Axial Coordination Modification of $M-N_4$ Single-Atom Catalysts to Regulate the Electrocatalytic CO_2 Reduction Reaction

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Catalyst models. Experimentally, various carbon-based conductive substrates, such as carbon nanotubes, graphene and amorphous or porous carbon have emerged as the supporting substrate to synthesize single-metal-atom catalysts. Especially, due to the strong binding with metal atoms and high electronic conductivity, the nitrogen-doped graphene is deemed as one of the most appealing substrates to stabilize single-metal-atom catalysts. In our work, a 5 × 5 × 1 supercell of graphene (lateral dimension of a = b =12.3 Å) with one doped metal that coordinated by four N atoms and one axial ligand L (-OH, $-CH_3$, $-SCH_2CH_3$, $-P(C_6H_5)_3$, -COOH, $-NH_2$, $-C{\equiv}CC_6H_5$, $-C_6H_7O_7$, $-NHC^{Me}$) is constructed to build the $M-N_4L$/Gra electrocatalysts (M = Fe, Co, Ni) (Figure 1a and 1b). Ultimately, a total of 30 catalyst structures with different metal centers and axial ligands are constructed (including the pristine pure $M-N_4$ structure without axial modification).

The optimized geometries of the 30 structural models are shown in Figure S1. One can see that the examined ligands are all chemically bonded to the Fe, Co and Ni center except for Ni-N_4[P(C_6H_5)$_3$]/Gra and Ni-N_4[NHC^{Me}]/Gra, where the neutral phosphine and NHC^{Me} ligands are physically interacted with the Ni atom. The bonding distance between the metal atom and the ligated atom (e.g., C, N, O, S, P) as well as the Bader charge carried by the central metal are listed in Table S1. In general, the bonding distances between metal and the ligands have the order of Ni (1.903 ~ 2.413Å) > Co (1.829 ~ 2.300Å) > Fe (1.817 ~ 2.169Å) (in some specific ligands such as -CH_3, -COOH, -$C_6H_7O_7$, the bonding distance with Fe is larger than Co). Moreover, the atomic charge of the metal center is greatly affected by the ligand functionalization. From the Bader charge analysis, the Ni atom bears more positive charge (+0.845 ~ +1.021 |*e*|) in Ni-N_4L/Gra compared to the Ni-N_4/Gra (+0.834 |*e*|) (Table S1). This indicates that the added axial ligands tend to attract the electron from the Ni atom, and the electron withdrawing becomes more evident for the -OH, -$C_6H_7O_7$, -NH_2 and -C≡CC_6H_5 groups. By contrast, most of the ligand functionalized Co atom carries much less positive charge (+0.816 ~ +1.063 |*e*|) than the Co atom in Co-N_4/Gra (+1.157 |*e*|), indicating that the ligand would donate electron to the Co center. An exception case is the -NH_2 functionalized Co, which carries a slightly higher positive charge (+1.202 |*e*|) and suggests that -NH_2 acts as an electron acceptor in this case. The atomic charge of Fe in Fe-N_4L/Gra systems is dramatically affected. The Fe center functionalized by -CH_3 (+1.219 |*e*|), -SCH_2CH_3 (+1.169 |*e*|), -P(C_6H_5)$_3$ (+0.842 |*e*|), -COOH (+1.382 |*e*|), and -$C_6H_7O_7$ (+1.339 |*e*|) is found to have much less positive charge than the pure Fe-N_4/Gra (+1.960 |*e*|), while the Fe atom bears magnitude of higher positive charge after modification by -OH (+3.612 |*e*|), $-NH_2$ (+3.642 |*e*|), $-C{\equiv}CC_6H_5$ (+2.935 |*e*|), and -NHC^{Me} (+3.638 |*e*|). The induced changes in the charge of the central metal imply that the introduction of axial ligands can greatly modulate the electronic structure of the active center and the CO_2RR catalytic performance would be intuitively affected. In our subsequent section, we will focus on the electrocatalytic performance of the designed M-N_4L/Gra structures.

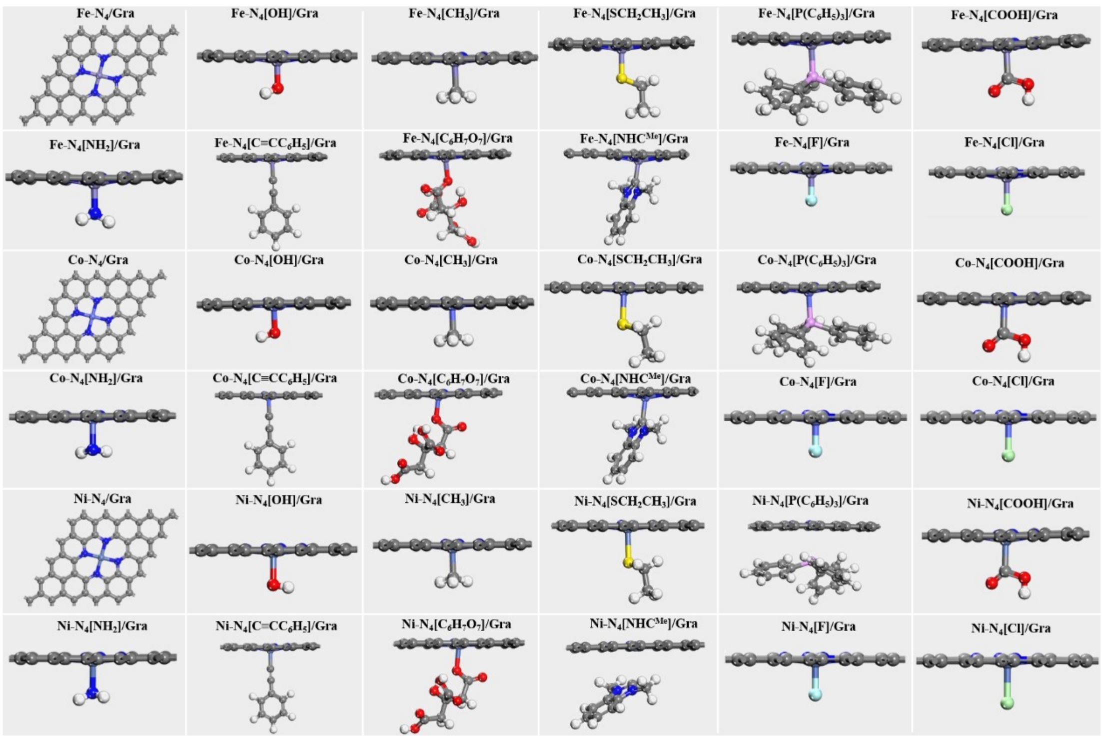


Figure S1. The optimized structures of the pure M-N_4/Gra (top view) and the ligand modified M-N_4L/Gra (side view) (M = Fe, Co, Ni) structures.

Table S1. The bonding distance (Å) between the central metal atom (Fe, Co, Ni) and the terminal atom (e.g., C, N, O, S, P, F, Cl) from the axial ligands. Here "q" stands for the charge carried by the central metal atom.

	Fe-N_4[L]/Gra	**Co-N_4[L]/Gra**	**NiN_4/[L]/Gra**

	d (Å)	q (*e*)	d (Å)	q (*e*)	d (Å)	q (*e*)
Pure		+1.960		+1.157		+0.834
-OH	1.817	+3.612	1.868	+1.053	2.000	+1.021
-CH_3	1.982	+1.219	1.958	+0.984	1.993	+0.907
-SCH_2CH_3	2.150	+1.169	2.216	+1.059	2.413	+0.860
-$P(C_6H_5)_3$	2.169	+0.842	2.300	+0.816	3.007	+0.845
-COOH	1.910	+1.382	1.889	+1.063	1.948	+0.897
-NH_2	1.838	+3.642	1.920	+1.202	2.075	+0.976
-C≡CC_6H_5	1.824	+2.935	1.829	+0.964	1.903	+0.936
-$C_6H_7O_7$	1.929	+1.339	1.927	+1.058	2.123	+0.989
-NHC^{Me}	1.910	+3.638	2.096	+0.920	3.014	+0.863
-F	1.822	+3.581	1.840	+1.218	1.957	+1.048
-Cl	2.196	+2.225	2.208	+1.056	2.361	+0.955

Table S2. The adsorption energies (eV) of *CO_2, *COOH and *CO on M-N_4L/Gra systems.

