11	-		-		
TiN_4-Gra/ben/NO_2[b]	-	-	-		–		
VN_4-Gra/ben/NO_2[c]	-	-	-1.47		–		
CrN_4-Gra/ben/NO_2	-3.90	-2.57	-1.34	3.98	1.93	0.96	0.29
MnN_4-Gra/ben/NO_2	-3.44	-2.54	-1.27	4.06	2.40	1.01	0.37
FeN_4-Gra/ben/NO_2	-3.44	-2.51	-1.46	3.90	2.40	1.03	0.21
CoN_4-Gra/ben/NO_2	-2.77	-2.06	-0.86	4.47	3.14	1.46	0.78
NiN_4-Gra/ben/NO_2	-2.75	-2.01	-0.82	4.51	3.15	1.35	0.82
CuN_4-Gra/ben/NO_2	-2.69	-1.34	-0.25	5.00	3.22	2.20	1.31
ZnN_4-Gra/ben/NO_2[d]	-2.74	-	-		-		
RuN_4-Gra/ben/NO_2	-3.40	-2.58	-1.55	3.80	2.42	0.97	0.26
RhN_4-Gra/ben/NO_2	-2.96	-2.31	-1.17	4.12	2.95	1.20	0.43
PdN_4-Gra/ben/NO_2	-3.00	-2.54	-1.32	4.00	2.91	0.95	0.31
IrN_4-Gra/ben/NO_2	-2.85	-2.60	-1.11	4.21	2.96	0.92	0.52
PtN_4-Gra/ben/NO_2	-2.71	-2.96	-1.30	4.03	3.17	0.58	0.65

[a]*OOH was not adsorbed on the ScN_4-Gra/ben/NO_2.

[b]The ligand ben/NO_2 falls off when *O, *OH and *OOH were adsorbed on the TiN_4-Gra/ben/NO_2, respectively.

[c]The ligand ben/NO_2 falls off when *O and *OH were adsorbed on the VN_4-Gra/ben/NO_2, respectively.

[d]*OH and *OOH were not adsorbed on the ZnN_4-Gra/ben/NO_2.

Table S6. Adsorption energies ΔE_{ads} (eV) for the most stable ORR intermediates and Gibbs adsorption free energies of the oxygenated intermediates (ΔG_{*OOH}, ΔG_{*O}, and ΔG_{*OH}) and overpotentials (η) for MN_4-Gra/ben catalysts.

	E_{ads} (eV)			ΔG (eV)			η(V)
	*O	*OH	*OOH	*OOH	*O	*OH	
ScN_4-Gra/ben[a]	-3.06	-1.12	-		-		
TiN_4-Gra/ben[b]	-	-	-1.14		-		
VN_4-Gra/ben[c]	-	-2.78	-1.39		-		
CrN_4-Gra/ben	-3.91	-2.57	-1.25	4.04	1.93	0.96	0.35
MnN_4-Gra/ben	-3.47	-2.56	-1.28	4.03	2.36	0.98	0.34
FeN_4-Gra/ben	-3.53	-2.59	-1.46	3.88	2.31	0.95	0.28
CoN_4-Gra/ben	-2.84	-2.10	-0.89	4.40	3.07	1.42	0.71
NiN_4-Gra/ben	-2.84	-2.08	-0.71	4.60	3.06	1.45	0.90
CuN_4-Gra/ben[d]	-2.74	-1.45	-		-		
ZnN_4-Gra/ben[e]	-2.76	-	-		-		
RuN_4-Gra/ben	-3.55	-2.62	-1.53	3.83	2.30	0.91	0.32
RhN_4-Gra/ben	-3.03	-2.34	-1.14	4.23	2.88	1.19	0.54
PdN_4-Gra/ben	-3.08	-2.60	-1.36	3.98	2.83	0.91	0.32
IrN_4-Gra/ben	-2.93	-2.60	-1.06	4.21	2.89	0.92	0.52
PtN_4-Gra/ben	-2.80	-2.96	-1.27	4.02	3.07	0.55	0.68

[a]*OOH was not adsorbed on the ScN_4-Gra/ben.

[b]The ligand ben falls off when *O and *OH were adsorbed on the TiN_4-Gra/ben, respectively.

[c]The ligand ben falls off when *O was adsorbed on the VN_4-Gra/ben.

[d]*OOH was not adsorbed on the CuN_4-Gra/ben.

[e]*OH and *OOH were not adsorbed on the ZnN_4-Gra/ben.

Table S7. Adsorption energies ΔE_{ads} (eV) for the most stable ORR intermediates and Gibbs adsorption free energies of the oxygenated intermediates (ΔG_{*OOH}, ΔG_{*O}, and ΔG_{*OH}) and overpotentials (η) for MN_4-Gra/ben/NH_2 catalysts.

