Supporting Information

Adsorption of Transition Metal Clusters on Graphene and N doped Graphene: A DFT Study

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Table S1. Part of 3*d*/4*d*/5*d* TM elements in Periodic Table, associated covalent radius (pm), and configuration of extra-nuclear electron (The elements we selected to calculate are marked in red lines)

3	4	5	6	7	8	9	10	11	12
21 **Sc** 144 $3d^1 4s^2$	22 **Ti** 136 $3d^2 4s^2$	23 **V** 125 $3d^3 4s^2$	24 **Cr** 127 $3d^5 4s^1$	25**Mn** 139 $3d^5 4s^2$	26 **Fe** 125 $3d^6 4s^2$	27 **Co** 126 $3d^7 4s^2$	28 **Ni** 121 $3d^8 4s^2$	29 **Cu** 138 $3d^{10} 4s^1$	30 **Zn** 131 $3d^{10} 4s^2$
39 **Y** 162 $4d^1 5s^2$	40 **Zr** 148 $4d^2 5s^2$	41 **Nb** 137 $4d^4 5s^1$	42**Mo** 145 $4d^5 5s^1$	43 **Tc** 156 $4d^5 5s^2$	44 **Ru** 126 $4d^7 5s^1$	45 **Rh** 135 $4d^8 5s^1$	46 **Pd** 131 $4d^{10}$	47 **Ag** 153 $4d^{10} 5s^1$	48 **Cd** 148 $4d^{10} 5s^2$
57~71 **La~Lu**	72 **Hf** 150 $5d^2 6s^2$	73 **Ta** 138 $5d^3 6s^2$	74 **W** 146 $5d^4 6s^2$	75 **Re** 159 $5d^5 6s^2$	76 **Os** 128 $5d^6 6s^2$	77 **Ir** 137 $5d^7 6s^2$	78 **Pt** 128 $5d^9 6s^1$	79 **Au** 144 $5d^{10} 6s^1$	80 **Hg** 149 $5d^{10} 6s^2$

Table S2. The comparison of standard DFT and DFT-D3 method

clusters	Gr		N-Gr	
	E_{ads}-D3	E_{ads} without D3	E_{ads}-D3	E_{ads} without D3
Mn_1	–0.50	–0.28	–0.42	–0.19
Mn_2	–1.10	–0.75	–1.08	–0.73
Mn_3	–1.98	–1.35	–2.18	–1.66
Mn_4	–1.97	–1.37	–2.06	–1.46
Tc_1	–1.58	–1.21	–1.92	–1.56
Tc_2	–1.27	–0.73	–1.57	–0.81
Tc_3	–2.80	–1.84	–2.99	–1.21
Tc_4	–2.56	–1.19	–2.95	–2.19
Re_1	–1.70	–1.40	–2.06	–1.36
Re_2	–1.75	–1.29	–2.03	–1.77
Re_3	–2.42	–1.59	–2.65	–1.83
Re_4	–1.64	–0.55	–2.21	–0.87
Fe_1	–1.04	–0.87	–1.18	–1.01
Fe_2	–1.11	–0.79	–1.19	–0.75
Fe_3	–1.90	–1.37	–1.93	–1.39
Fe_4	–2.14	–1.34	–2.10	–1.32
Ru_1	–2.67	–2.40	–2.92	–2.66
Ru_2	–1.71	–1.11	–2.05	–1.44
Ru_3	–1.89	–1.14	–2.60	–1.80
Ru_4	–2.11	–1.05	–2.61	–1.37
Os_1	–1.37	–1.10	–1.76	–1.49
Os_2	–2.02	–1.67	–2.15	–1.80
Os_3	–2.52	–2.01	–2.78	–2.27
Os_4	–1.99	–1.33	–2.47	–1.55
Co_1	–1.29	–1.15	–1.43	–1.30
Co_2	–1.44	–1.19	–1.57	–1.35
Co_3	–2.13	–1.77	–2.31	–1.94
Co_4	–2.07	–1.39	–2.10	–1.43
Rh_1	–2.17	–1.98	–2.60	–2.36
Rh_2	–1.70	–1.25	–2.10	–1.65
Rh_3	–1.86	–1.19	–2.32	–1.63
Rh_4	–2.19	–1.37	–2.72	–1.86
Ir_1	–1.64	–1.35	–2.25	–1.98
Ir_2	–2.08	–1.72	–2.54	–2.01
Ir_3	–2.04	–1.52	–2.55	–1.84
Ir_4	–1.52	–0.89	–2.36	–1.44
Ni_1	–1.60	–1.47	–1.59	–1.37
Ni_2	–1.19	–0.95	–1.48	–1.05
Ni_3	–2.19	–1.66	–2.36	–1.81
Ni_4	–2.57	–1.93	–2.76	–2.12
Pd_1	–1.39	–1.12	–1.44	–1.16
Pd_2	–2.00	–1.48	–2.20	–1.68
Pd_3	–1.67	–0.88	–2.21	–1.39
Pd_4	–1.66	–0.92	–2.14	–1.23

Pt_1	–1.92	–1.63	–2.28	–1.99
Pt_2	–1.34	–0.96	–2.05	–1.46
Pt_3	–2.13	–1.45	–2.73	–2.03
Pt_4	–2.32	–1.48	–3.10	–2.08
Cu_1	–0.55	–0.34	–0.77	–0.55
Cu_2	–0.88	–0.59	–0.86	–0.58
Cu_3	–1.49	–0.98	–1.46	–0.95
Cu_4	–1.15	–0.55	–1.16	–0.56
Ag_1	–0.28	0.01	–0.38	–0.10
Ag_2	–0.43	–0.12	–0.44	–0.13
Ag_3	–0.99	–0.57	–0.95	–0.36
Ag_4	–0.85	–0.24	–0.83	–0.21
Au_1	–0.42	–0.15	–1.02	–0.74
Au_2	–0.82	–0.48	–0.90	–0.56
Au_3	–1.06	–0.35	–1.61	–0.91
Au_4	–1.22	–0.50	–1.34	–0.61

Table S3. The convergence test for TM_4 cluster within different cubic supercell

cluster	cubic supercell (pm)							
	1000	1200	1300	1400	1500	1600	1700	1800
Mn_4	–25.420	–25.471	–25.474	–25.476	–25.476	–25.475	–25.475	–25.475
Tc_4	–27.395	–27.460	–27.462	–27.462	–27.461	–27.460	–27.460	–27.459
Re_4	–33.079	–33.069	–33.066	–33.065	–33.065	–33.064	–33.064	–33.064
Fe_4	–22.377	–22.405	–22.405	–22.406	–22.406	–22.405	–22.405	–22.405
Ru_4	–22.719	–22.697	–22.695	–22.695	–22.695	–22.695	–22.695	–22.696
Os_4	–27.907	–27.913	–27.913	–27.914	–27.914	–27.913	–27.913	–27.914
Co_4	–17.300	–17.315	–17.316	–17.316	–17.316	–17.315	–17.315	–17.315
Rh_4	–17.363	–17.336	–17.332	–17.331	–17.331	–17.330	–17.330	–17.330
Ir_4	–20.836	–20.854	–20.855	–20.854	–20.854	–20.854	–20.854	–20.853
Ni_4	–12.129	–12.136	–12.135	–12.136	–12.135	–12.135	–12.134	–12.135
Pd_4	–12.887	–12.863	–12.859	–12.859	–12.858	–12.857	–12.856	–12.857
Pt_4	–13.344	–13.349	–13.349	–13.348	–13.347	–13.347	–13.347	–13.347
Cu_4	–7.463	–7.466	–7.465	–7.466	–7.465	–7.464	–7.464	–7.465
Ag_4	–6.119	–6.123	–6.126	–6.128	–6.127	–6.127	–6.126	–6.127
Au_4	–7.434	–7.426	–7.424	–7.422	–7.422	–7.421	–7.421	–7.421