Species	E_{ads}(*CO_2)	E_{ads}(*COOH)	E_{ads}(*CO)
Fe-N_4/Gra	-0.29	-0.37	-1.27
Fe-N_4[OH]/Gra	-0.33	0.14	-0.64
Fe-N_4[CH_3]/Gra	-0.31	0.39	-0.43
Fe-N_4[SCH_2CH_3]/Gra	-0.32	0.32	-0.36
Fe-N_4[$P(C_6H_5)_3$]/Gra	-0.33	0.08	-0.61

$Fe-N_4[COOH]/Gra$	-0.34	0.37	-0.48
$Fe-N_4[NH_2]/Gra$	-0.31	0.24	-0.44
$Fe-N_4[C{\equiv}CC_6H_5]/Gra$	-0.31	0.36	-0.55
$Fe-N_4[C_6H_7O_7]/Gra$	-0.31	-0.07	-1.02
$Fe-N_4[NHC^{Me}]/Gra$	-0.34	0.18	-0.51
$Fe-N_4[F]/Gra$	-0.40	0.10	-0.92
$Fe-N_4[Cl]/Gra$	-0.34	0.27	-0.82
$Co-N_4/Gra$	-0.34	-0.58	-0.56
$Co-N_4[OH]/Gra$	-0.32	-0.12	-0.38
$Co-N_4[CH_3]/Gra$	-0.32	0.34	-0.01
$Co-N_4[SCH_2CH_3]/Gra$	-0.32	0.11	-0.01
$Co-N_4[P(C_6H_5)_3]/Gra$	-0.36	-0.09	0.17
$Co-N_4[COOH]/Gra$	-0.31	0.35	0.12
$Co-N_4[NH_2]/Gra$	-0.31	0.08	-0.2
$Co-N_4[C{\equiv}CC_6H_5]/Gra$	-0.31	0.17	0.00
$Co-N_4[C_6H_7O_7]/Gra$	-0.32	-0.37	-0.31
$Co-N_4[NHC^{Me}]/Gra$	-0.36	-0.14	0.18
$Co-N_4[F]/Gra$	-0.32	-0.27	-0.52
$Co-N_4[Cl]/Gra$	-0.33	-0.11	-0.17
$Ni-N_4/Gra$	-0.33	0.82	0.24
$Ni-N_4[OH]/Gra$	-0.33	0.31	0.23
$Ni-N_4[CH_3]/Gra$	-0.34	0.44	0.21

Ni-N_4[SCH_2CH_3]/Gra	-0.34	0.52	0.22
Ni-N_4[$P(C_6H_5)_3$]/Gra	-0.35	0.79	0.2
Ni-N_4[COOH]/Gra	-0.34	0.45	0.22
Ni-N_4[NH_2]/Gra	-0.34	0.36	0.22
Ni-N_4[$C \equiv CC_6H_5$]/Gra	-0.34	0.37	0.21
Ni-N_4[$C_6H_7O_7$]/Gra	-0.33	0.49	0.23
Ni-N_4[NHC^{Me}]/Gra	-0.52	0.64	0.01
Ni-N_4[F]/Gra	-0.24	0.38	0.21
Ni-N_4[Cl]/Gra	-0.34	0.63	0.23

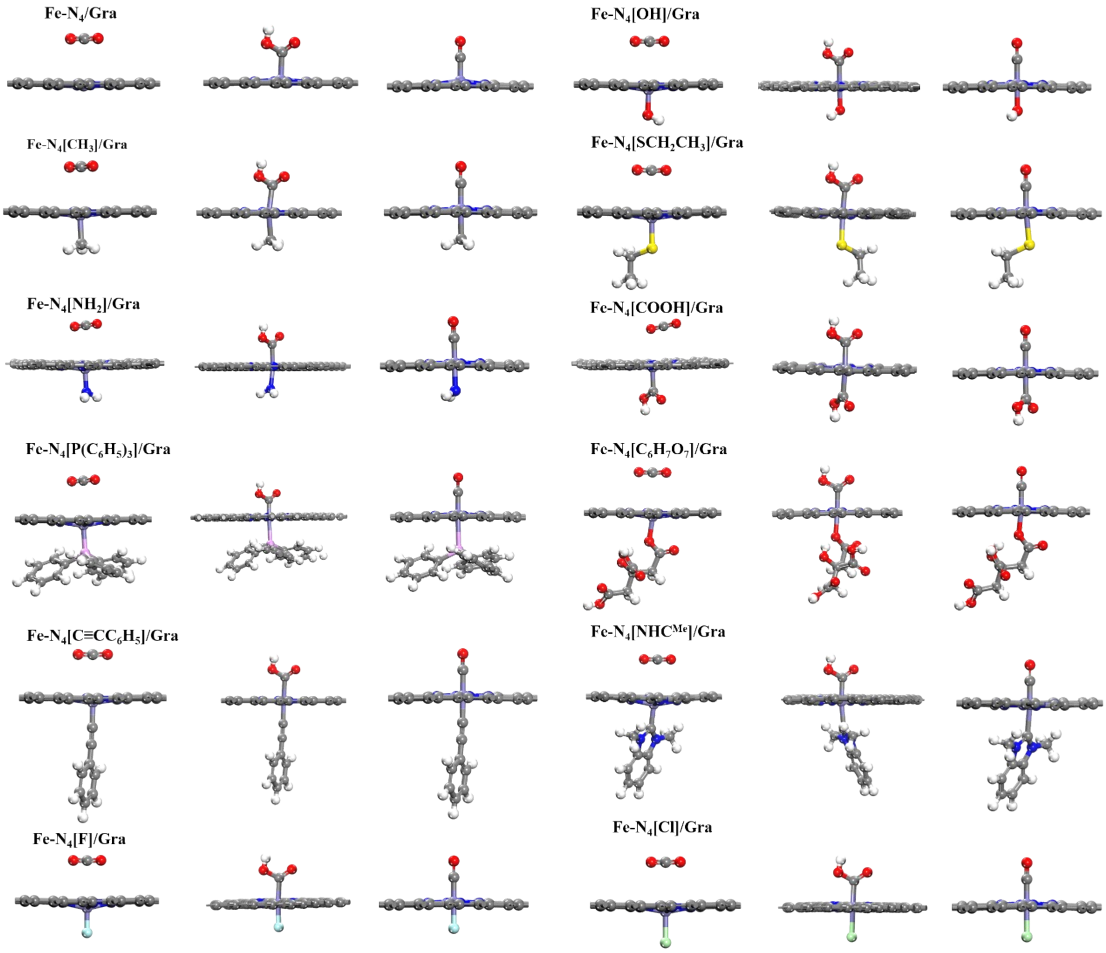


Figure S2. The most stable structures of $*CO_2$, *COOH and *CO adsorbed on Fe-N_4L/Gra.

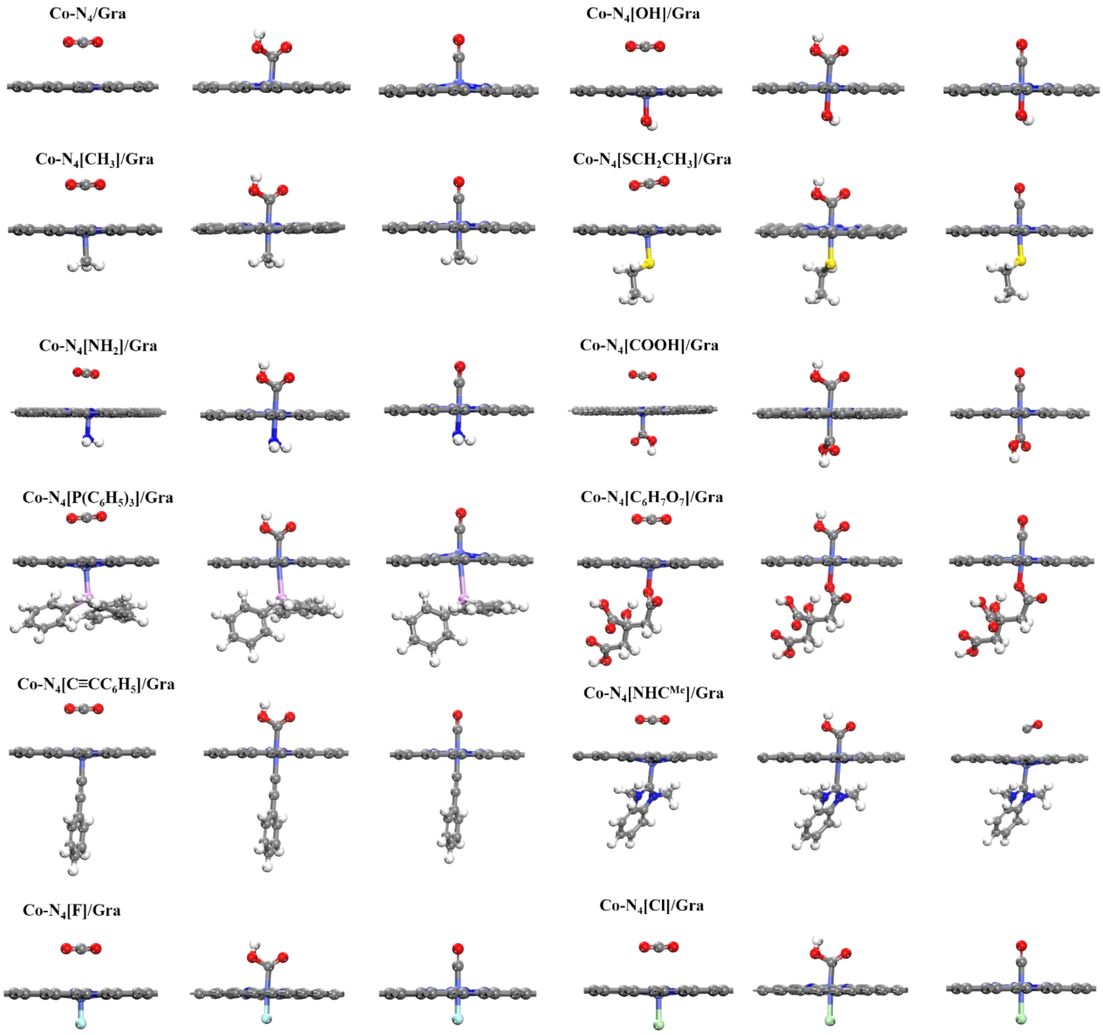


Figure S3. The most stable structures of $*CO_2$, *COOH and *CO adsorbed on $Co\text{-}N_4L/Gra$.