	E_{ads} (eV)			ΔG (eV)			η(V)
	*O	*OH	*OOH	*OOH	*O	*OH	
ScN_4-Gra/ben/NH_2[a]	-3.09	-1.13	-		-		
TiN_4-Gra/ben/NH_2[b]	-	-	-1.05		-		
VN_4-Gra/ben/NH_2[c]	-	-2.69	-1.20		-		
CrN_4-Gra/ben/NH_2	-3.89	-2.57	-1.27	4.06	1.94	0.96	0.37
MnN_4-Gra/ben/NH_2	-3.51	-2.61	-1.31	4.00	2.34	0.92	0.32
FeN_4-Gra/ben/NH_2	-3.36	-2.44	-1.27	4.06	2.48	1.11	0.37
CoN_4-Gra/ben/NH_2	-2.85	-2.13	-0.90	4.47	3.06	1.40	0.78
NiN_4-Gra/ben/NH_2	-2.87	-2.13	-0.97	4.37	3.03	1.42	0.68
CuN_4-Gra/ben/NH_2[d]	-2.73	-1.47	-		-		
ZnN_4-Gra/ben/NH_2[e]	-2.59	-	-		-		
RuN_4-Gra/ben/NH_2	-3.61	-2.67	-1.54	3.80	2.23	0.87	0.36
RhN_4-Gra/ben/NH_2	-3.04	-2.37	-1.14	4.16	2.86	1.15	0.47
PdN_4-Gra/ben/NH_2	-3.12	-2.65	-1.39	4.00	2.78	0.88	0.35
IrN_4-Gra/ben/NH_2	-3.00	-2.66	-1.08	4.21	2.82	0.87	0.53
PtN_4-Gra/ben/NH_2	-2.83	-2.99	-1.34	3.99	3.05	0.52	0.71

[a]*OOH was not adsorbed on the ScN_4-Gra/ben/NH_2.

[b]The ligand ben/NH_2 falls off when *O and *OH were adsorbed on the TiN_4-Gra/ben/NH_2, respectively.

[c]The ligand ben/NH_2 falls off when *O was adsorbed on the VN_4-Gra/ben/NH_2.

[d]*OOH was not adsorbed on the CuN_4-Gra/ben/NH_2.

[e]*OH and *OOH were not adsorbed on the ZnN_4-Gra/ben/NH_2.

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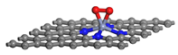
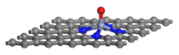
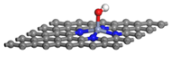
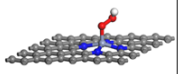
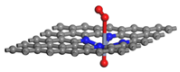
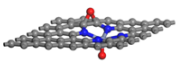
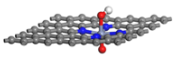
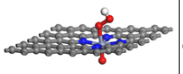
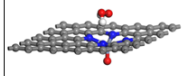
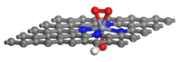
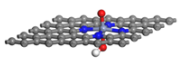
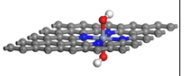
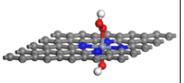
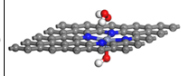
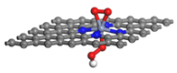
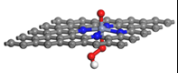
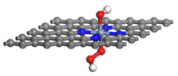
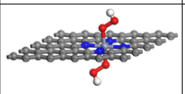
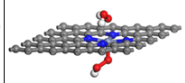
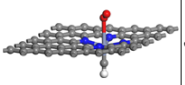
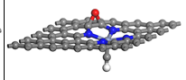
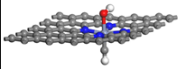
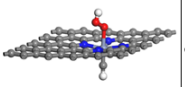
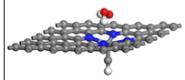
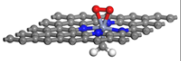
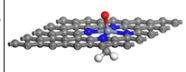
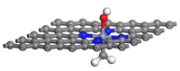
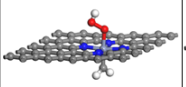
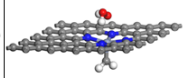
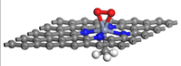
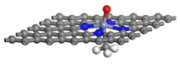
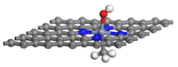
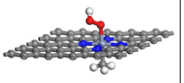
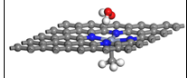
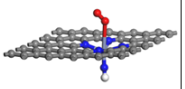
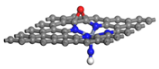
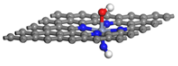
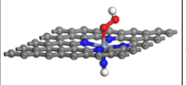
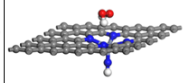
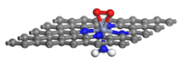
CrN_4-Gra					-
CrN_4-Gra/O					
CrN_4-Gra/OH					
CrN_4-Gra/OOH					
CrN_4-Gra/CH					
CrN_4-Gra/CH_2					
CrN_4-Gra/CH_3					
CrN_4-Gra/NH					
CrN_4-Gra/NH_2					
CrN_4-Gra/NH_3					-
CrN_4-Gra/Benzene					
CrN_4-Gra/Benzene/NH_2					
CrN_4-Gra/Benzene/NO_2					

Figure S1. The optimized structures of O_2, *O, *OH, *OOH and HOOH intermediates on the CrN_4-Gra surfaces with different axial ligands.