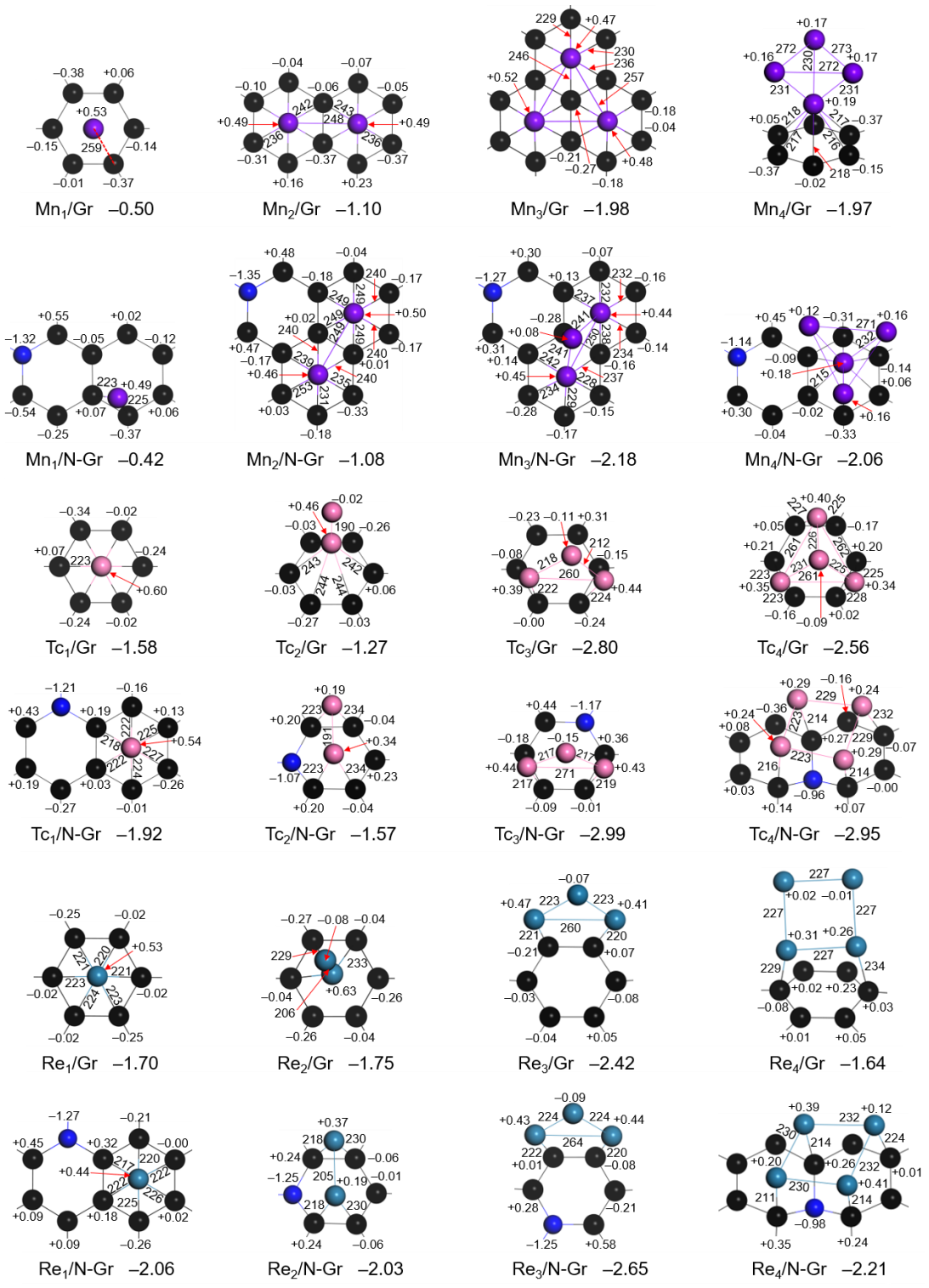

Figure S1. Bond lengths (pm), E_{ads} (eV), and Bader charges (*e*) for the most stable configurations of TM_n clusters (TM = Mn, Tc and Re; n = 1–4) adsorption on Gr and N-Gr surfaces. Mn, Tc and Re atoms are shown in violet, pink, and green balls; C and N in black and deep blue balls for all figures.

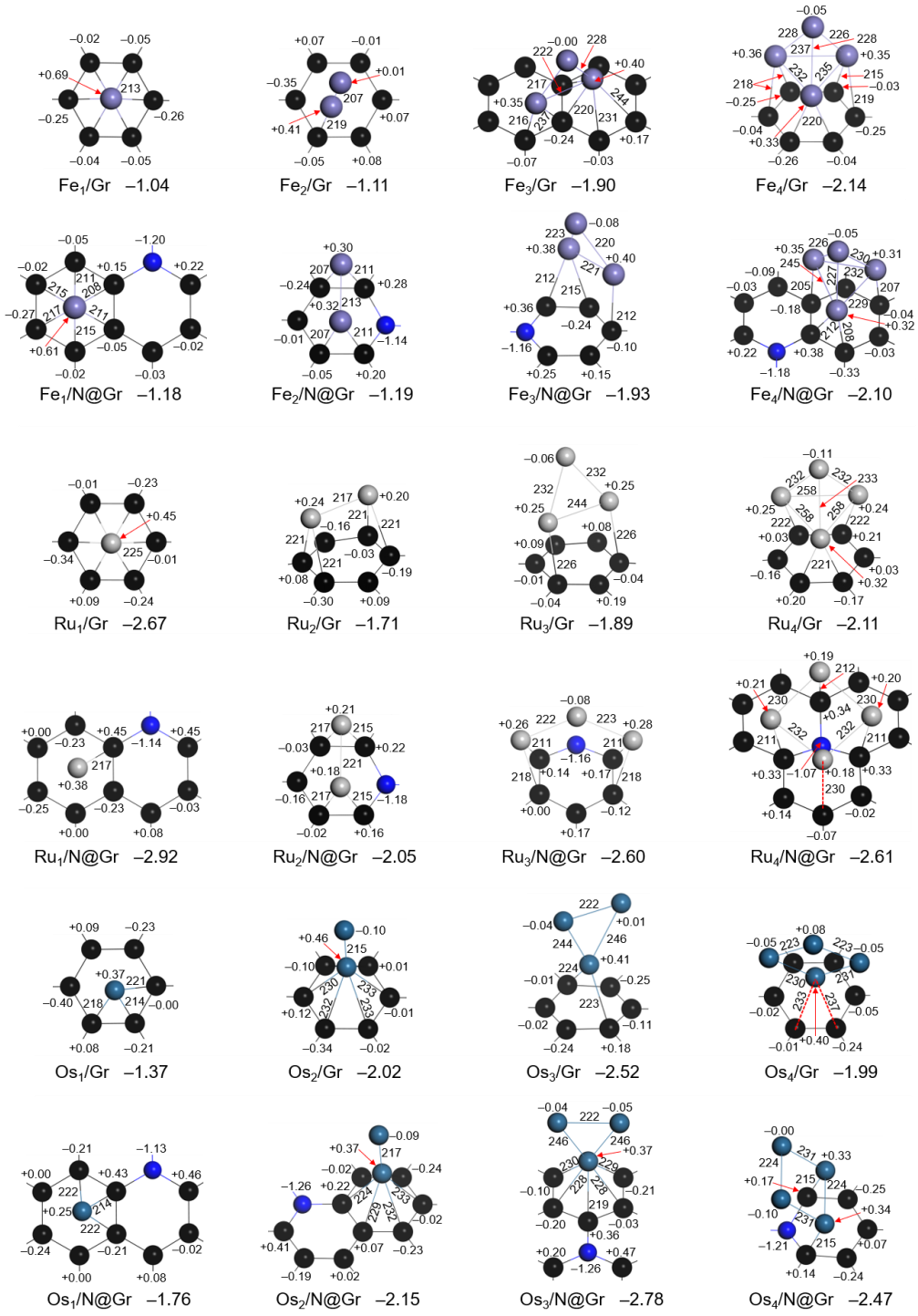

Figure S2. Bond lengths (pm), E_{ads} (eV), and Bader charges (e) for the most stable configuration of TM_n clusters (TM = Fe, Ru and Os; n = 1–4) adsorption on Gr and N-Gr surfaces. Fe, Ru and Os atoms are shown in purple, grey, and deep green balls, respectively.

