catalysts

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Supporting Information

Dual Metal Site Fe Single Atom Catalyst with Improved Stability in Acidic Conditions

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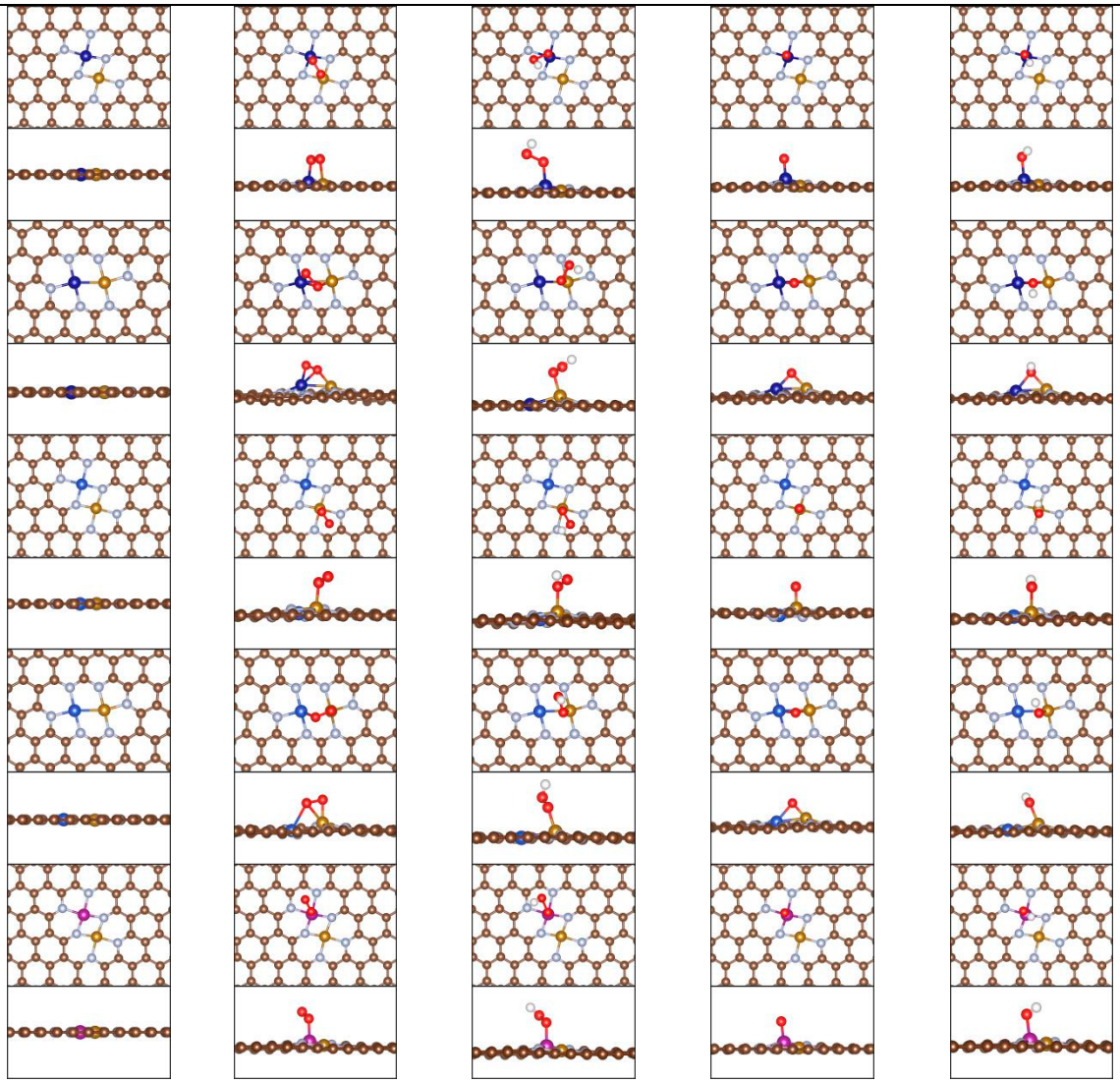
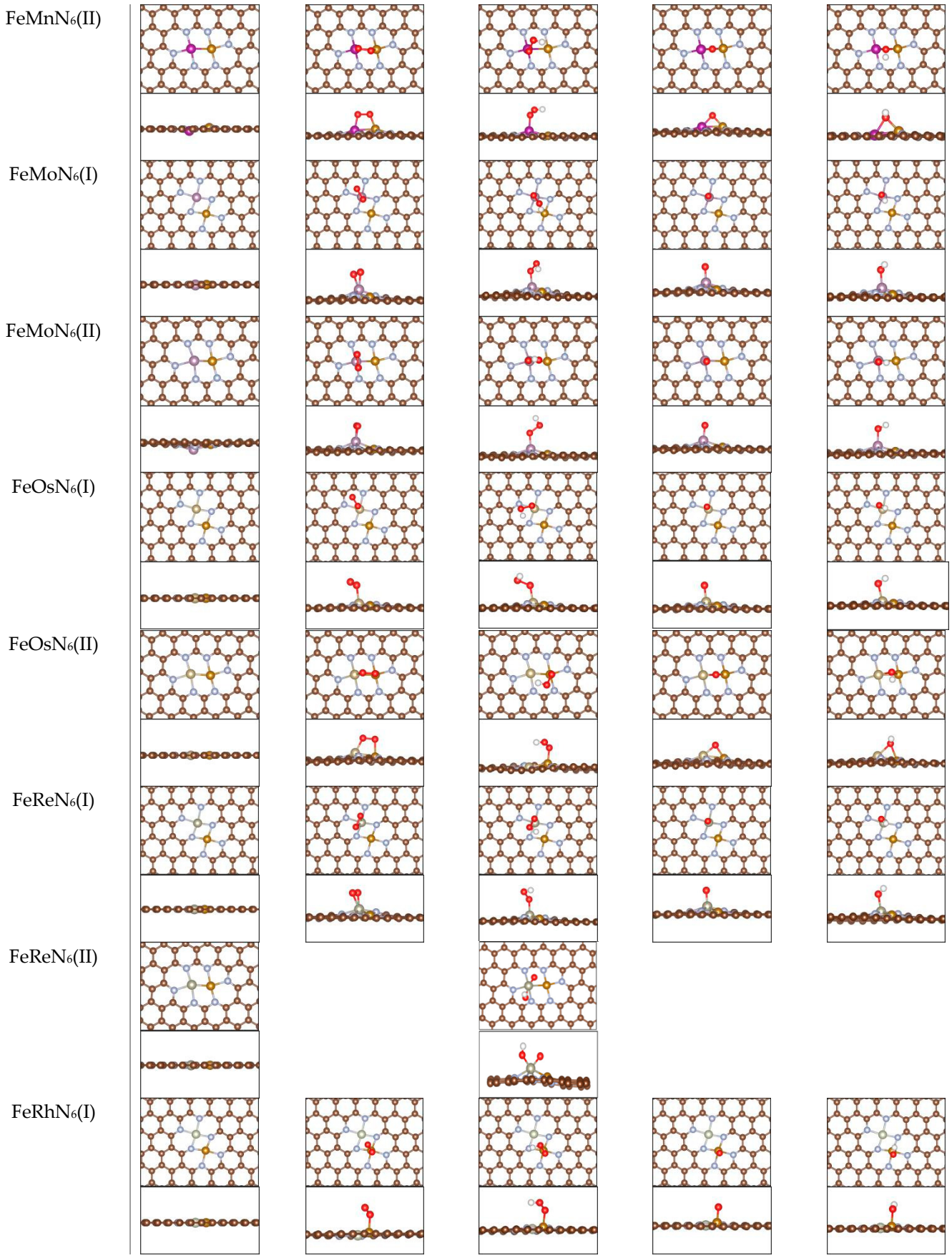
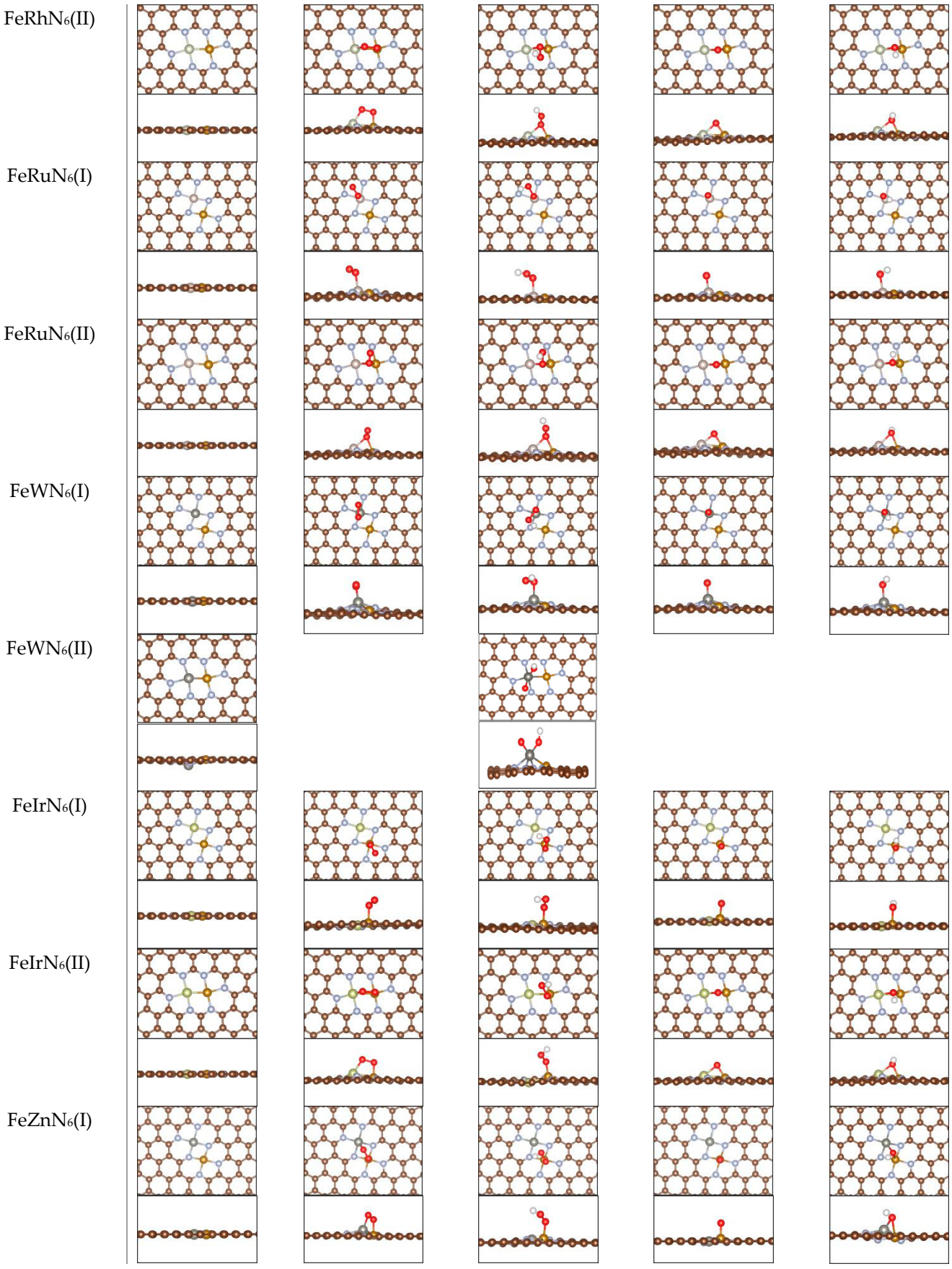
Table S1. Structural evolution of electrochemical ORR for the designed catalysts, top view and side view.