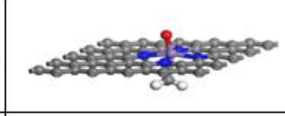
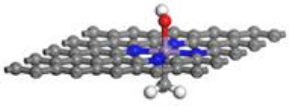
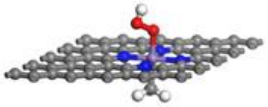
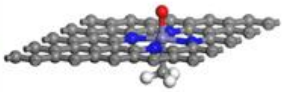
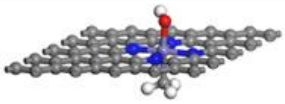
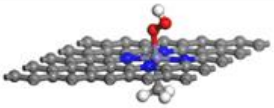
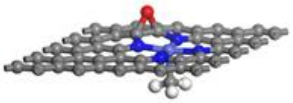
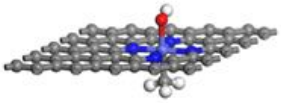
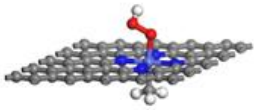
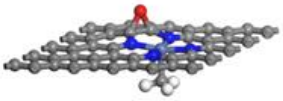
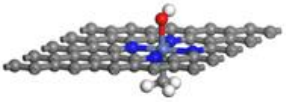
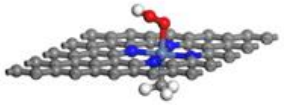
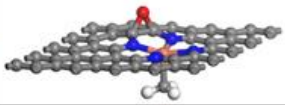
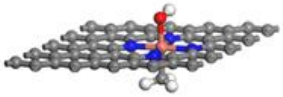
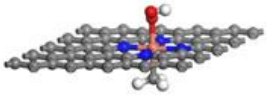
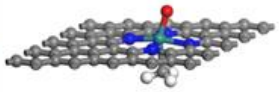
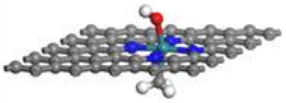
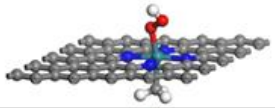
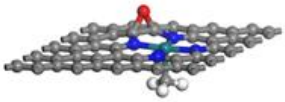
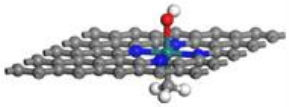
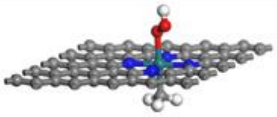
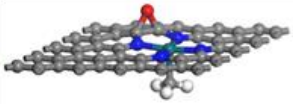
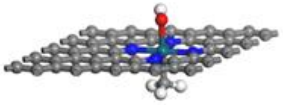
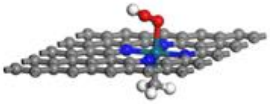
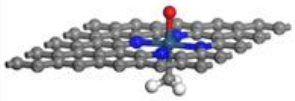
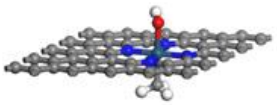
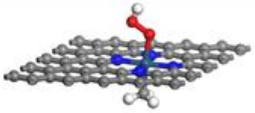
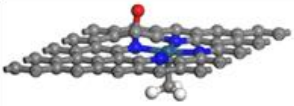
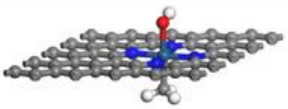
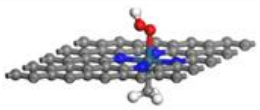
	*O	*OH	*OOH
MnN_4-Gra/CH_3			
FeN_4-Gra/CH_3			
CoN_4-Gra/CH_3			
NiN_4-Gra/CH_3			
CuN_4-Gra/CH_3			
RuN_4-Gra/CH_3			
RhN_4-Gra/CH_3			
PdN_4-Gra/CH_3			
IrN_4-Gra/CH_3			
PtN_4-Gra/CH_3			

Figure S2. The optimized structures of *O, *OH and *OOH intermediates on the MN_4-Gra/CH_3 surfaces.