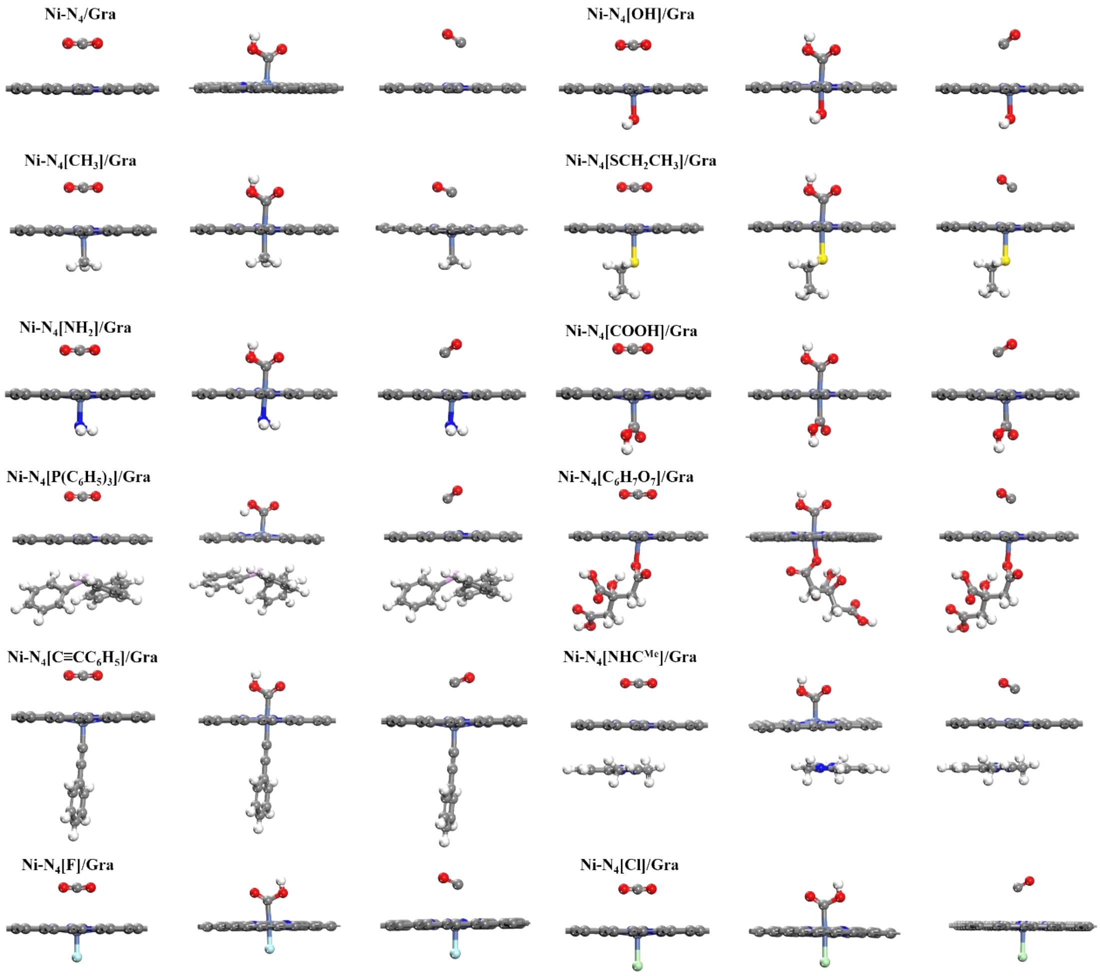


Figure S4. The most stable structures of $*CO_2$, *COOH and *CO adsorbed on Ni-N_4L/Gra.

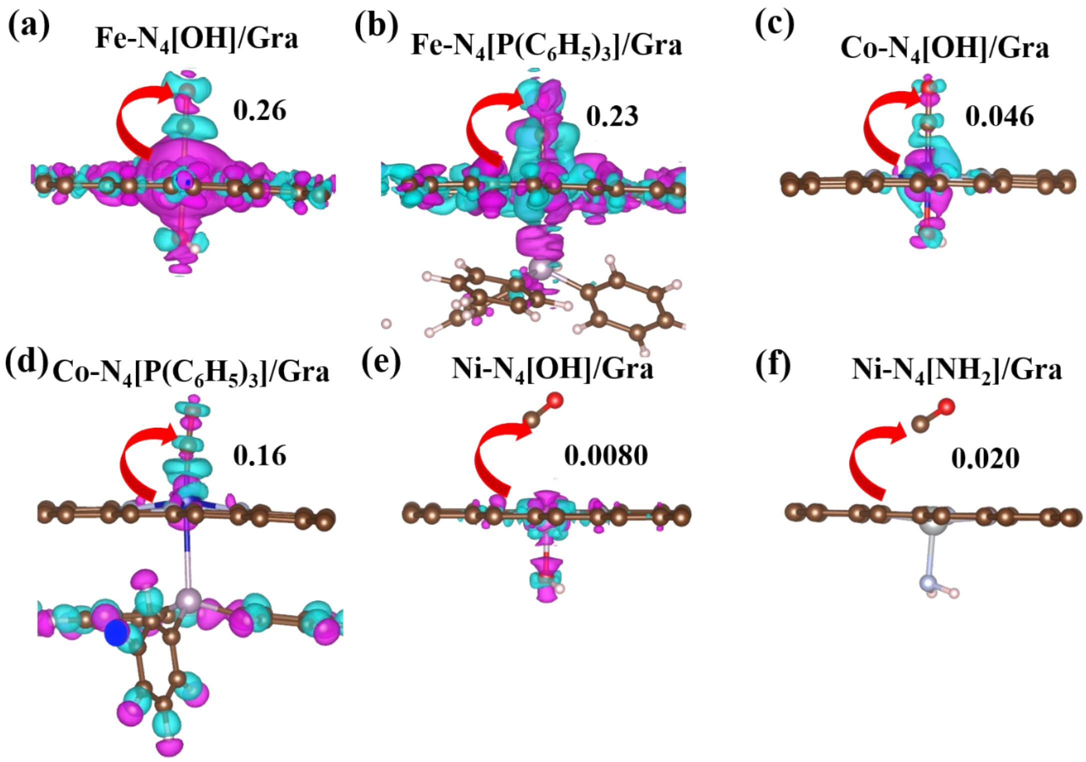


Figure S5. The charge density difference of CO adsorption over Fe-N_4[OH]/Gra (a), Fe-N_4[P(C_6H_5)$_3$]/Gra (b), Co-N_4[OH]/Gra (c), Co-N_4[P(C_6H_5)$_3$]/Gra (d), Ni-N_4[OH]/Gra (e), and Ni-N_4[NH_2]/Gra (f), with isosurface level of 0.005 e Å^{-3}. The cyan and magenta region represents electron depletion and accumulation, respectively.

Table S3. The detailed electronic energy (E_*, eV), zero-point energy (E_{ZPE}, eV), entropy corrections (TS, eV), and free energy (G, eV) of critical intermediate (*CO_2, *COOH, *CO, *H) in M-N_4L/Gra systems during electrochemical CO_2RR.

Species	E_{*CO_2}	E_{ZPE}	TS	G_{*CO_2}
Fe-N_4/Gra	-471.17	0.31	0.23	-471.09
FeN_4[OH]/Gra	-481.82	0.32	0.17	-481.67
Fe-N_4[CH_3]/Gra	-491.29	0.31	0.19	-491.16
Fe-N_4[SCH_2CH_3]/Gra	-512.75	0.31	0.19	-512.63
Fe-N_4[P(C_6H_5)$_3$]/Gra	-695.37	0.31	0.18	-695.24

Fe-N_4[COOH]/Gra	-497.88	0.32	0.18	-497.74
Fe-N_4[NH_2]/Gra	-486.96	0.31	0.19	-486.83
Fe-N_4[C≡CC_6H_5]/Gra	-560.01	0.32	0.30	-560.00
Fe-N_4[$C_6H_7O_7$]/Gra	-600.20	0.32	0.24	-600.13
Fe-N_4[NHC]/Gra	-606.24	0.31	0.13	-606.06
Fe-N_4[F]/Gra	-475.88	0.32	0.23	-475.79
Fe-N_4[Cl]/Gra	-474.52	0.32	0.24	-474.44
Co-N_4/Gra	-470.20	0.31	0.17	-470.06
Co-N_4[OH]/Gra	-480.36	0.32	0.23	-480.27
Co-N_4[CH_3]/Gra	-490.33	0.31	0.12	-490.14
Co-N_4[SCH_2CH_3]/Gra	-511.43	0.31	0.12	-511.24
Co-N_4[P(C_6H_5)$_3$]/Gra	-694.18	0.31	0.13	-693.99
Co-N_4[COOH]/Gra	-496.91	0.31	0.07	-496.66
Co-N_4[NH_2]/Gra	-485.62	0.32	0.18	-485.48
Co-N_4[C≡CC_6H_5]/Gra	-558.86	0.31	0.19	-558.73
Co-N_4[$C_6H_7O_7$]/Gra	-598.98	0.31	0.06	-598.74
Co-N_4[NHC]/Gra	-604.92	0.31	0.18	-604.78
Co-N_4[F]/Gra	-474.34	0.31	0.18	-474.21
Co-N_4[Cl]/Gra	-473.25	0.31	0.12	-473.07
Ni-N_4/Gra	-468.95	0.31	0.18	-468.82
Ni-N_4[OH]/Gra	-478.16	0.31	0.19	-478.03
Ni-N_4[CH_3]/Gra	-487.79	0.32	0.18	-487.65
Ni-N_4[SCH_2CH_3]/Gra	-509.17	0.31	0.18	-509.04
Ni-N_4[P(C_6H_5)$_3$]/Gra	-692.32	0.31	0.20	-692.21
Ni-N_4[COOH]/Gra	-494.29	0.32	0.17	-494.14
Ni-N_4[NH_2]/Gra	-483.27	0.31	0.12	-483.09
Ni-N_4[C≡CC_6H_5]/Gra	-556.29	0.32	0.28	-556.25
Ni-N_4[$C_6H_7O_7$]/Gra	-597.06	0.31	0.12	-596.87
Ni-N_4[NHC]/Gra	-603.27	0.31	0.18	-603.14
Ni-N_4[F]/Gra	-472.33	0.31	0.19	-472.20
Ni-N_4[Cl]/Gra	-471.27	0.31	0.14	-471.09
	E_{*COOH}	E_{ZPE}	TS	$G_{(*COOH)}$
Fe-N_4/Gra	-474.63	0.63	0.14	-474.14
FeN_4[OH]/Gra	-484.73	0.61	0.17	-484.29
Fe-N_4[CH_3]/Gra	-493.97	0.60	0.07	-493.44
Fe-N_4[SCH_2CH_3]/Gra	-515.50	0.61	0.17	-515.06
Fe-N_4[P(C_6H_5)$_3$]/Gra	-698.34	0.60	0.19	-697.93
Fe-N_4[COOH]/Gra	-500.55	0.60	0.13	-500.09
Fe-N_4[NH_2]/Gra	-489.79	0.61	0.13	-489.31
Fe-N_4[C≡CC_6H_5]/Gra	-562.72	0.61	0.14	-562.25
Fe-N_4[$C_6H_7O_7$]/Gra	-603.35	0.60	0.14	-602.89
Fe-N_4[NHC]/Gra	-609.11	0.63	0.05	-608.53
Fe-N_4[F]/Gra	-478.86	0.61	0.16	-478.41