DMSC	CATA	$*O_2$	*OOH	*O	*OH
$FeCrN_6$(I)					
$FeCrN_6$(II)					
$FeCuN_6$(I)					
$FeCuN_6$(II)					
$FeMnN_6$(I)					


FeMnN6(II)
FeMoN6(I)
FeMoN6(II)
FeOsN6(I)
FeOsN6(II)
FeReN6(I)
FeReN6(II)
FeRhN6(I)


FeRhN6(II)
FeRuN6(I)
FeRuN6(II)
FeWN6(I)
FeWN6(II)
FeIrN6(I)
FeIrN6(II)
FeZnN6(I)

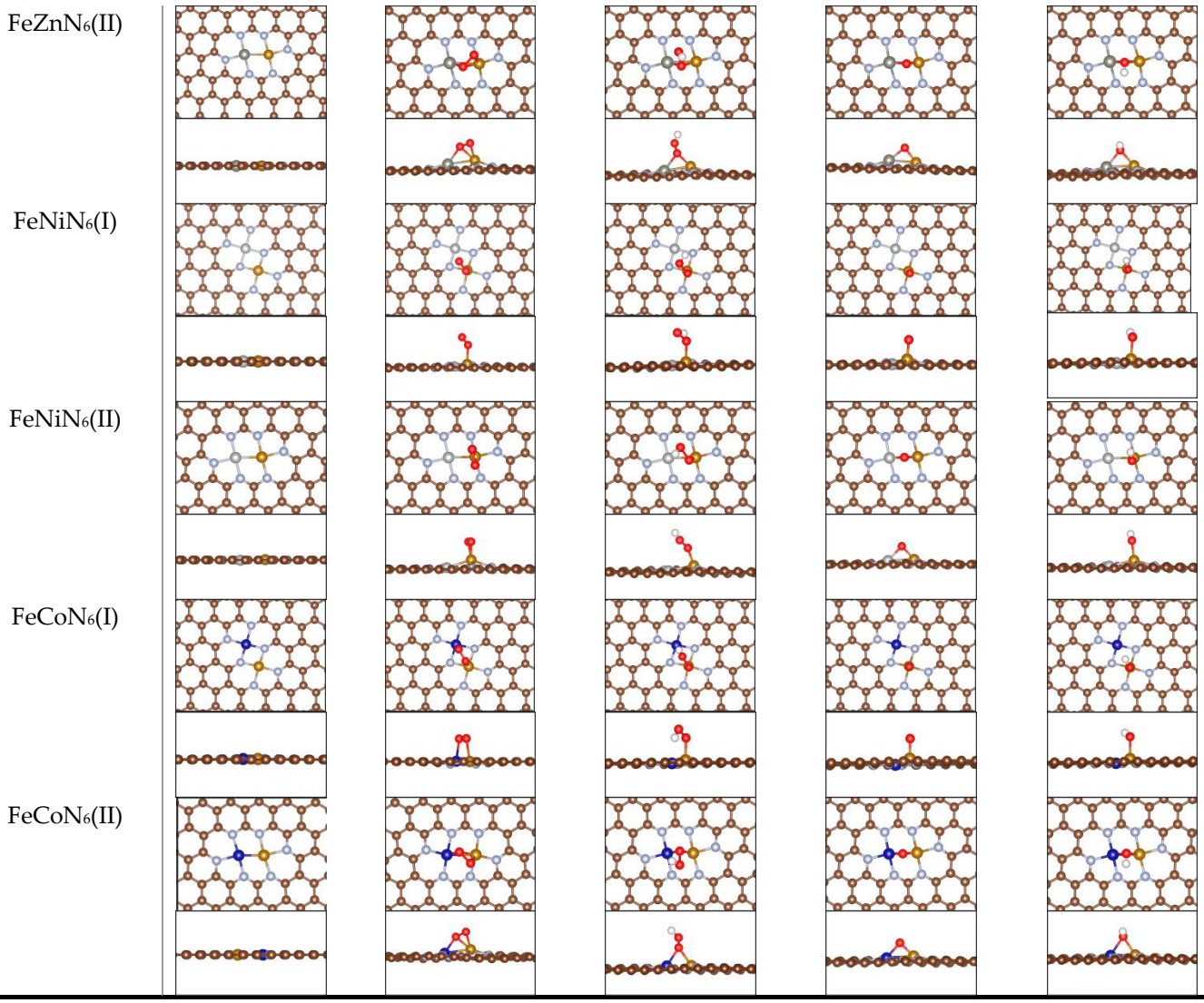

FeZnN6(II)
FeNiN6(I)
FeNiN6(II)
FeCoN6(I)
FeCoN6(II)

Table S2. The bond lengths of M1-M2 and $*O_2$. Adsorption energies of the O_2 with DMSCs.