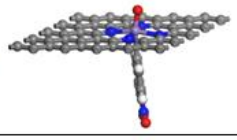
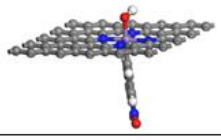
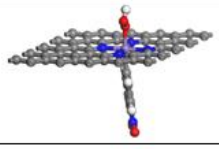
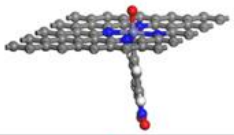
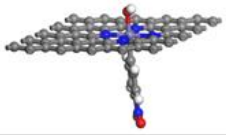
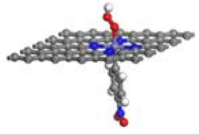
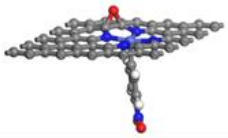
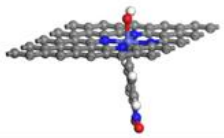
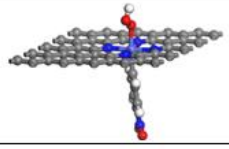
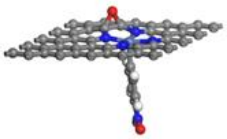
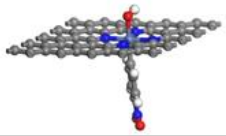
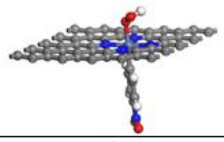
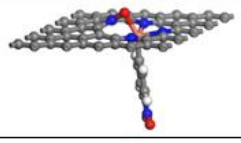
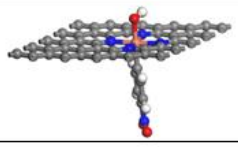
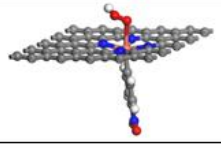
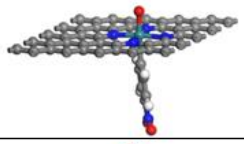
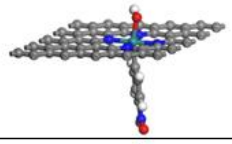
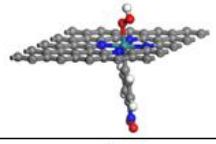
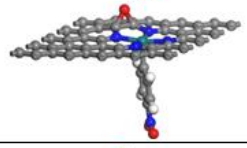
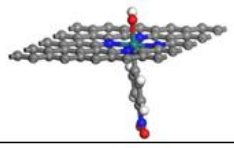
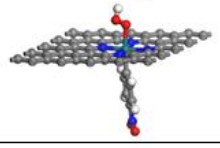
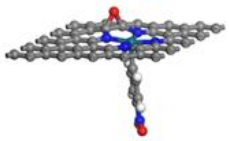
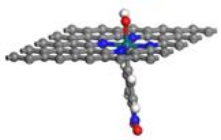
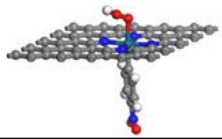
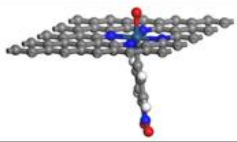
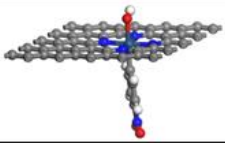
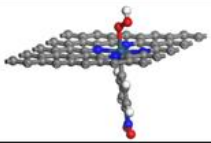
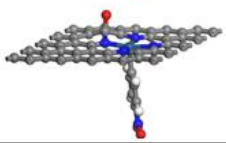
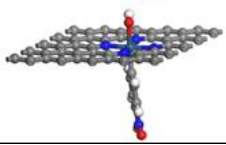
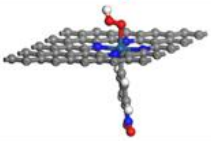
	*O	*OH	*OOH
MnN_4-Gra/Benzene/NO_2			
FeN_4-Gra/Benzene/NO_2			
CoN_4-Gra/Benzene/NO_2			
NiN_4-Gra/Benzene/NO_2			
CuN_4-Gra/Benzene/NO_2			
RuN_4-Gra/Benzene/NO_2			
RhN_4-Gra/Benzene/NO_2			
PdN_4-Gra/Benzene/NO_2			
IrN_4-Gra/Benzene/NO_2			
PtN_4-Gra/Benzene/NO_2			

Figure S3. The optimized structures of *O, *OH and *OOH intermediates on the MN_4-Gra/ben/NO_2 surfaces.