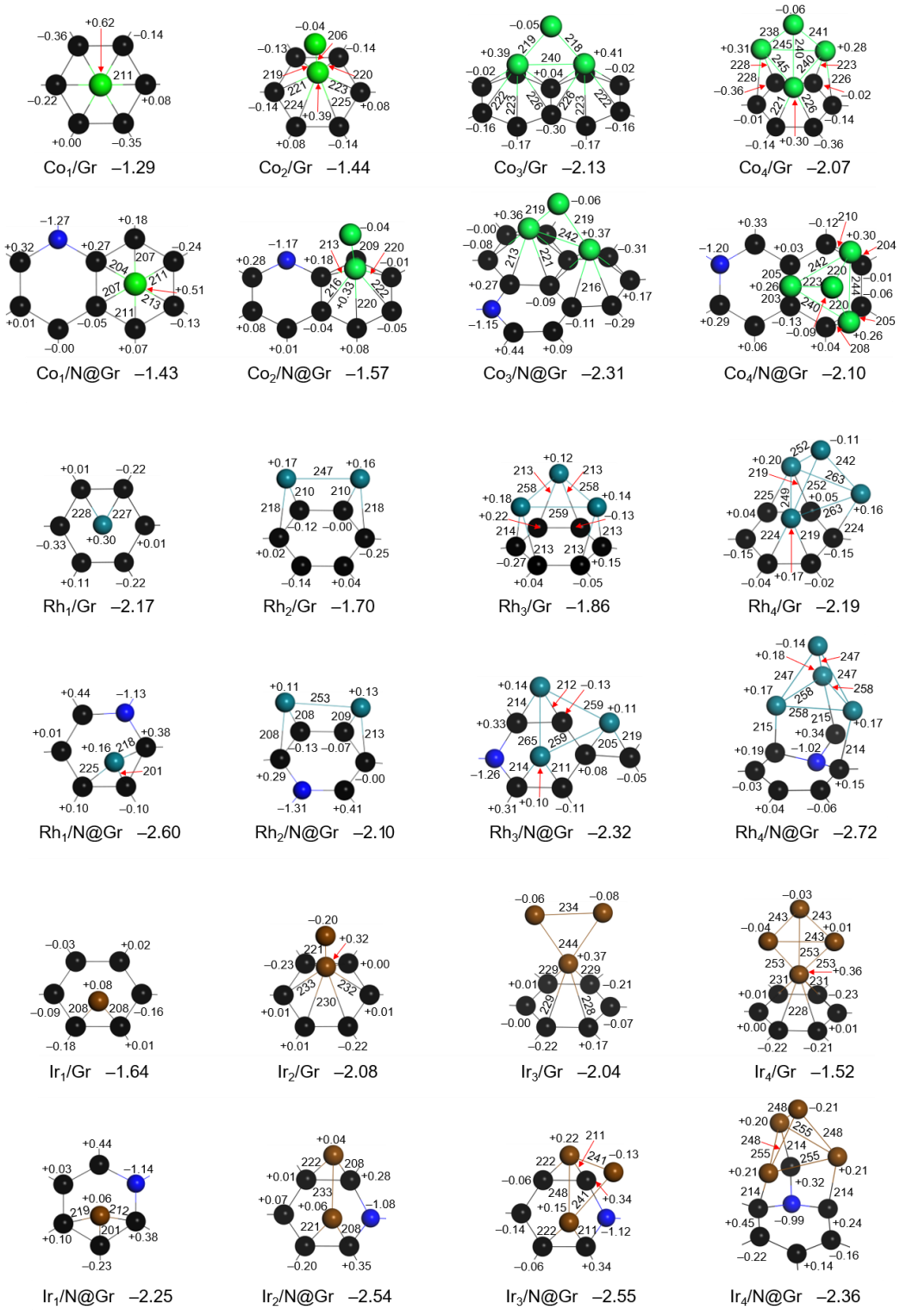

Figure S3. Bond lengths (pm), E_{ads} (eV), and Bader charges (e) for the most stable configurations of TM_n clusters (TM = Co, Rh and Ir; n = 1–4) adsorption on Gr and N-Gr surfaces. Co, Rh and Ir atoms are shown in light green, deep green, and brown balls, respectively.

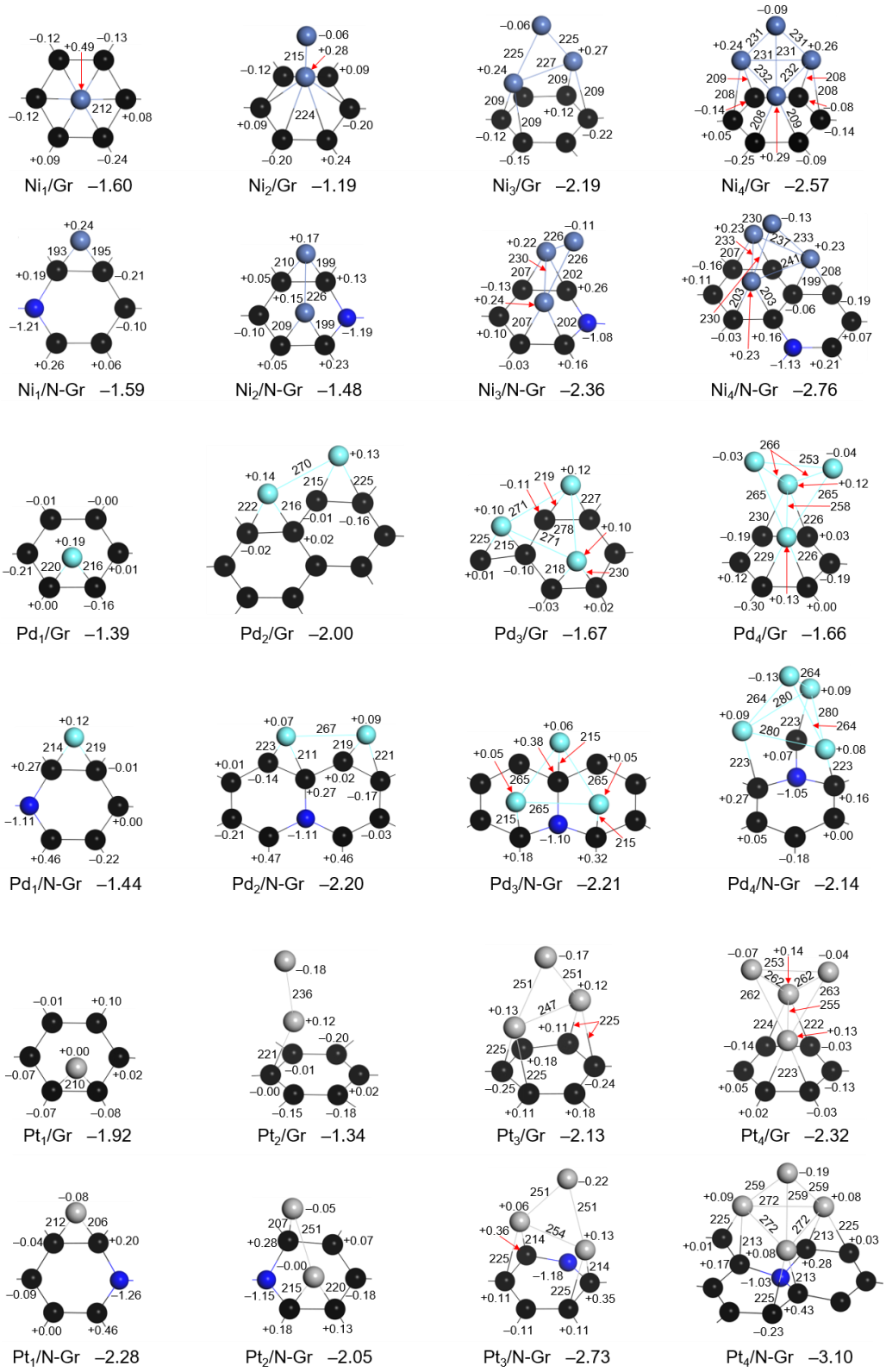

Figure S4. Bond lengths (pm), E_{ads} (eV), and Bader charges (e) for the most stable configurations of TM_n clusters (TM = Ni, Pd and Pt; n = 1–4) adsorption on Gr and N-Gr surfaces. Ni, Pd and Pt atoms are shown in blue, cyan, and grey balls, respectively.