DMSC	d_{M1-M2} (Å)	d_{M1-M2} (Å) $*O_2$	$*O_2$ (Å)	ΔE_{ads}(eV)
$FeCrN_6$(I)	2.26	2.27	1.40	−2.11
$FeCrN_6$(II)	2.41	2.57	1.49	−3.38
$FeCuN_6$(I)	2.47	2.50	1.30	−0.89
$FeCuN_6$(II)	2.41	2.49	1.38	−1.67
$FeMnN_6$(I)	2.28	2.26	1.40	−1.08
$FeMnN_6$(II)	2.35	2.39	1.43	−2.80
$FeMoN_6$(I)	2.31	2.45	1.49	−3.3
$FeMoN_6$(II)	2.11	2.27	1.46	−3.60
$FeOsN_6$(I)	2.31	2.33	1.32	−0.78
$FeOsN_6$(II)	2.19	2.36	1.40	−2.27
$FeReN_6$(I)	2.31	2.40	1.48	−2.18
$FeRhN_6$(I)	2.33	2.34	1.29	−0.67
$FeRhN_6$(II)	2.25	2.48	1.40	−1.60
$FeRuN_6$(I)	2.30	2.33	1.30	−0.82
$FeRuN_6$(II)	2.17	2.30	1.34	−1.60
$FeWN_6$(I)	2.32	1.92	1.51	−3.81
$FeIrN_6$(I)	2.33	2.35	1.29	−0.78
$FeIrN_6$(II)	2.26	2.48	1.43	−1.73
$FeZnN_6$(I)	2.54	2.55	1.36	−1.47
$FeZnN_6$(II)	2.41	2.62	1.44	−2.80
$FeNiN_6$(I)	2.48	2.48	1.29	−0.79
$FeNiN_6$(II)	2.30	2.43	1.39	−1.59
$FeCoN_6$(I)	2.48	2.46	1.29	−0.62
$FeCoN_6$(II)	2.18	2.53	1.38	−1.60

Table S3. Bader charge (in units of e). Q(Fe), Q(Other) refer to the charge on Fe, other transition metals to DMSCs.

DMSC	Q(Fe)	Q(Fe*O_2)	DMSC	Q(Fe)	Q(Fe*O_2)
Fe/Cr(I)	−1.11	−1.27	Fe/Cr(II)	−0.71	−1.04
Fe/Cu(I)	−1.21	−1.37	Fe/Cu(II)	−0.97	−1.23
Fe/Mn(I)	−1.04	−1.28	Fe/Mn(II)	−0.74	−1.08
Fe/Mo(I)	−1.01	−1.02	Fe/Mo(II)	−0.72	−0.85
Fe/Os(I)	−1.03	−1.02	Fe/Os(II)	−0.91	−1.11
Fe/Re(I)	−1.05	−1.02	--	--	--
Fe/Rh(I)	−1.10	−1.29	Fe/Rh(II)	−1.01	−1.18
Fe/Ru(I)	−0.95	−1.03	Fe/Ru(II)	−0.84	−1.14
Fe/W(I)	−0.95	−1.02	--	--	--
Fe/Ir(I)	−1.07	−1.28	Fe/Ir(II)	−0.90	−1.16
Fe/Zn(I)	−1.46	−1.60	Fe/Zn(II)	−0.74	−1.20
Fe/Ni(I)	−1.46	−1.58	Fe/Ni(II)	−0.90	−1.18
Fe/Co(I)	−1.05	−1.35	Fe/Co(II)	−2.35	−1.10

Table S4. Adsorption free energies (ΔG_{*ads}, eV) of the key ORR intermediate species associated with DMSCs.

DMSC	ΔG_{*OOH}	ΔG_{*O}	ΔG_{*OH}	η_{ORR}
$FeCrN_6$(I)	2.86	−0.20	−0.27	1.50
$FeCrN_6$(II)	−0.75	−1.42	−1.24	2.47
$FeCuN_6$(I)	3.82	1.73	0.75	0.48
$FeCuN_6$(II)	2.95	0.67	−0.12	1.35
$FeMnN_6$(I)	3.70	1.50	0.69	0.54
$FeMnN_6$(II)	2.82	−0.86	−0.94	2.17
$FeMoN_6$(I)	1.86	−1.69	−1.32	2.55
$FeMoN_6$(II)	3.30	−1.50	−1.05	2.28
$FeOsN_6$(I)	3.78	1.40	0.74	0.57
$FeOsN_6$(II)	3.36	−0.24	−0.34	1.57
$FeReN_6$(I)	2.89	−0.53	−0.25	1.51
$FeRhN_6$(I)	3.98	2.31	1.02	0.30
$FeRhN_6$(II)	3.19	0.46	0.28	1.05
$FeRuN_6$(I)	3.84	2.01	0.81	0.42
$FeRuN_6$(II)	2.85	0.06	−0.14	1.37
$FeWN_6$(I)	6.26	−2.09	−1.70	2.57
$FeIrN_6$(I)	3.95	2.41	1.03	0.26
$FeIrN_6$(II)	3.53	0.34	0.23	1.12
$FeZnN_6$(I)	3.96	2.05	0.82	0.41
$FeZnN_6$(II)	2.28	−0.44	−0.88	2.11
$FeNiN_6$(I)	3.52	3.11	0.53	0.70
$FeNiN_6$(II)	3.18	0.49	0.08	1.15
$FeCoN_6$(I)	4.03	2.23	1.07	0.34
$FeCoN_6$(II)	3.65	0.23	0.26	1.26

Table S5. O-O bond distance in $*O_2$, theoretical overpotential, half-wave potential ($E_{1/2}$) and onset potential (E_{onset}) in literature and this work.

catalysts	$E_{1/2}$	E_{onset}	η	d_{O-O}	Ref.
Fe-N-C	0.875V		0.79V		Energy Environ. Sci., 2022,15, 1601 [29]
Fe/Co-N-C				1.40Å	J. Am. Chem. Soc. 2017, 139, 17281 [26]
Fe/Cu-N-C		0.92V	0.38V	1.39Å	Adv. Funct. Mater. 2021, 31, 2006533 [22]
Fe/Ni-N-C	0.861V	1.005V			Applied Catalysis B: Environmental 2021, 285, 119778 [28]
Fe/Zn-N-C	0.906V		0.41V		Energy Environ. Sci., 2022,15, 1601 [29]
Co/Ni-N-C	0.76V	--	0.35V		Adv. Mater. 2019, 31, 1905622 [46]
Fe/Co-N-C			0.34V	1.29Å	
Fe/Ir-N-C			0.26V	1.29Å	
Fe/Ru-N-C			0.42V	1.40Å	This work
Fe/Rh-N-C			0.30V	1.29Å	
Fe/Os-N-C			0.57V	1.32Å	

Table S6. Structural evolution of electrochemical ORR for DMSCs with *H and 2*H, top view and side view.