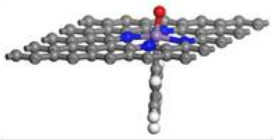
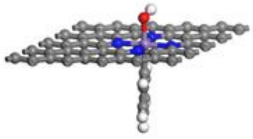
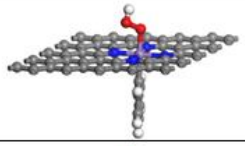
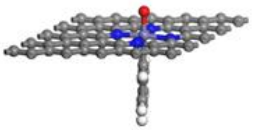
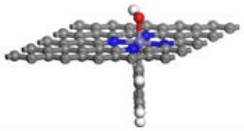
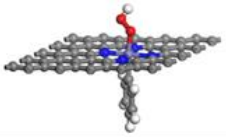
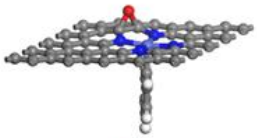
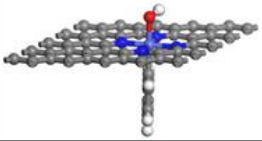
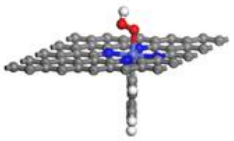
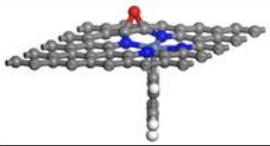
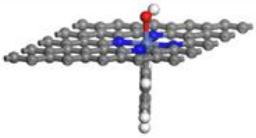
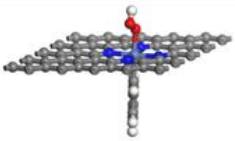
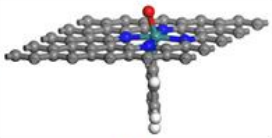
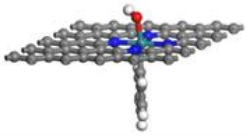
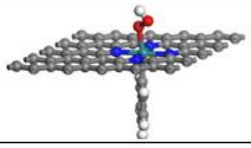
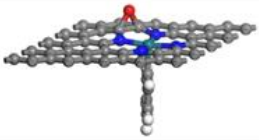
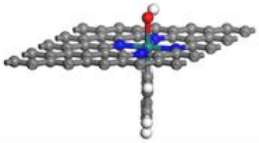
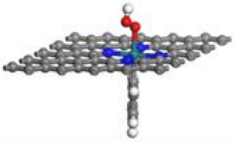
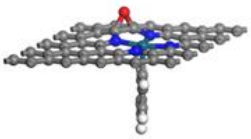
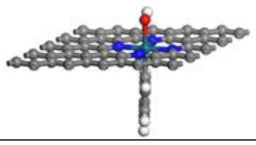
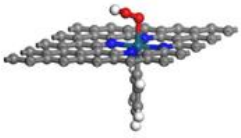
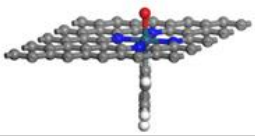
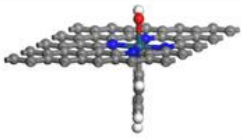
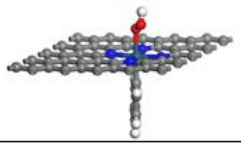
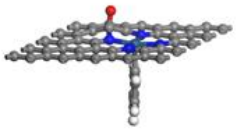
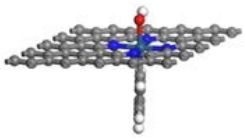
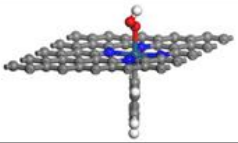
	*O	*OH	*OOH
MnN_4-Gra/Benzene			
FeN_4-Gra/Benzene			
CoN_4-Gra/Benzene			
NiN_4-Gra/Benzene			
RuN_4-Gra/Benzene			
RhN_4-Gra/Benzene			
PdN_4-Gra/Benzene			
IrN_4-Gra/Benzene			
PtN_4-Gra/Benzene			

Figure S4. The optimized structures of *O, *OH and *OOH intermediates on the MN_4-Gra/ben surfaces.

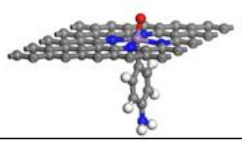
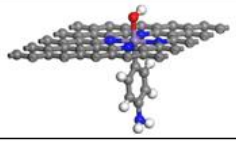
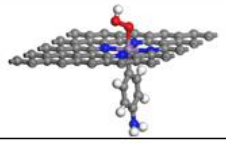
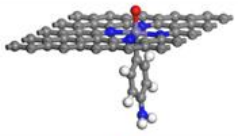
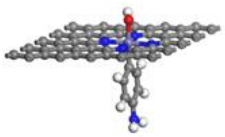
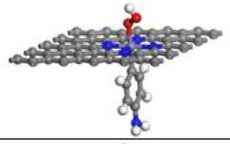
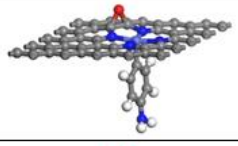
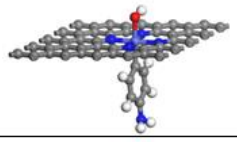
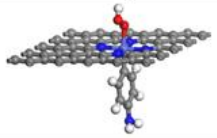
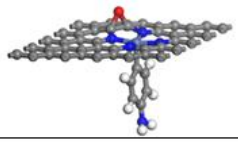
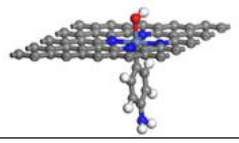
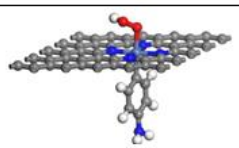
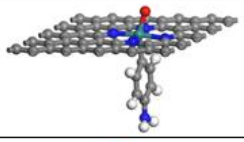
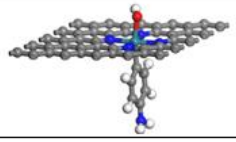
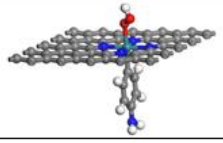
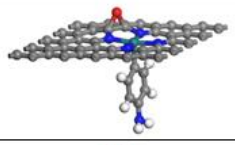
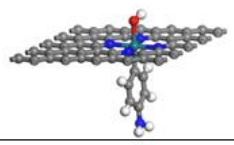
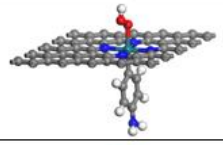
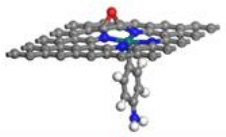
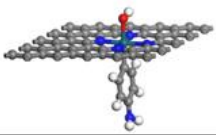
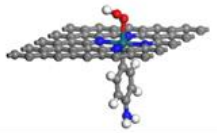
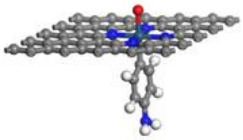
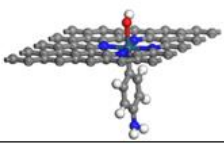
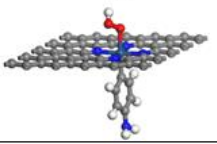
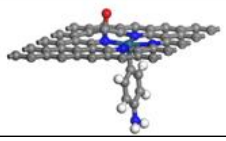
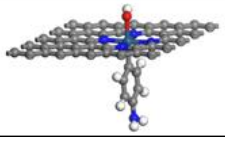
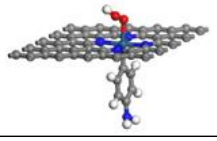
	*O	*OH	*OOH
MnN_4-Gra/Benzene/NH_2			
FeN_4-Gra/Benzene/NH_2			
CoN_4-Gra/Benzene/NH_2			
NiN_4-Gra/Benzene/NH_2			
RuN_4-Gra/Benzene/NH_2			
RhN_4-Gra/Benzene/NH_2			
PdN_4-Gra/Benzene/NH_2			
IrN_4-Gra/Benzene/NH_2			
PtN_4-Gra/Benzene/NH_2			