$Fe-N_4[Cl]/Gra$	-477.39	0.60	0.12	-476.91
$Co-N_4/Gra$	-473.82	0.62	0.11	-473.32
$Co-N_4[OH]/Gra$	-483.54	0.61	0.11	-483.04
$Co-N_4[CH_3]/Gra$	-493.05	0.62	0.22	-492.65
$Co-N_4[SCH_2CH_3]/Gra$	-514.38	0.62	0.16	-513.91
$Co-N_4[P(C_6H_5)_3]/Gra$	-697.29	0.64	0.21	-696.87
$Co-N_4[COOH]/Gra$	-499.63	0.62	0.16	-499.17
$Co-N_4[NH_2]/Gra$	-488.61	0.62	0.17	-488.16
$Co-N_4[C{\equiv}CC_6H_5]/Gra$	-561.76	0.62	0.17	-561.31
$Co-N_4[C_6H_7O_7]/Gra$	-602.41	0.62	0.11	-601.90
$Co-N_4[NHC]/Gra$	-608.08	0.63	0.16	-607.60
$Co-N_4[F]/Gra$	-477.78	0.62	0.15	-477.31
$Co-N_4[Cl]/Gra$	-476.52	0.62	0.16	-476.05
$Ni-N_4/Gra$	-471.18	0.61	0.19	-470.76
$Ni-N_4[OH]/Gra$	-480.90	0.62	0.16	-480.43
$Ni-N_4[CH_3]/Gra$	-490.40	0.61	0.17	-489.96
$Ni-N_4[SCH_2CH_3]/Gra$	-511.68	0.62	0.16	-511.23
$Ni-N_4[P(C_6H_5)_3]/Gra$	-694.56	0.62	0.16	-694.10
$Ni-N_4[COOH]/Gra$	-496.88	0.61	0.16	-496.43
$Ni-N_4[NH_2]/Gra$	-485.95	0.62	0.22	-485.56
$Ni-N_4[C{\equiv}CC_6H_5]/Gra$	-558.96	0.63	0.15	-558.49
$Ni-N_4[C_6H_7O_7]/Gra$	-599.63	0.62	0.11	-599.11
$Ni-N_4[NHC]/Gra$	-605.48	0.60	0.12	-605.01
$Ni-N_4[F]/Gra$	-475.09	0.63	0.22	-474.68
$Ni-N_4[Cl]/Gra$	-473.78	0.64	0.19	-472.33
	E_{*CO}	E_{ZPE}	TS	$G_{(*CO)}$
$Fe-N_4/Gra$	-464.47	0.21	0.09	-464.35
$FeN_4[OH]/Gra$	-474.45	0.21	0.09	-474.32
$Fe-N_4[CH_3]/Gra$	-483.73	0.21	0.09	-483.61
$Fe-N_4[SCH_2CH_3]/Gra$	-505.11	0.21	0.08	-504.98
$Fe-N_4[P(C_6H_5)_3]/Gra$	-687.97	0.22	0.13	-687.89
$Fe-N_4[COOH]/Gra$	-490.34	0.21	0.08	-490.21
$Fe-N_4[NH_2]/Gra$	-479.41	0.22	0.08	-479.27
$Fe-N_4[C{\equiv}CC_6H_5]/Gra$	-552.57	0.21	0.08	-552.43
$Fe-N_4[C_6H_7O_7]/Gra$	-593.24	0.22	0.07	-593.09
$Fe-N_4[NHC]/Gra$	-598.73	0.22	0.07	-598.58
$Fe-N_4[F]/Gra$	-468.72	0.22	0.07	-468.57
$Fe-N_4[Cl]/Gra$	-467.31	0.22	0.07	-467.16
$Co-N_4/Gra$	-462.74	0.18	0.05	-462.62
$Co-N_4[OH]/Gra$	-472.74	0.21	0.09	-472.62
$Co-N_4[CH_3]/Gra$	-482.34	0.20	0.04	-482.18
$Co-N_4[SCH_2CH_3]/Gra$	-503.44	0.21	0.10	-503.33
$Co-N_4[P(C_6H_5)_3]/Gra$	-685.97	0.18	0.06	-685.85

Co-N_4[COOH]/Gra	-488.80	0.20	0.10	-488.70
Co-N_4[NH_2]/Gra	-477.83	0.21	0.10	-477.72
Co-N_4[C≡CC_6H_5]/Gra	-550.87	0.21	0.10	-550.76
Co-N_4[$C_6H_7O_7$]/Gra	-591.29	0.22	0.14	-591.20
Co-N_4[NHC]/Gra	-596.70	0.15	0.20	-596.74
Co-N_4[F]/Gra	-466.87	0.22	0.14	-466.79
Co-N_4[Cl]/Gra	-465.41	0.22	0.09	-465.28
Ni-N_4/Gra	-460.70	0.15	0.23	-460.78
Ni-N_4[OH]/Gra	-469.91	0.14	0.16	-469.92
Ni-N_4[CH_3]/Gra	-479.56	0.15	0.12	-479.53
Ni-N_4[SCH_2CH_3]/Gra	-500.92	0.15	0.14	-500.91
Ni-N_4[P(C_6H_5)$_3$]/Gra	-684.09	0.15	0.14	-684.08
Ni-N_4[COOH]/Gra	-486.05	0.15	0.22	-486.13
Ni-N_4[NH_2]/Gra	-475.04	0.14	0.16	-475.06
Ni-N_4[C≡CC_6H_5]/Gra	-548.06	0.15	0.27	-548.18
Ni-N_4[$C_6H_7O_7$]/Gra	-588.82	0.15	0.14	-588.82
Ni-N_4[NHC]/Gra	-595.05	0.16	0.24	-595.13
Ni-N_4[F]/Gra	-464.10	0.15	0.19	-464.14
Ni-N_4[Cl]/Gra	-463.01	0.15	0.19	-463.06
	E_{*H}	E_{ZPE}	TS	$G_{(*H)}$
Fe-N_4/Gra	-451.34	0.24	0.00	-451.10
FeN_4[OH]/Gra	-461.44	0.16	0.00	-461.28
Fe-N_4[CH_3]/Gra	-470.76	0.19	0.01	-470.58
Fe-N_4[SCH_2CH_3]/Gra	-491.58	0.15	0.01	-491.43
Fe-N_4[P(C_6H_5)$_3$]/Gra	-675.04	0.16	0.00	-674.88
Fe-N_4[COOH]/Gra	-477.32	0.20	0.01	-477.12
Fe-N_4[NH_2]/Gra	-466.53	0.21	0.01	-466.33
Fe-N_4[C≡CC_6H_5]/Gra	-539.42	0.18	0.01	-539.25
Fe-N_4[$C_6H_7O_7$]/Gra	-580.11	0.14	0.00	-579.97
Fe-N_4[NHC]/Gra	-585.84	0.09	0.01	-585.75
Fe-N_4[F]/Gra	-455.62	0.25	0.00	-455.37
Fe-N_4[Cl]/Gra	-454.23	0.15	0.00	-454.08
Co-N_4/Gra	-450.45	0.21	0.01	-450.25
Co-N_4[OH]/Gra	-460.19	0.21	0.01	-459.98
Co-N_4[CH_3]/Gra	-469.62	0.19	0.01	-469.43
Co-N_4[SCH_2CH_3]/Gra	-491.04	0.21	0.01	-490.84
Co-N_4[P(C_6H_5)$_3$]/Gra	-674.06	0.23	0.00	-673.83
Co-N_4[COOH]/Gra	-476.23	0.20	0.01	-476.04
Co-N_4[NH_2]/Gra	-465.25	0.21	0.01	-465.05
Co-N_4[C≡CC_6H_5]/Gra	-538.37	0.21	0.01	-538.17
Co-N_4[$C_6H_7O_7$]/Gra	-579.11	0.23	0.00	-578.89
Co-N_4[NHC]/Gra	-584.83	0.24	0.00	-584.60
Co-N_4[F]/Gra	-454.45	0.22	0.01	-454.23

$Co-N_4[Cl]/Gra$	-453.20	0.22	0.01	-452.99
$Ni-N_4/Gra$	-447.78	0.13	0.01	-447.66
$Ni-N_4[OH]/Gra$	-457.68	0.22	0.00	-457.46
$Ni-N_4[CH_3]/Gra$	-467.06	0.20	0.01	-466.86
$Ni-N_4[SCH_2CH_3]/Gra$	-488.43	0.21	0.01	-488.23
$Ni-N_4[P(C_6H_5)_3]/Gra$	-671.19	0.16	0.01	-671.04
$Ni-N_4[COOH]/Gra$	-473.60	0.21	0.01	-473.39
$Ni-N_4[NH_2]/Gra$	-462.69	0.21	0.01	-462.48
$Ni-N_4[C{\equiv}CC_6H_5]/Gra$	-535.73	0.24	0.01	-535.50
$Ni-N_4[C_6H_7O_7]/Gra$	-576.48	0.23	0.01	-576.26
$Ni-N_4[NHC]/Gra$	-581.95	0.08	0.01	-581.87
$Ni-N_4[F]/Gra$	-451.92	0.23	0.00	-451.69
$Ni-N_4[Cl]/Gra$	-450.61	0.21	0.01	-450.41

Table S4. The detailed electronic energy (E_*, eV), zero-point energy (E_{ZPE}, eV), entropy corrections (TS, eV), and free energy (G, eV) of isolated molecule during electrochemical CO_2RR.