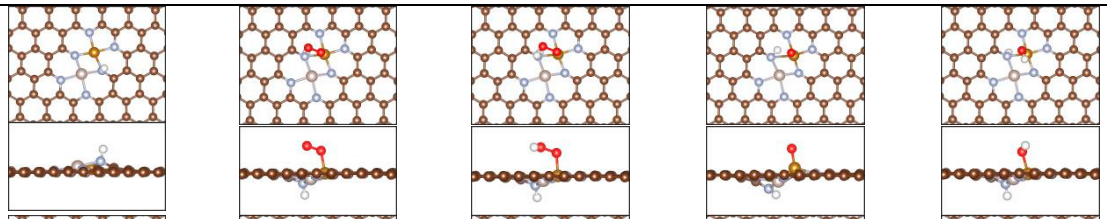
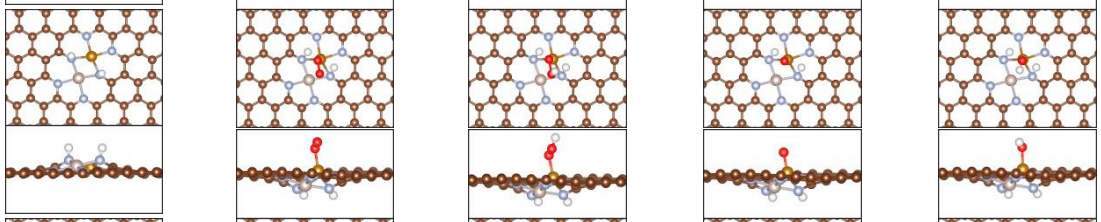
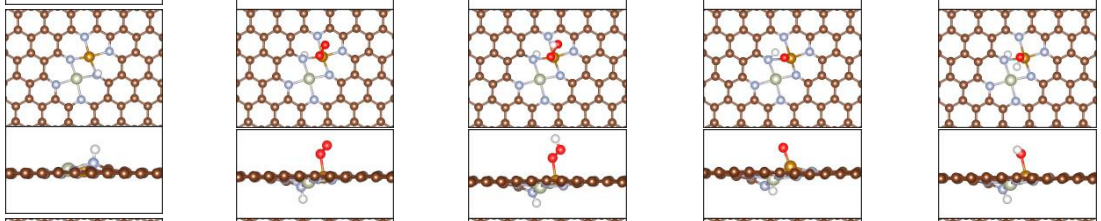
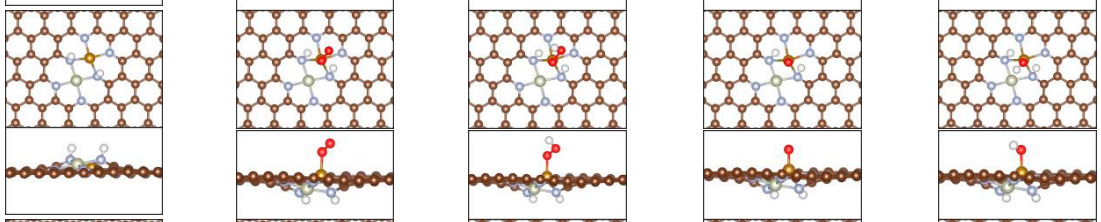
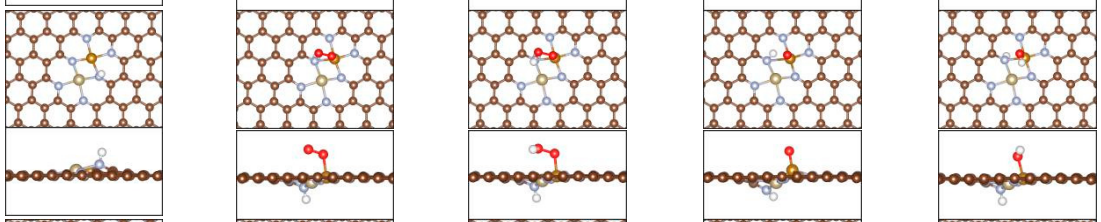
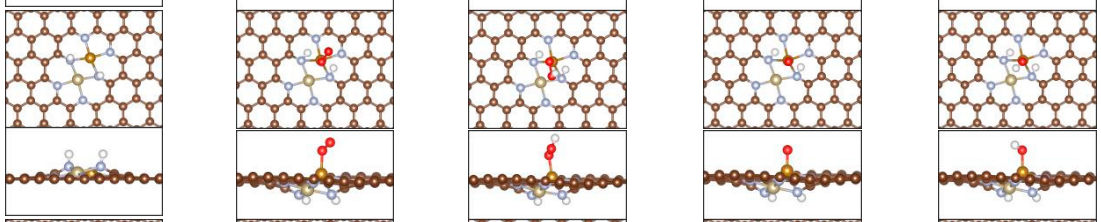