Figure S5. The optimized structures of *O, *OH and *OOH intermediates on the MN_4-Gra/ben/NH_2 surfaces.

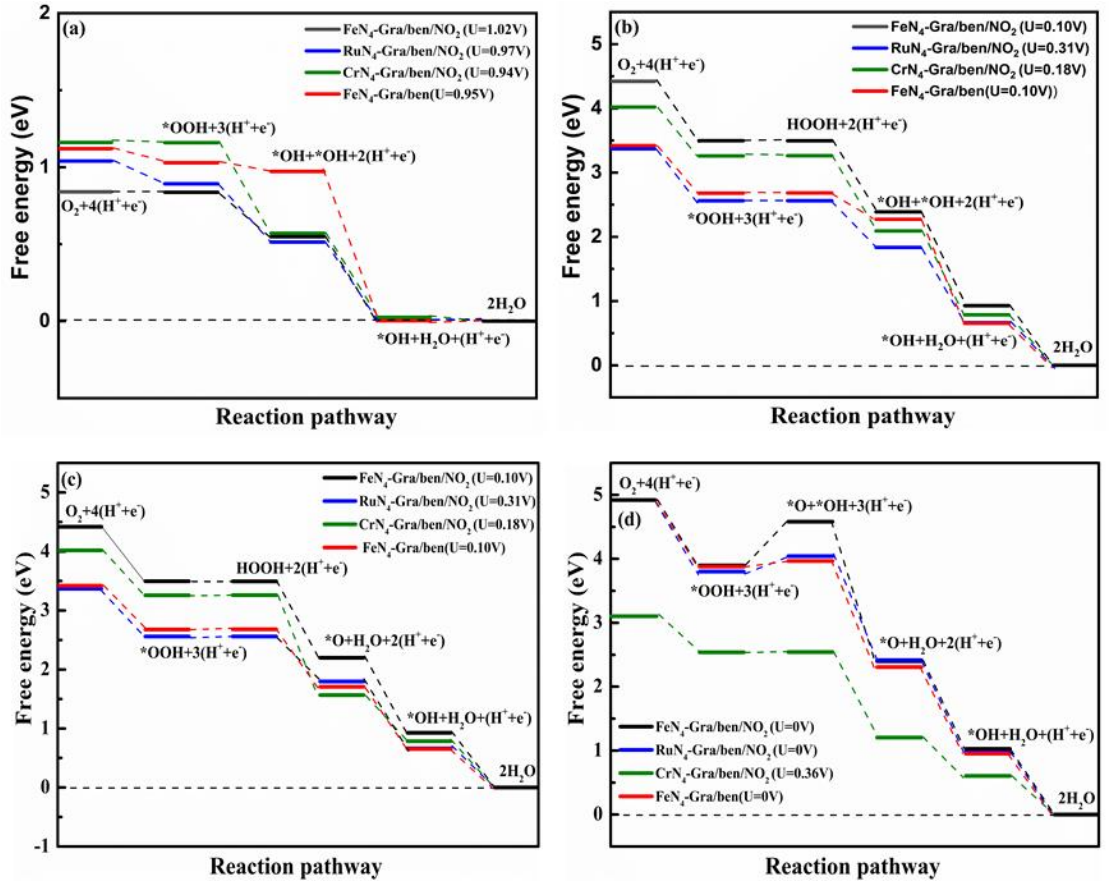


Figure S6. The free energy diagrams of the different ORR pathways for FeN_4-Gra/ben/NO_2, RuN_4-Gra/ben/NO_2, CrN_4-Gra/ben/NO_2, and FeN_4-Gra/ben.