Species	E_*	E_{ZPE}	TS	G
CO_2	-22.96	0.31	0.66	-23.31
H_2	-6.76	0.27	0.40	-6.89
CO	-14.84	0.13	0.61	-15.32
H_2O	-14.25	0.59	0.58	-14.24

Table S5. The free energy change (eV) of the four elementary reaction steps (ΔG_1, ΔG_2, ΔG_3, ΔG_4) of CO_2RR and the adsorption Gibbs free energy of H (ΔG_H) on the M-N_4L/Gra systems.

	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔG_H
$Fe-N_4/Gra$	0.14	0.15	-1.10	0.66	0.38
$FeN_4[OH]/Gra$	0.17	0.58	-0.91	0.03	0.79
$Fe-N_4[CH_3]/Gra$	0.17	0.92	-1.06	-0.17	1.00
$Fe-N_4[SCH_2CH_3]/Gra$	0.16	0.77	-0.81	-0.25	1.59
$Fe-N_4[P(C_6H_5)_3]/Gra$	0.15	0.51	-0.84	0.04	0.75
$Fe-N_4[COOH]/Gra$	0.15	0.86	-1.01	-0.14	1.01
$Fe-N_4[NH_2]/Gra$	0.17	0.71	-0.84	-0.18	0.92
$Fe-N_4[C{\equiv}CC_6H_5]/Gra$	0.05	0.95	-1.07	-0.07	1.04
$Fe-N_4[C_6H_7O_7]/Gra$	0.11	0.44	-1.09	0.39	0.51
$Fe-N_4[NHC^{Me}]/Gra$	0.20	0.73	-0.94	-0.12	0.74
$Fe-N_4[F]/Gra$	0.04	0.58	-1.05	0.29	0.70
$Fe-N_4[Cl]/Gra$	0.09	0.73	-1.15	0.19	0.68

Co-N_4/Gra	0.15	-0.06	-0.19	-0.04	0.20
Co-N_4[OH]/Gra	0.12	0.43	-0.47	-0.22	0.65
Co-N_4[CH_3]/Gra	0.22	0.68	-0.41	-0.63	1.17
Co-N_4[SCH_2CH_3]/Gra	0.22	0.52	-0.30	-0.58	0.85
Co-N_4[$P(C_6H_5)_3$]/Gra	0.18	0.32	0.13	-0.77	0.58
Co-N_4[COOH]/Gra	0.28	0.69	-0.42	-0.70	1.15
Co-N_4[NH_2]/Gra	0.18	0.52	-0.45	-0.39	0.86
Co-N_4[$C{\equiv}CC_6H_5$]/Gra	0.17	0.62	-0.34	-0.59	0.97
Co-N_4[$C_6H_7O_7$]/Gra	0.27	0.04	-0.19	-0.26	0.36
Co-N_4[NHC^{Me}]/Gra	0.12	0.38	-0.03	-0.61	0.55
Co-N_4[F]/Gra	0.16	0.10	-0.36	-0.04	0.39
Co-N_4[Cl]/Gra	0.21	0.21	-0.12	-0.44	0.53
Ni-N_4/Gra	0.15	1.26	-0.91	-0.64	1.55
Ni-N_4[OH]/Gra	0.14	0.80	-0.38	-0.70	0.95
Ni-N_4[CH_3]/Gra	0.15	0.89	-0.46	-0.73	1.18
Ni-N_4[SCH_2CH_3]/Gra	0.14	1.01	-0.57	-0.71	1.19
Ni-N_4[$P(C_6H_5)_3$]/Gra	0.11	1.30	-0.87	-0.69	1.52
Ni-N_4[COOH]/Gra	0.16	0.91	-0.59	-0.62	1.15
Ni-N_4[NH_2]/Gra	0.20	0.73	-0.39	-0.68	1.04
Ni-N_4[$C{\equiv}CC_6H_5$]/Gra	0.05	0.96	-0.58	-0.57	1.05
Ni-N_4[$C_6H_7O_7$]/Gra	0.21	0.95	-0.59	-0.71	1.07
Ni-N_4[NHC^{Me}]/Gra	-0.04	1.32	-1.01	-0.42	1.47
Ni-N_4[F]/Gra	0.14	0.72	-0.35	-0.65	0.89
Ni-N_4[Cl]/Gra	0.18	0.95	-0.61	-0.67	1.11

Table S6. The limiting potential (V) of CO_2RR and HER on the M-N_4L/Gra systems.

Species	**$U_L(CO_2RR)$**	**$U_L(HER)$**
Fe-N_4/Gra	-0.66	-0.38
Fe-N_4[OH]/Gra	-0.58	-0.79
Fe-N_4[CH_3]/Gra	-0.92	-1.00
Fe-N_4[SCH_2CH_3]/Gra	-0.77	-1.59
Fe-N_4[$P(C_6H_5)_3$]/Gra	-0.51	-0.75
Fe-N_4[COOH]/Gra	-0.86	-1.01
Fe-N_4[NH_2]/Gra	-0.71	-0.92

$Fe-N_4[C{\equiv}CC_6H_5]/Gra$	-0.95	-1.04
$Fe-N_4[C_6H_7O_7]/Gra$	-0.44	-0.51
$Fe-N_4[NHC^{Me}]/Gra$	-0.73	-0.74
$Fe-N_4[F]/Gra$	-0.58	-0.70
$Fe-N_4[Cl]/Gra$	-0.73	-0.68
$Co-N_4/Gra$	-0.15	-0.20
$Co-N_4[OH]/Gra$	-0.43	-0.65
$Co-N_4[CH_3]/Gra$	-0.68	-1.17
$Co-N_4[SCH_2CH_3]/Gra$	-0.52	-0.85
$Co-N_4[P(C_6H_5)_3]/Gra$	-0.32	-0.58
$Co-N_4[COOH]/Gra$	-0.69	-1.15
$Co-N_4[NH_2]/Gra$	-0.52	-0.86
$Co-N_4[C{\equiv}CC_6H_5]/Gra$	-0.62	-0.97
$Co-N_4[C_6H_7O_7]/Gra$	-0.27	-0.36
$Co-N_4[NHC^{Me}]/Gra$	-0.38	-0.55
$Co-N_4[F]/Gra$	-0.16	-0.39
$Co-N_4[Cl]/Gra$	-0.21	-0.53
$Ni-N_4/Gra$	-1.26	-1.55
$Ni-N_4[OH]/Gra$	-0.80	-0.95
$Ni-N_4[CH_3]/Gra$	-0.89	-1.18
$Ni-N_4[SCH_2CH_3]/Gra$	-1.01	-1.19
$Ni-N_4[P(C_6H_5)_3]/Gra$	-1.30	-1.52

Ni-N_4[COOH]/Gra	-0.91	-1.15
Ni-N_4[NH_2]/Gra	-0.73	-1.04
Ni-N_4[C≡CC_6H_5]/Gra	-0.96	-1.05
Ni-N_4[$C_6H_7O_7$]/Gra	-0.95	-1.07
Ni-N_4[NHC^{Me}]/Gra	-1.32	-1.47
Ni-N_4[F]/Gra	-0.72	-0.89
Ni-N_4[Cl]/Gra	-0.95	-1.11