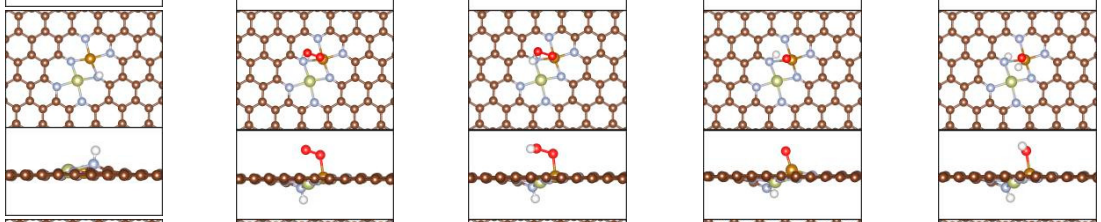
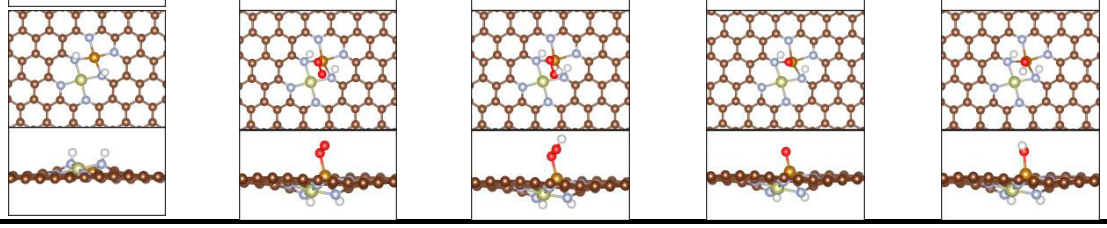
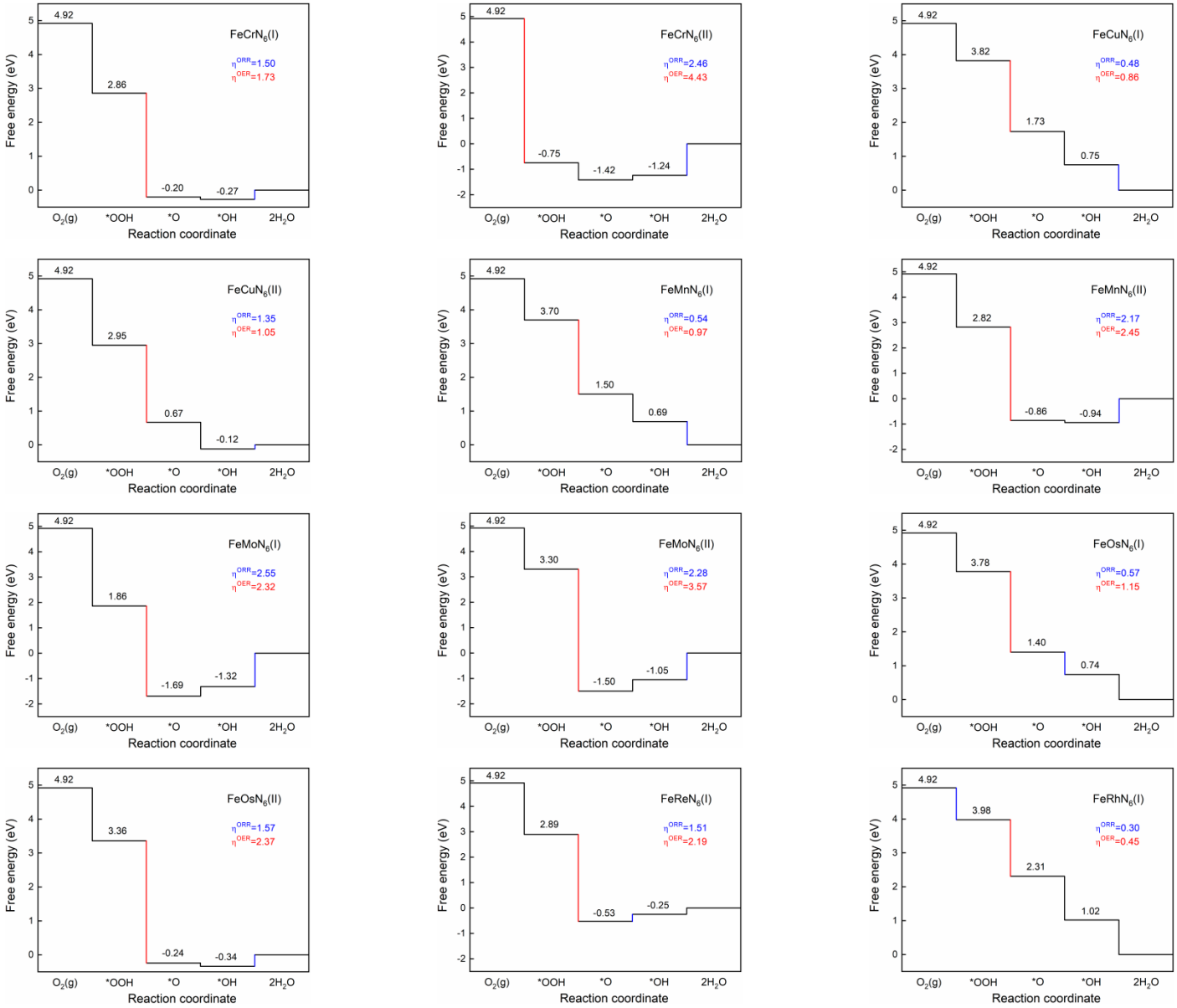
DMSC	CATA	$*O_2$	*OOH	*O	*OH
Fe/Ru(I)*H					
Fe/Ru(I)*2H					
Fe/Rh(I)*H					
Fe/Rh(I)*2H					
Fe/Os(I)*H					
Fe/Os(I)*2H					
Fe/Ir(I)*H					
Fe/Ir(I)*2H					