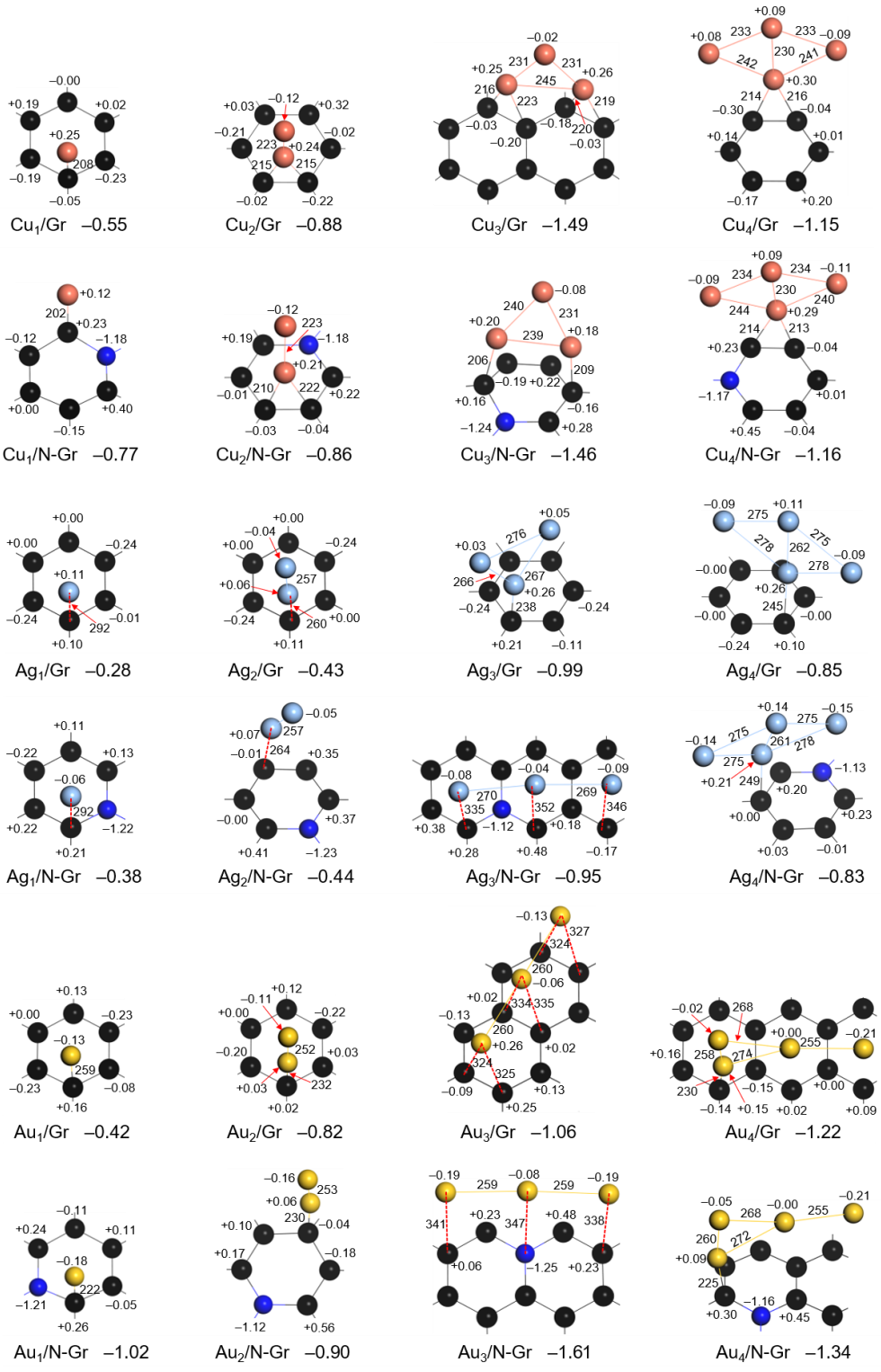

Figure S5. Bond lengths (pm), E_{ads} (eV), and Bader charges (*e*) for the most stable configurations of TM_n clusters (TM = Cu, Ag and Au; n = 1–4) adsorption on Gr and N-Gr surfaces. Cu, Ag and Au atoms are shown in copper, light blue, and gold balls, respectively.

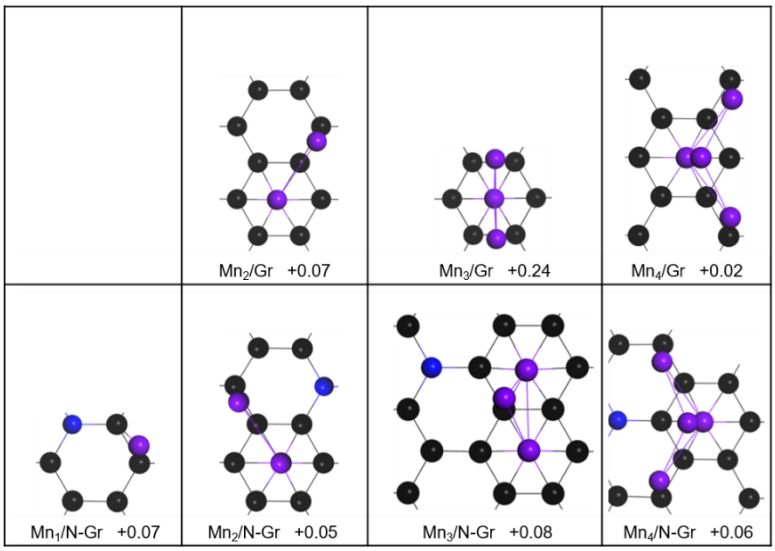

Figure S6. The sub-stable structures of Mn_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

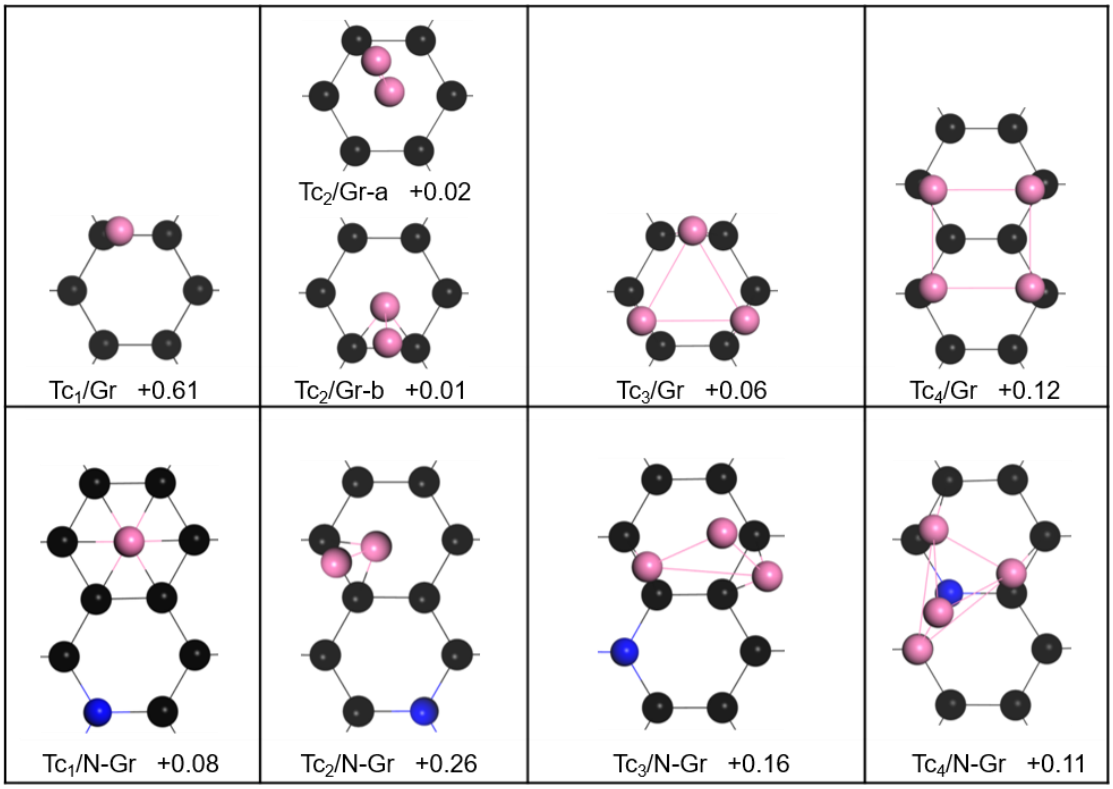

Figure S7. The sub-stable structures of Tc_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