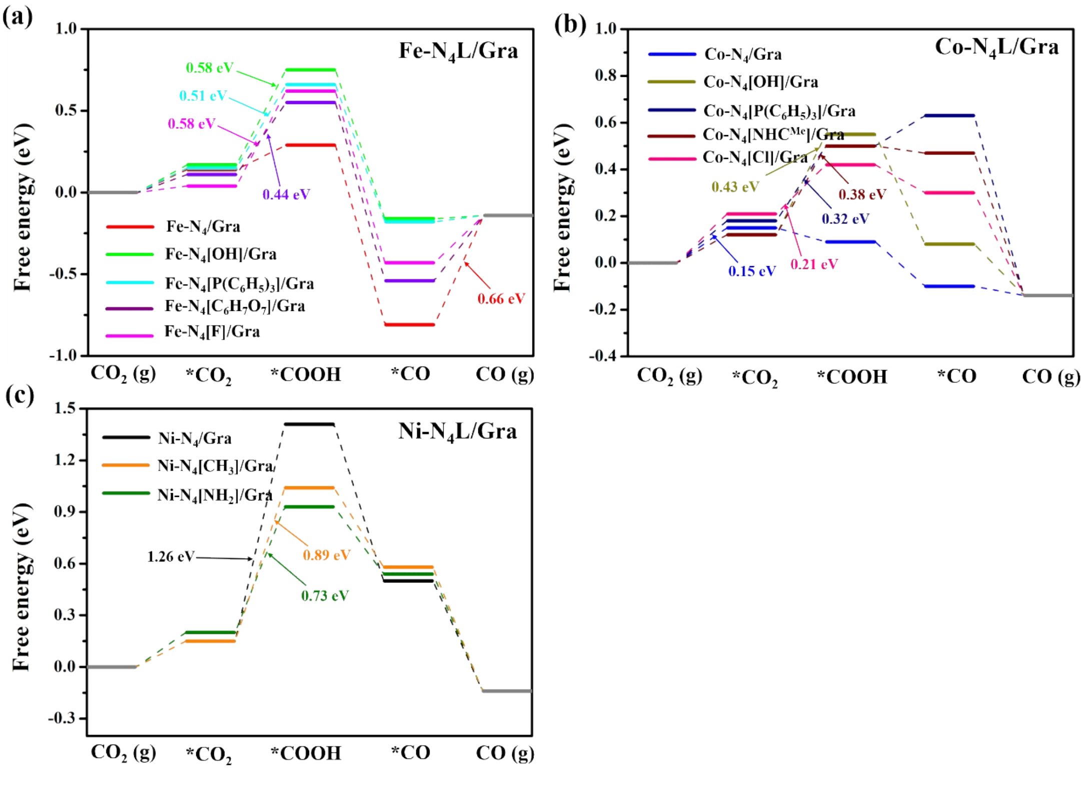


Figure S6. Free energy diagrams of CO_2RR on several selected candidates: Fe-N_4L/Gra (a), Co-N_4L/Gra (b) and Ni-N_4L/Gra (c).

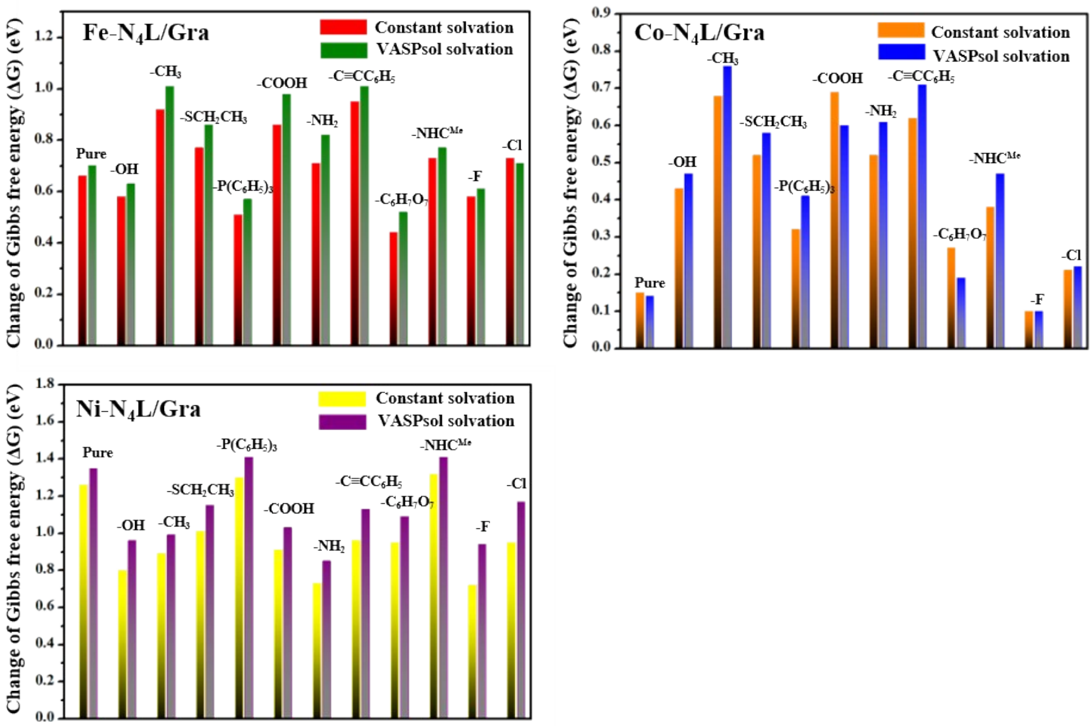


Figure S7. Comparison of the Gibbs free energy change Δ*G* (the largest free energy change among the elementary steps) on various M-N_4L/Gra catalysts based on the constant solvation and the VASPsol solvation.

Table S7. The adsorption Gibbs free energy (eV) of *COOH and *CO on the M-N_4L/Gra systems.

Species	***G*(*COOH)**	***G*(*CO)**
Fe-N_4/Gra	0.55	-0.66
Fe-N_4[OH]/Gra	1.00	-0.03
Fe-N_4[CH_3]/Gra	1.34	0.18
Fe-N_4[SCH_2CH_3]/Gra	1.18	0.26
Fe-N_4[$P(C_6H_5)_3$]/Gra	0.92	-0.04
Fe-N_4[COOH]/Gra	1.26	0.14
Fe-N_4[NH_2]/Gra	1.14	0.18
Fe-N_4[$C{\equiv}CC_6H_5$]/Gra	1.25	0.07

$Fe-N_4[C_6H_7O_7]/Gra$	0.81	-0.39
$Fe-N_4[NHC^{Me}]/Gra$	1.18	0.13
$Fe-N_4[F]/Gra$	0.87	-0.29
$Fe-N_4[Cl]/Gra$	1.07	-0.19
$Co-N_4/Gra$	0.35	0.05
$Co-N_4[OH]/Gra$	0.81	0.23
$Co-N_4[CH_3]/Gra$	1.16	0.63
$Co-N_4[SCH_2CH_3]/Gra$	0.99	0.58
$Co-N_4[P(C_6H_5)_3]/Gra$	0.75	0.77
$Co-N_4[COOH]/Gra$	1.23	0.70
$Co-N_4[NH_2]/Gra$	0.96	0.39
$Co-N_4[C\equiv CC_6H_5]/Gra$	1.04	0.59
$Co-N_4[C_6H_7O_7]/Gra$	0.57	0.26
$Co-N_4[NHC^{Me}]/Gra$	0.76	0.62
$Co-N_4[F]/Gra$	0.51	0.04
$Co-N_4[Cl]/Gra$	0.67	0.44
$Ni-N_4/Gra$	1.67	0.64
$Ni-N_4[OH]/Gra$	1.20	0.70
$Ni-N_4[CH_3]/Gra$	1.30	0.73
$Ni-N_4[SCH_2CH_3]/Gra$	1.40	0.72
$Ni-N_4[P(C_6H_5)_3]/Gra$	1.67	0.69
$Ni-N_4[COOH]/Gra$	1.33	0.63

Ni-N_4[NH_2]/Gra	1.18	0.68
Ni-N_4[C≡CC_6H_5]/Gra	1.27	0.58
Ni-N_4[$C_6H_7O_7$]/Gra	1.42	0.72
Ni-N_4[NHC^{Me}]/Gra	1.54	0.42
Ni-N_4[F]/Gra	1.11	0.65
Ni-N_4[Cl]/Gra	1.39	0.67

Table S8. The total magnetic moment (μ_B) of the M-N_4L/Gra catalysts.

Fe-N_4[L]/Gra		**Co-N_4[L]/Gra**		**Ni-N_4[L]/Gra**	
Fe-N_4/Gra	2.00	Co-N_4/Gra	0.99	Ni-N_4/Gra	0.00
Fe-N_4[OH]/Gra	1.00	Co-N_4[OH]/Gra	0.00	Ni-N_4[OH]/Gra	0.56
Fe-N_4[CH_3]/Gra	1.00	Co-N_4[CH_3]/Gra	0.00	Ni-N_4[CH_3]/Gra	0.56
Fe-N_4[SCH_2CH_3]/Gra	1.00	Co-N_4[SCH_2CH_3]/Gra	0.00	Ni-N_4[SCH_2CH_3]/Gra	0.56
Fe-N_4[$P(C_6H_5)_3$]/Gra	0.00	Co-N_4[$P(C_6H_5)_3$]/Gra	0.56	Ni-N_4[$P(C_6H_5)_3$]/Gra	0.00
Fe-N_4[COOH]/Gra	1.00	Co-N_4[COOH]/Gra	0.00	Ni-N_4[COOH]/Gra	0.56
Fe-N_4[NH_2]/Gra	1.00	Co-N_4[NH_2]/Gra	0.00	Ni-N_4[NH_2]/Gra	0.56
Fe-N_4[C≡CC_6H_5]/Gra	1.00	Co-N_4[C≡CC_6H_5]/Gra	0.00	Ni-N_4[C≡CC_6H_5]/Gra	0.56
Fe-N_4[$C_6H_7O_7$]/Gra	1.44	Co-N_4[$C_6H_7O_7$]/Gra	0.00	Ni-N_4[$C_6H_7O_7$]/Gra	0.56
Fe-N_4[NHC^{Me}]/Gra	0.00	Co-N_4[NHC^{Me}]/Gra	0.56	Ni-N_4[NHC^{Me}]/Gra	0.00
Fe-N_4[F]/Gra	2.56	Co-N_4[F]/Gra	0.00	Ni-N_4[F]/Gra	0.56
Fe-N_4[F]/Gra	1.44	Co-N_4[Cl]/Gra	0.00	Ni-N_4[Cl]/Gra	0.56