Table S7. Adsorption free energies (ΔG_{*ads}, eV) of the key ORR intermediate species for DMSCs with *H and 2*H.

DMSC	*OOH	*O	*OH	η
Fe/Ru(I)	3.84	2.01	0.81	0.42
Fe/Ru(I)*H	3.87	1.83	0.95	0.35
Fe/Ru(I) 2*H	3.53	1.37	0.33	0.90
Fe/Rh(I)	3.98	2.31	1.02	0.30
Fe/Rh(I)*H	3.76	1.59	0.68	0.54
Fe/Rh(I)2*H	3.28	1.30	0.02	1.21
Fe/Os(I)	3.78	1.40	0.74	0.57
Fe/Os(I)*H	3.79	1.73	0.88	0.38
Fe/Os(I)2*H	3.47	1.42	0.04	1.19
Fe/Ir(I)	3.95	2.41	1.03	0.26
Fe/Ir(I)*H	3.79	1.64	0.71	0.52
Fe/Ir(I)2*H	3.25	1.28	0.08	1.15



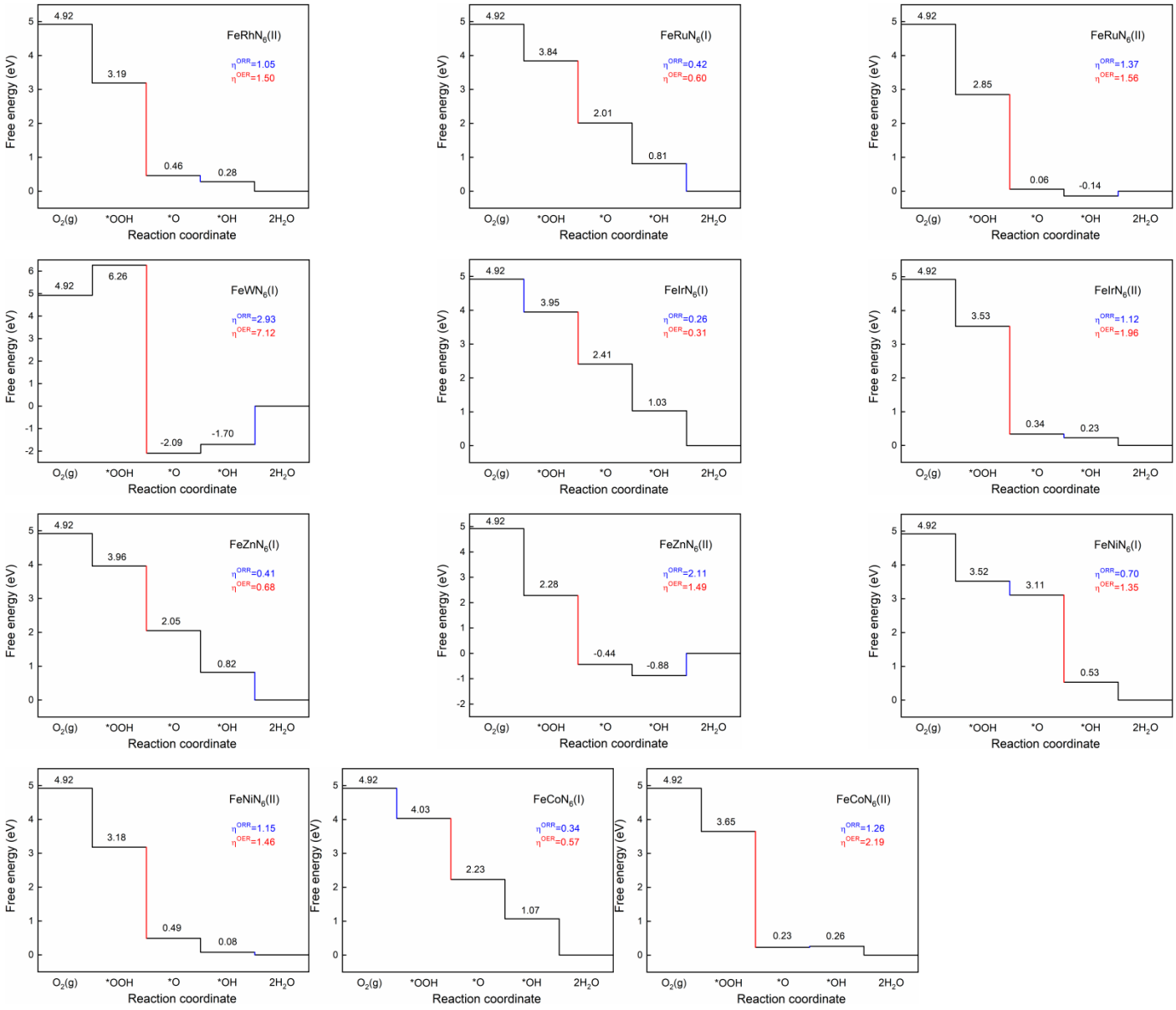


Figure S1. Gibbs free energy profiles for the designed catalysts.