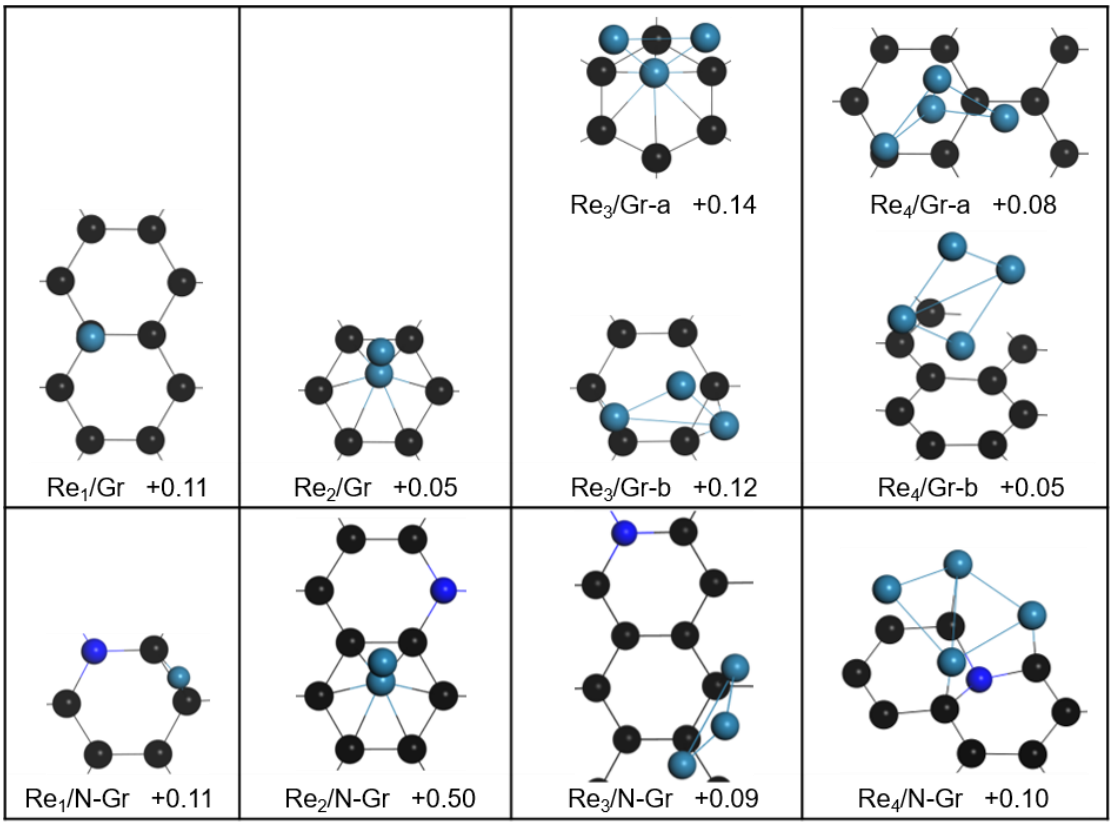

Figure S8. The sub-stable structures of Re_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

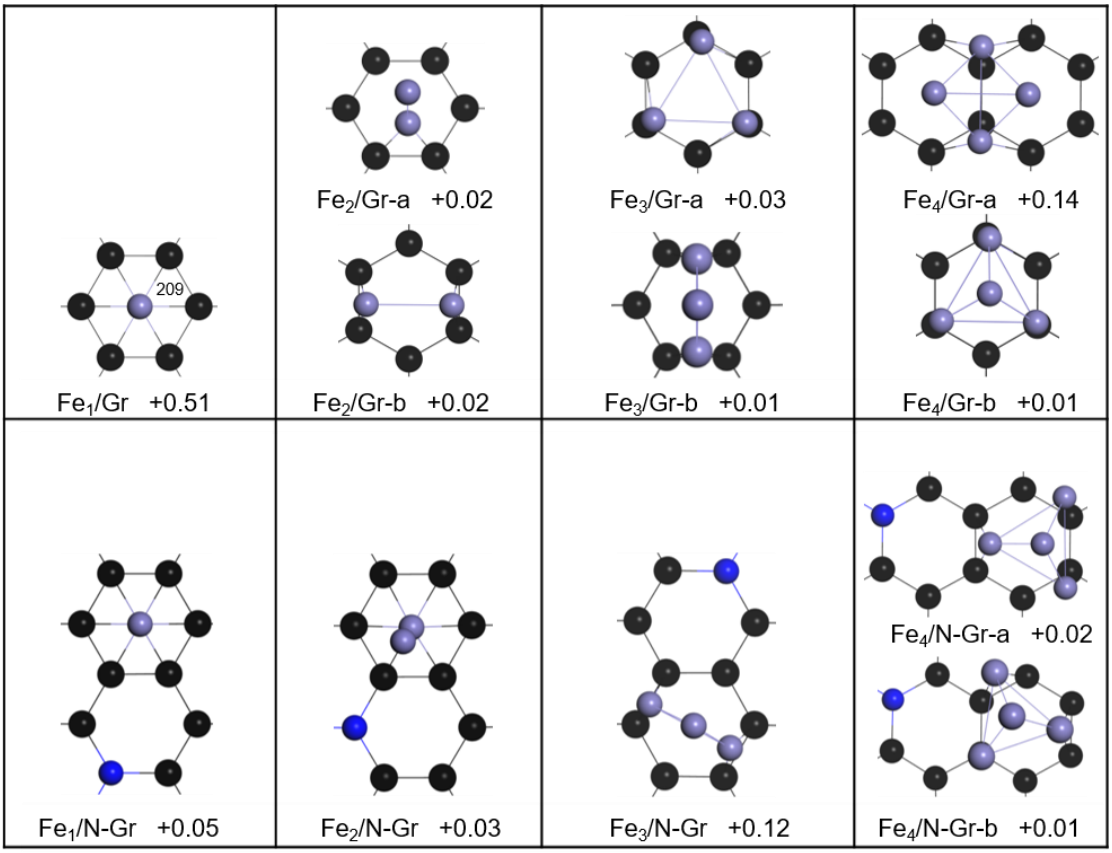

Figure S9. The sub-stable structures of Fe_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