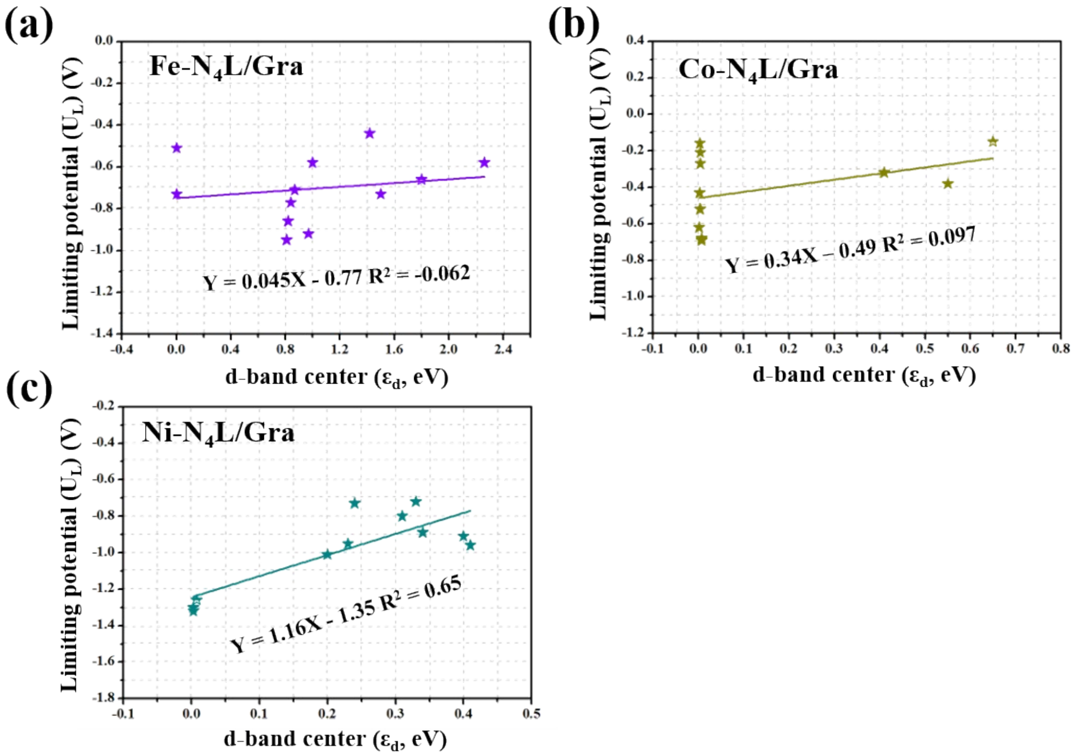
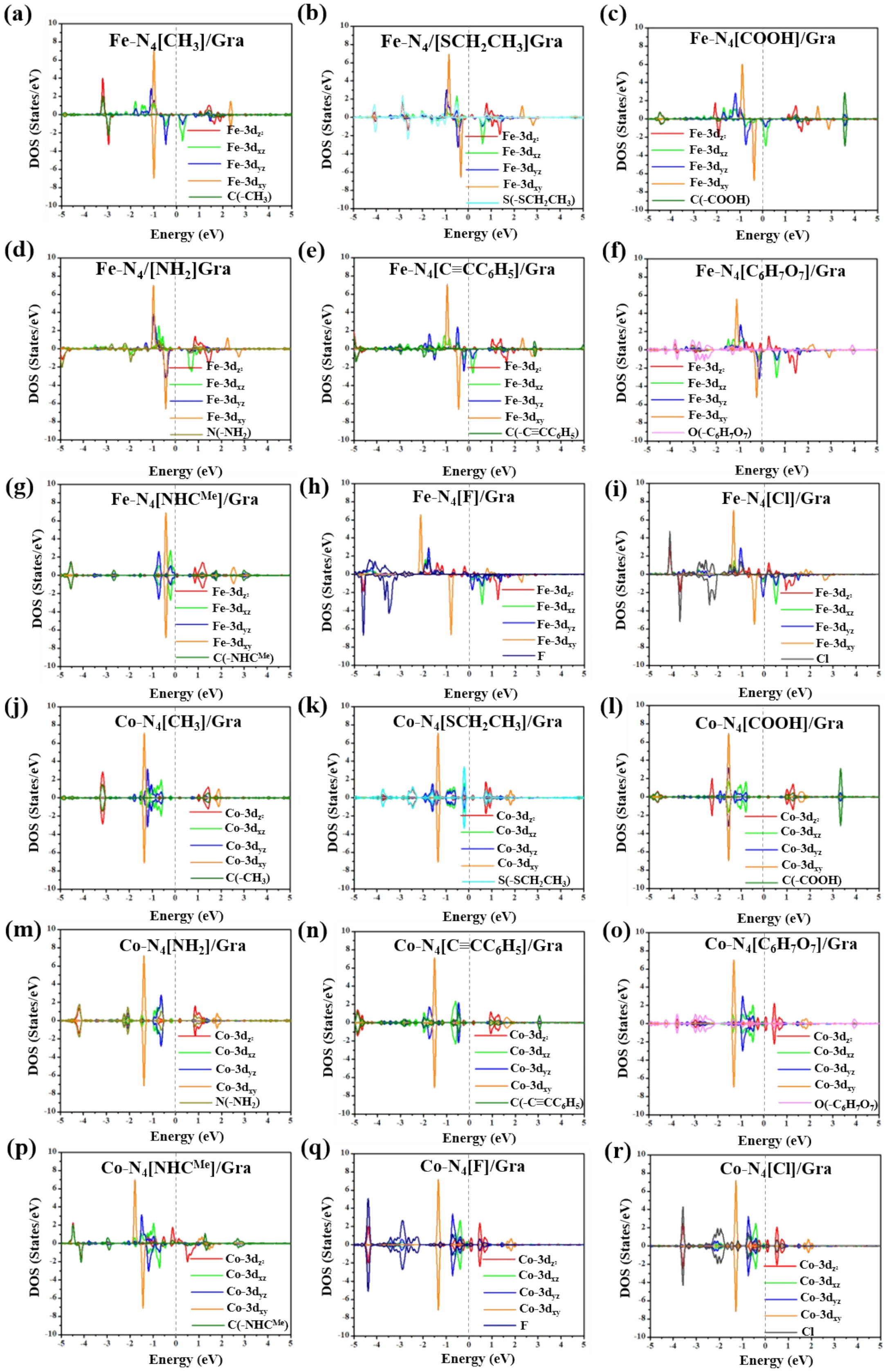


Figure S8. Correlation between the limiting potential (U_L) and the d-band center gap (Δd) on Fe-N_4L/Gra (a), Co-N_4L/Gra (b) and Ni-N_4L/Gra (c).


(a)
Fe-N4[CH3]/Gra
Fe-3dz2
Fe-3dxz
Fe-3dyz
Fe-3dxy
C(-CH3)
(b)
Fe-N4/[SCH2CH3]Gra
Fe-3dz2
Fe-3dxz
Fe-3dyz
Fe-3dxy
S(-SCH2CH3)
(c)
Fe-N4[COOH]/Gra
Fe-3dz2
Fe-3dxz
Fe-3dyz
Fe-3dxy
C(-COOH)
(d)
Fe-N4/[NH2]Gra
Fe-3dz2
Fe-3dxz
Fe-3dyz
Fe-3dxy
N(-NH2)
(e)
Fe-N4[C≡CC6H5]/Gra
Fe-3dz2
Fe-3dxz
Fe-3dyz
Fe-3dxy
C(-C≡CC6H5)
(f)
Fe-N4[C6H7O7]/Gra
Fe-3dz2
Fe-3dxz
Fe-3dyz
Fe-3dxy
O(-C6H7O7)
(g)
Fe-N4[NHCMe]/Gra
Fe-3dz2
Fe-3dxz
Fe-3dyz
Fe-3dxy
C(-NHCMe)
(h)
Fe-N4[F]/Gra
Fe-3dz2
Fe-3dxz
Fe-3dyz
Fe-3dxy
F
(i)
Fe-N4[Cl]/Gra
Fe-3dz2
Fe-3dxz
Fe-3dyz
Fe-3dxy
Cl
(j)
Co-N4[CH3]/Gra
Co-3dz2
Co-3dxz
Co-3dyz
Co-3dxy
C(-CH3)
(k)
Co-N4[SCH2CH3]/Gra
Co-3dz2
Co-3dxz
Co-3dyz
Co-3dxy
S(-SCH2CH3)
(l)
Co-N4[COOH]/Gra
Co-3dz2
Co-3dxz
Co-3dyz
Co-3dxy
C(-COOH)
(m)
Co-N4[NH2]/Gra
Co-3dz2
Co-3dxz
Co-3dyz
Co-3dxy
N(-NH2)
(n)
Co-N4[C≡CC6H5]/Gra
Co-3dz2
Co-3dxz
Co-3dyz
Co-3dxy
C(-C≡CC6H5)
(o)
Co-N4[C6H7O7]/Gra
Co-3dz2
Co-3dxz
Co-3dyz
Co-3dxy
O(-C6H7O7)
(p)
Co-N4[NHCMe]/Gra
Co-3dz2
Co-3dxz
Co-3dyz
Co-3dxy
C(-NHCMe)
(q)
Co-N4[F]/Gra
Co-3dz2
Co-3dxz
Co-3dyz
Co-3dxy
F
(r)
Co-N4[Cl]/Gra
Co-3dz2
Co-3dxz
Co-3dyz
Co-3dxy
Cl
DOS (States/eV)
Energy (eV)