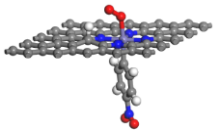
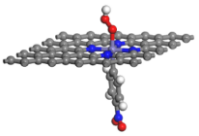
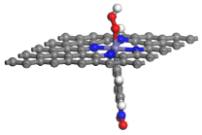
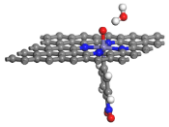
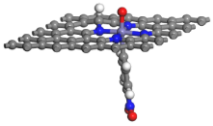
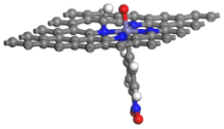
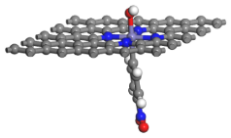
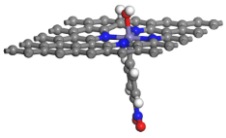
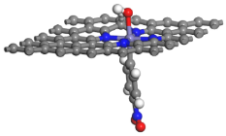
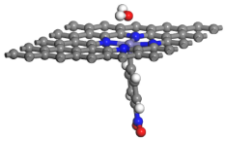
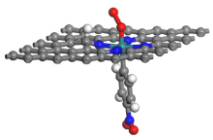
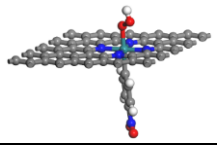
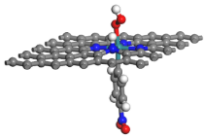
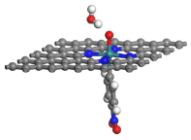
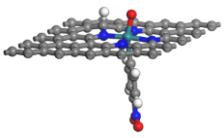
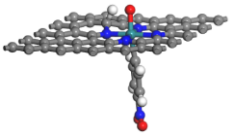
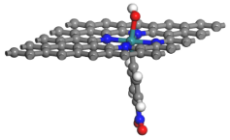
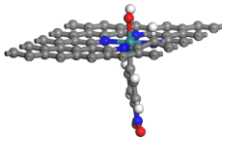
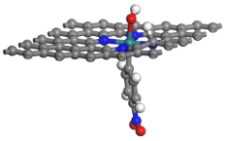
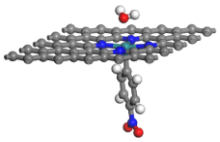
	IS	TS	FS
FeN_4-Gra/Benzene/NO_2: O2 → *OOH			
*OOH → *O + H_2O			
*O → *OH			
*OH → H_2O			
RuN_4-Gra/Benzene/NO_2: O2 → *OOH			
*OOH → *O + H_2O			
*O → *OH			
*OH → H_2O			

Figure S7. Atomic structures of the initial state (IS), the transition state (TS), and the final state (FS) for ORR on FeN_4-Gra/ben/NO_2 and RuN_4-Gra/ben/NO_2.

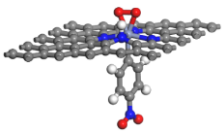
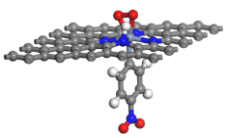
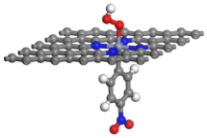
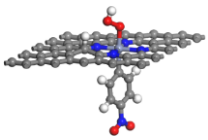
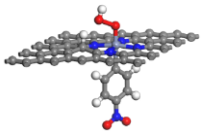
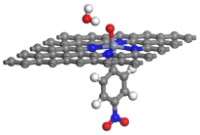
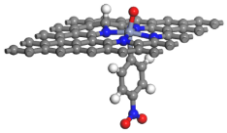
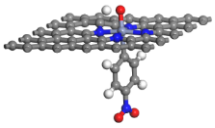
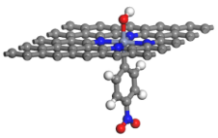
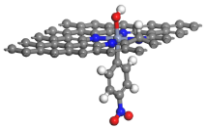
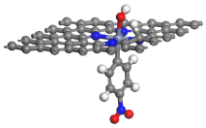
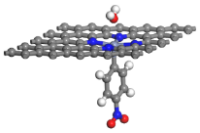
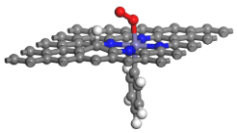
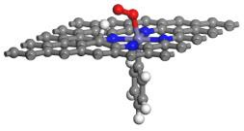
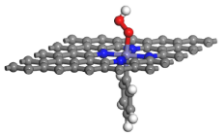
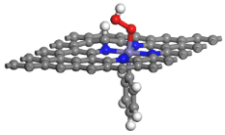
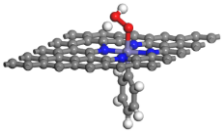
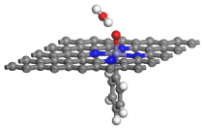
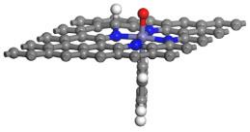
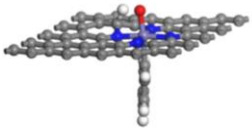
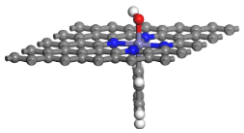
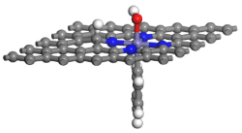
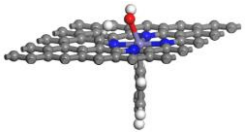
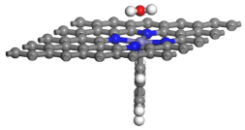
	IS	TS	FS
CrN_4-Gra/Benzene/NO_2: O2 → *OOH			
*OOH → *O + H_2O			
*O → *OH			
*OH → H_2O			
FeN_4-Gra/Benzene: O2 → *OOH			
*OOH → *O + H_2O			
*O → *OH			
*OH → H_2O			