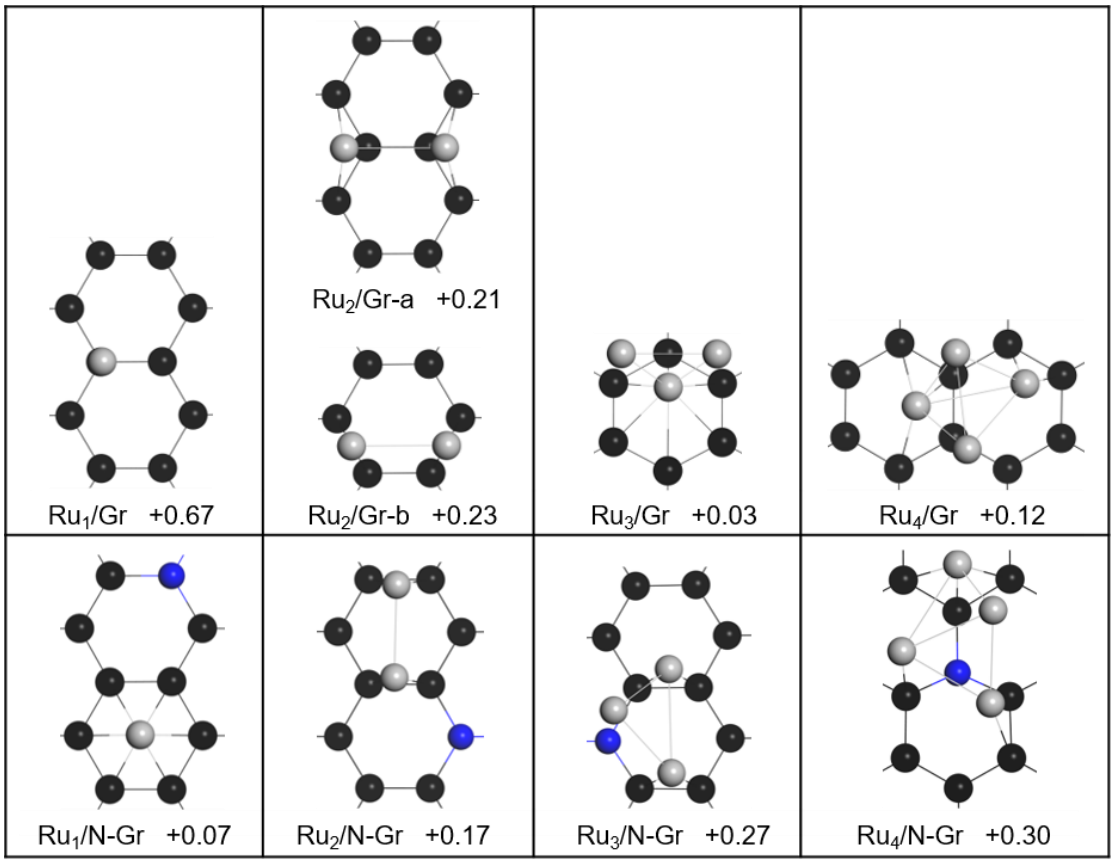

Figure S10. The sub-stable structures of Ru_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

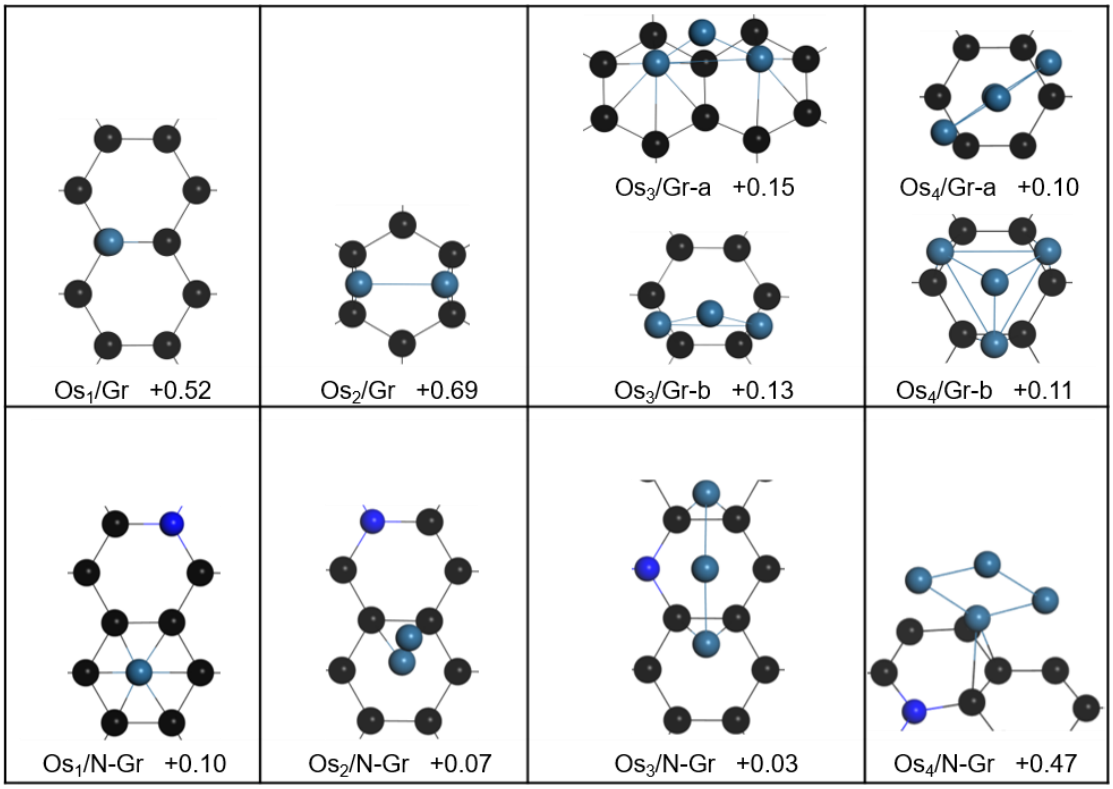

Figure S11. The sub-stable structures of Os_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

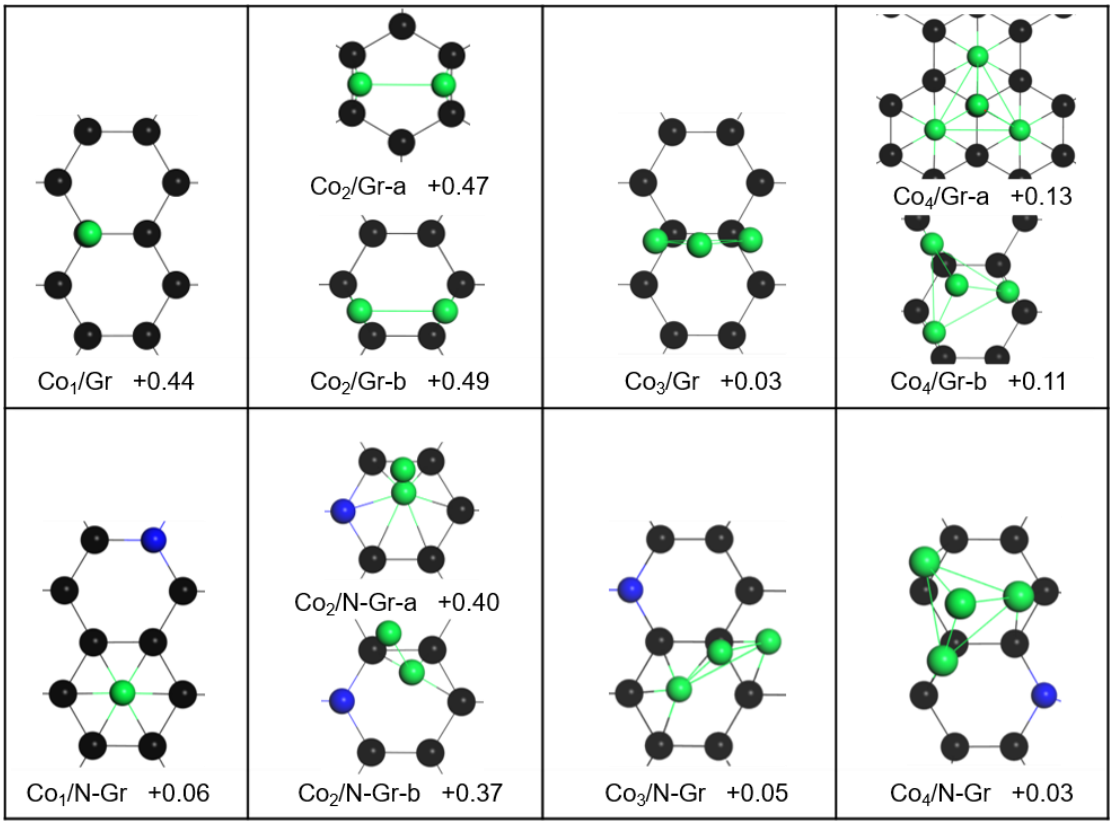

Figure S12. The sub-stable structures of Co_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