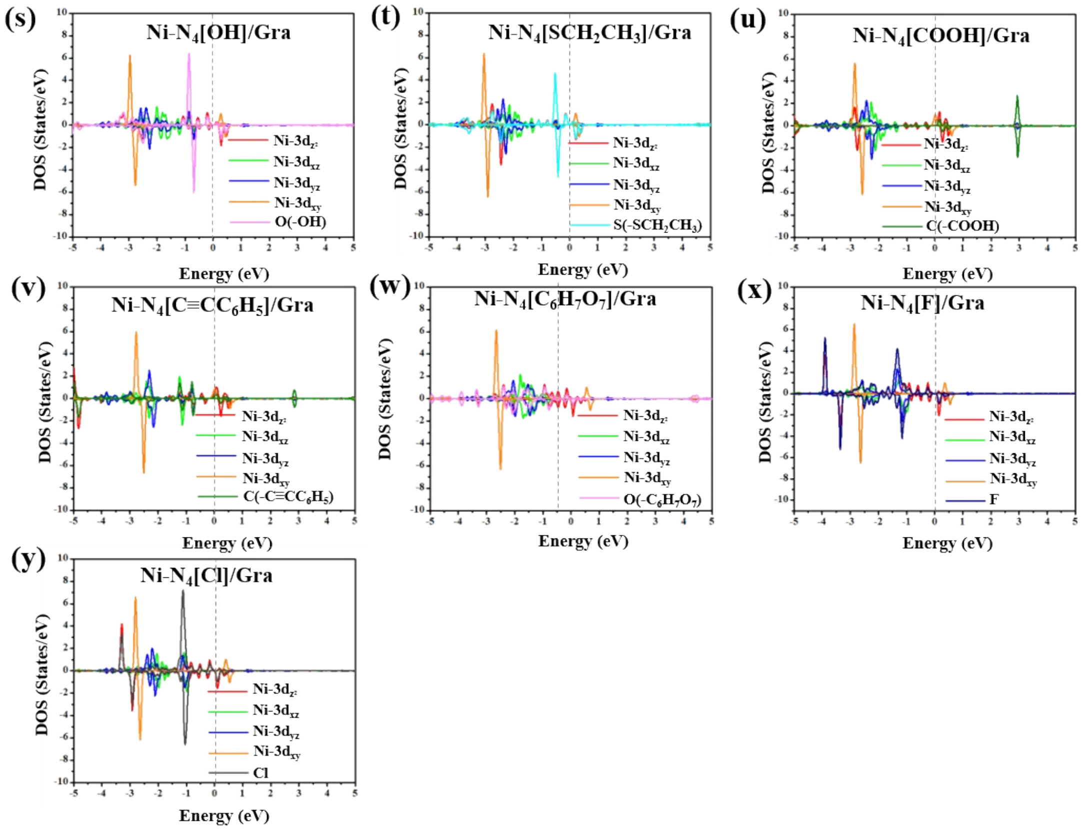


Figure S9. Projected density of states (PDOS) of Fe-N$_4$L/Gra (a-i), Co-N$_4$L/Gra (j-r) and Ni-N$_4$L/Gra (s-y). The Fermi level is set to 0 eV and denoted by vertical dotted line.

Table S9. The d-band center gap of spin state (Δd) of M-N$_4$L/Gra. (The unit is eV).

Fe-N$_4$L/Gra		**Co-N$_4$L/Gra**		**Ni-N$_4$L/Gra**	
Fe-N$_4$/Gra	1.80	Co-N$_4$/Gra	0.65	Ni-N$_4$/Gra	0.0076
Fe-N$_4$[OH]/Gra	1.00	Co-N$_4$[OH]/Gra	0.0028	Ni-N$_4$[OH]/Gra	0.31
Fe-N$_4$[CH$_3$]/Gra	0.97	Co-N$_4$[CH$_3$]/Gra	0.0072	Ni-N$_4$[CH$_3$]/Gra	0.34
Fe-N$_4$[SCH$_2$CH$_3$]/Gra	0.84	Co-N$_4$[SCH$_2$CH$_3$]/Gra	0.0035	Ni-N$_4$[SCH$_2$CH$_3$]/Gra	0.20
Fe-N$_4$[P(C$_6$H$_5$)$_3$]/Gra	0.0031	Co-N$_4$[P(C$_6$H$_5$)$_3$]/Gra	0.41	Ni-N$_4$[P(C$_6$H$_5$)$_3$]/Gra	0.0027
Fe-N$_4$[COOH]/Gra	0.82	Co-N$_4$[COOH]/Gra	0.0073	Ni-N$_4$[COOH]/Gra	0.40

Fe-$N_4[NH_2]$/Gra	0.87	Co-$N_4[NH_2]$/Gra	0.0043	Ni-$N_4[NH_2]$/Gra	0.24
Fe-$N_4[C{\equiv}CC_6H_5]$/Gra	0.81	Co-$N_4[C{\equiv}CC_6H_5]$/Gra	0.0015	Ni-$N_4[C{\equiv}CC_6H_5]$/Gra	0.41
Fe-$N_4[C_6H_7O_7]$/Gra	1.42	Co-$N_4[C_6H_7O_7]$/Gra	0.0043	Ni-$N_4[C_6H_7O_7]$/Gra	0.23
Fe-$N_4[NHC^{Me}]$/Gra	0.0026	Co-$N_4[NHC^{Me}]$/Gra	0.55	Ni-$N_4[NHC^{Me}]$/Gra	0.0031
Fe-N_4[F]/Gra	2.26	Co-N_4[F]/Gra	0.0033	Ni-N_4[F]/Gra	0.33
Fe-N_4[Cl]/Gra	1.50	Co-N_4[Cl]/Gra	0.0046	Ni-N_4[Cl]/Gra	0.23

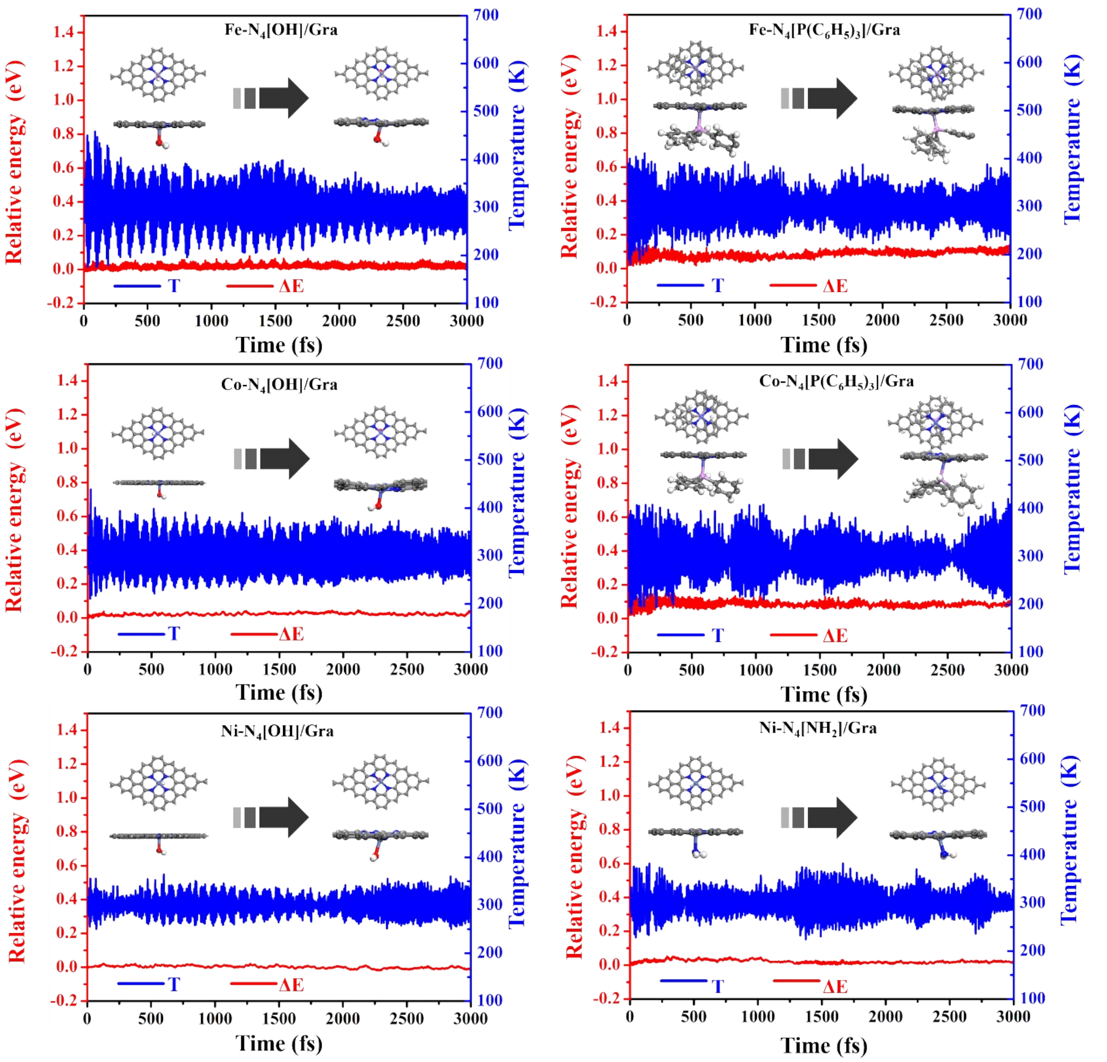


Figure S10. In the AIMD simulation, the temperature and potential energy curve with time for 3 ps under 300 K with a time step of 1 fs for Fe-N_4[OH]/Gra (a), Fe-$N_4[P(C_6H_5)_3]$/Gra (b), Co-

N_4[OH]/Gra (c), Co-N_4[P(C_6H_5)$_3$]/Gra (d), Ni-N_4[OH]/Gra (e), and Ni-N_4[NH_2]/Gra (f). Here, the relative energy of the initial configuration is set to zero for reference.