Figure S8. Atomic structures of the initial state (IS), the transition state (TS), and the final state (FS) for ORR on CrN_4-Gra/ben/NO_2 and FeN_4-Gra/ben.

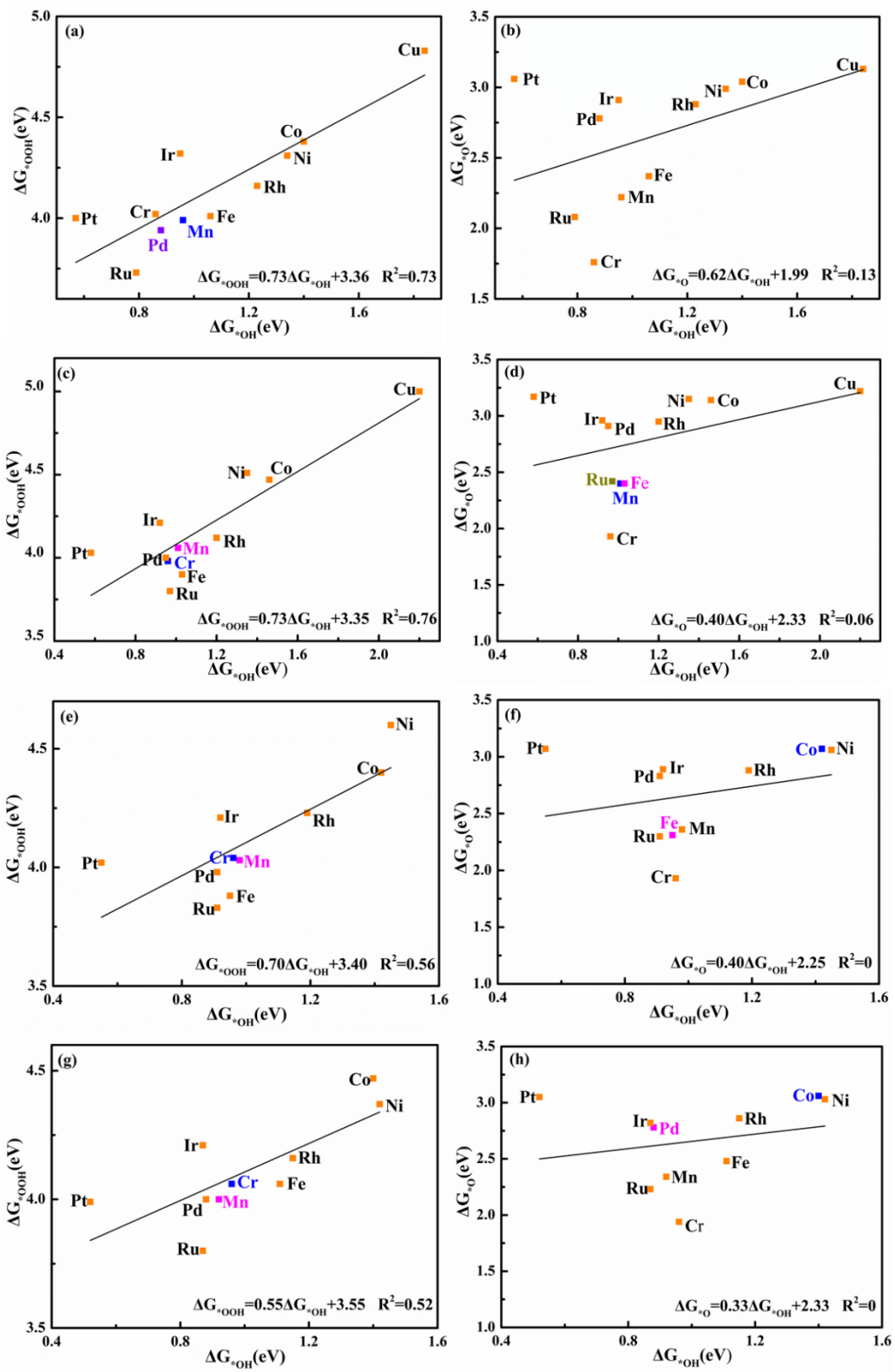


Figure S9. The scaling relationship for Gibbs adsorption free energies of *OH versus *OOH and *OH versus *O for MN_4-Gra/CH_3 (a,b) MN_4-Gra/ben/NO_2 (c,d) MN_4-Gra/ben (e,f) and MN_4-Gra/ben/NH_2 (g,h).