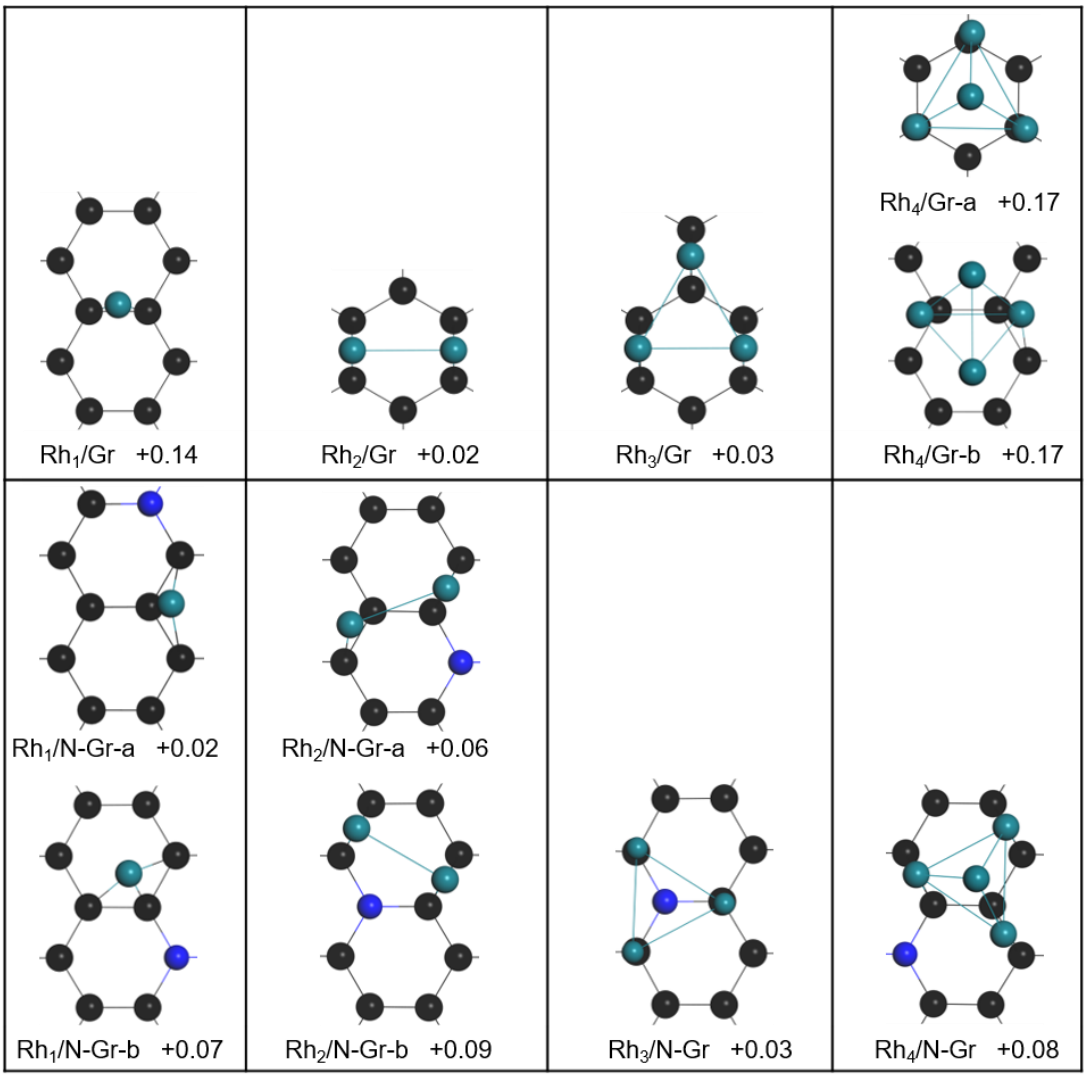

Figure S13. The sub-stable structures of Rh_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

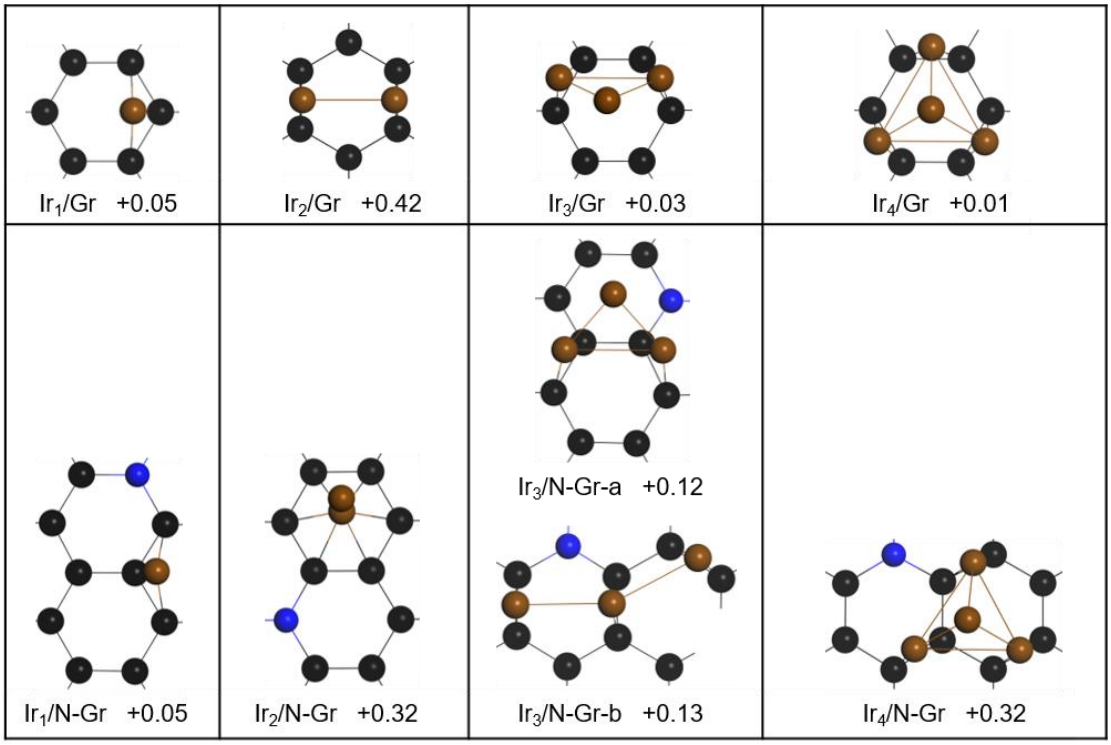

Figure S14. The sub-stable structures of Ir_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