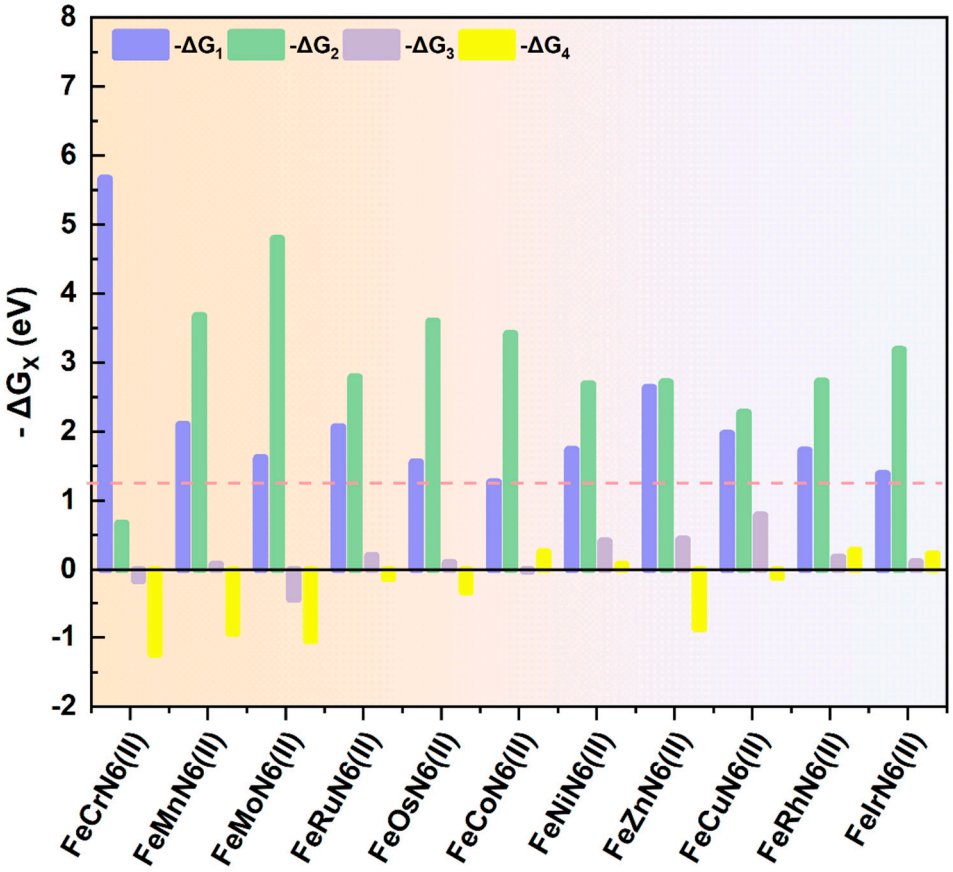


Figure S2. Free energy diagram for $FeTMN_6$(II) (TM = Cr, Mn, Mo, Ru, W, Re, Os, Co, Ni, CuRe, Os, Co, Ni, Cu, Zn, Rh and Ir) moieties.

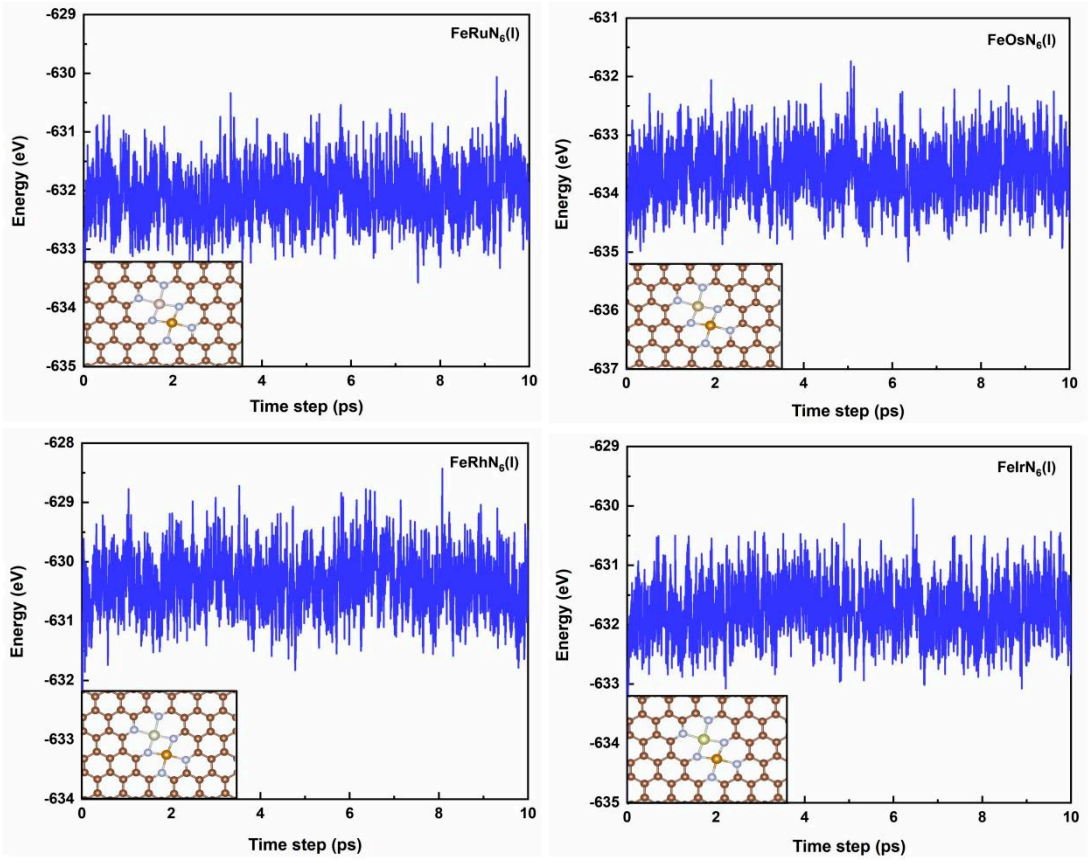


Figure S3. Energy evolution at 300 K for $FeRuN_6$(I), $FeOsN_6$(I), $FeRhN_6$(I), and $FeIrN_6$(I).