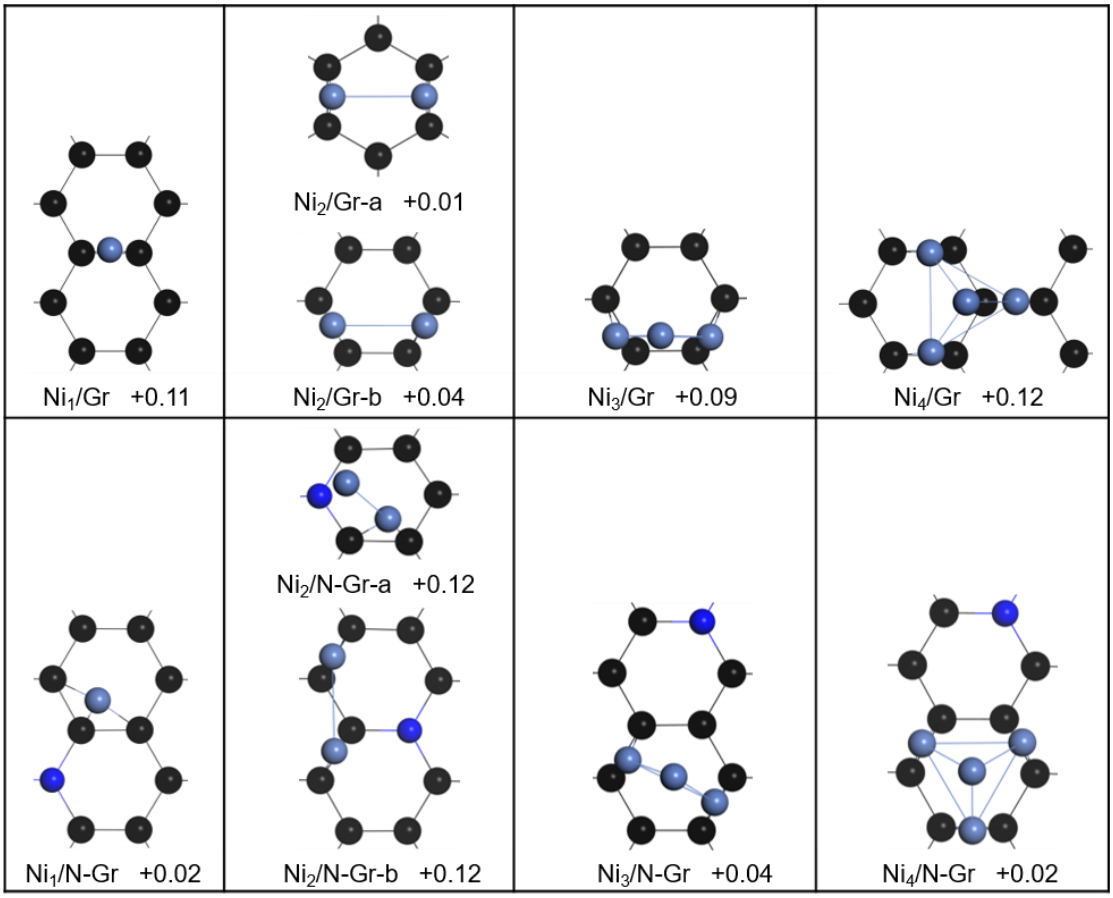

Figure S15. The sub-stable structures of Ni_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

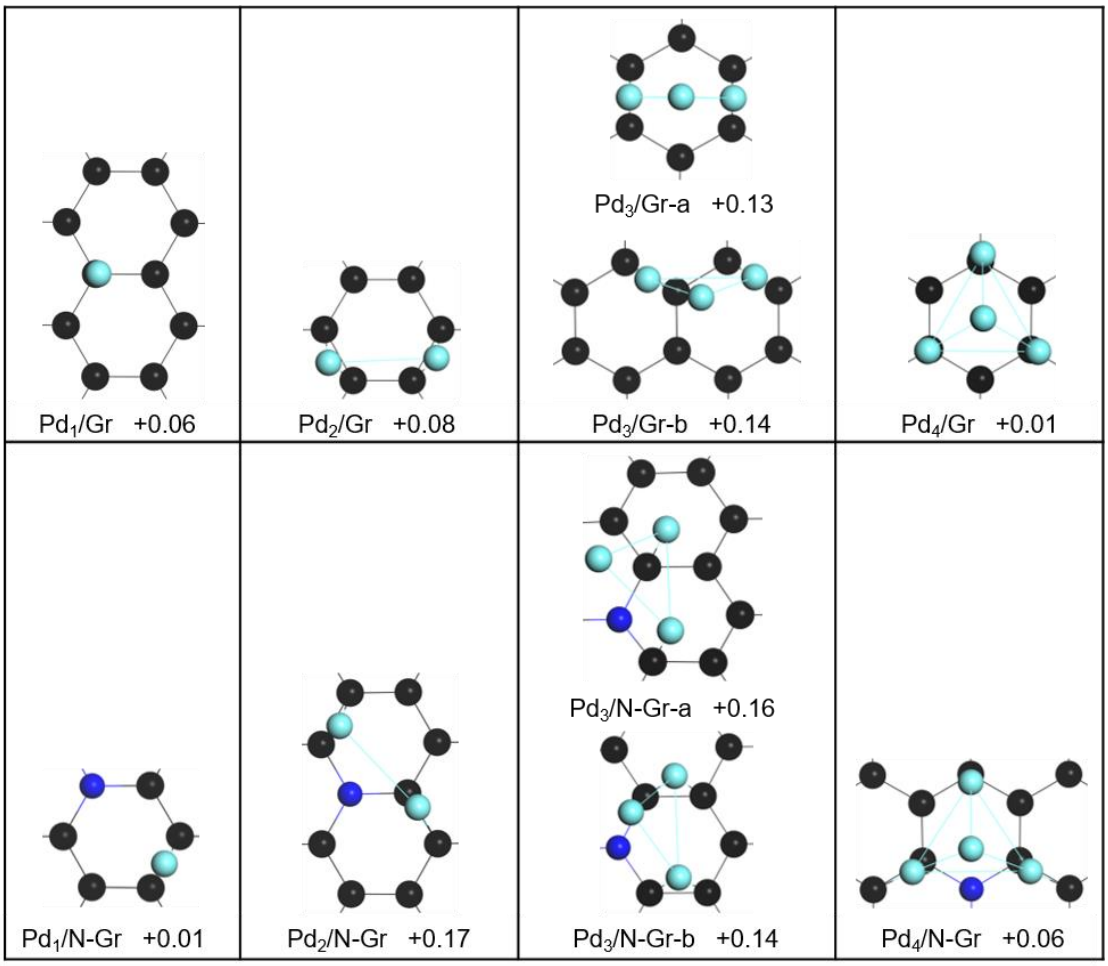

Figure S16. The sub-stable structures of Pd_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

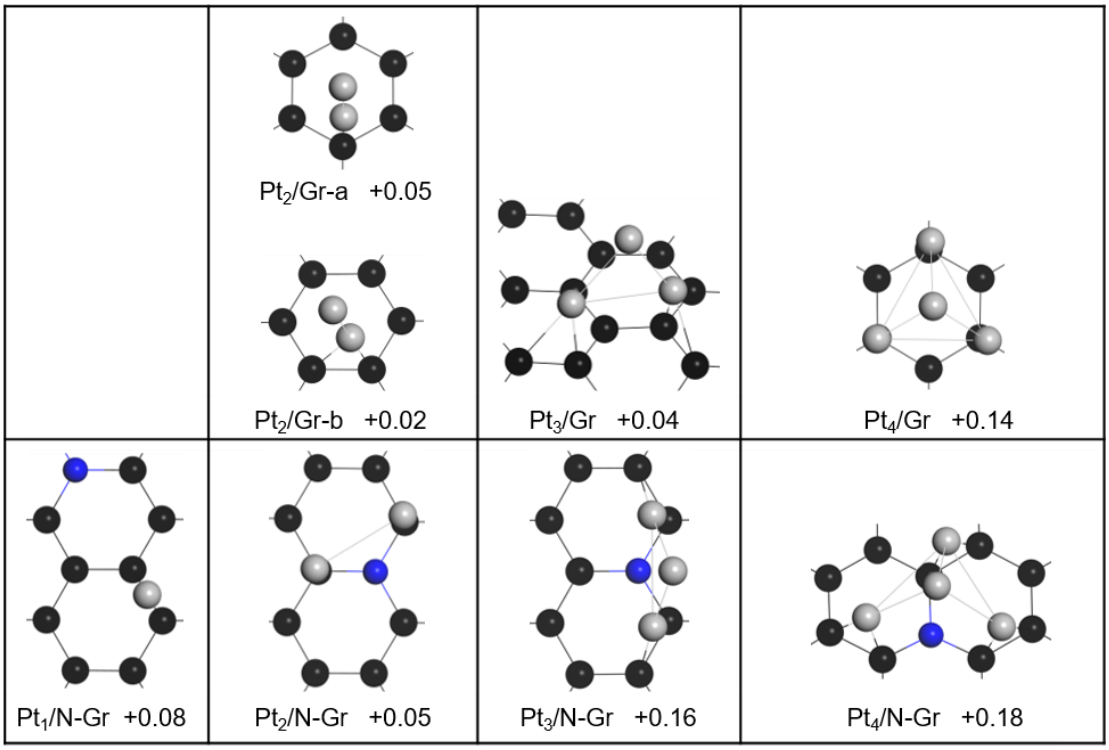

Figure S17. The sub-stable structures of Pt_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

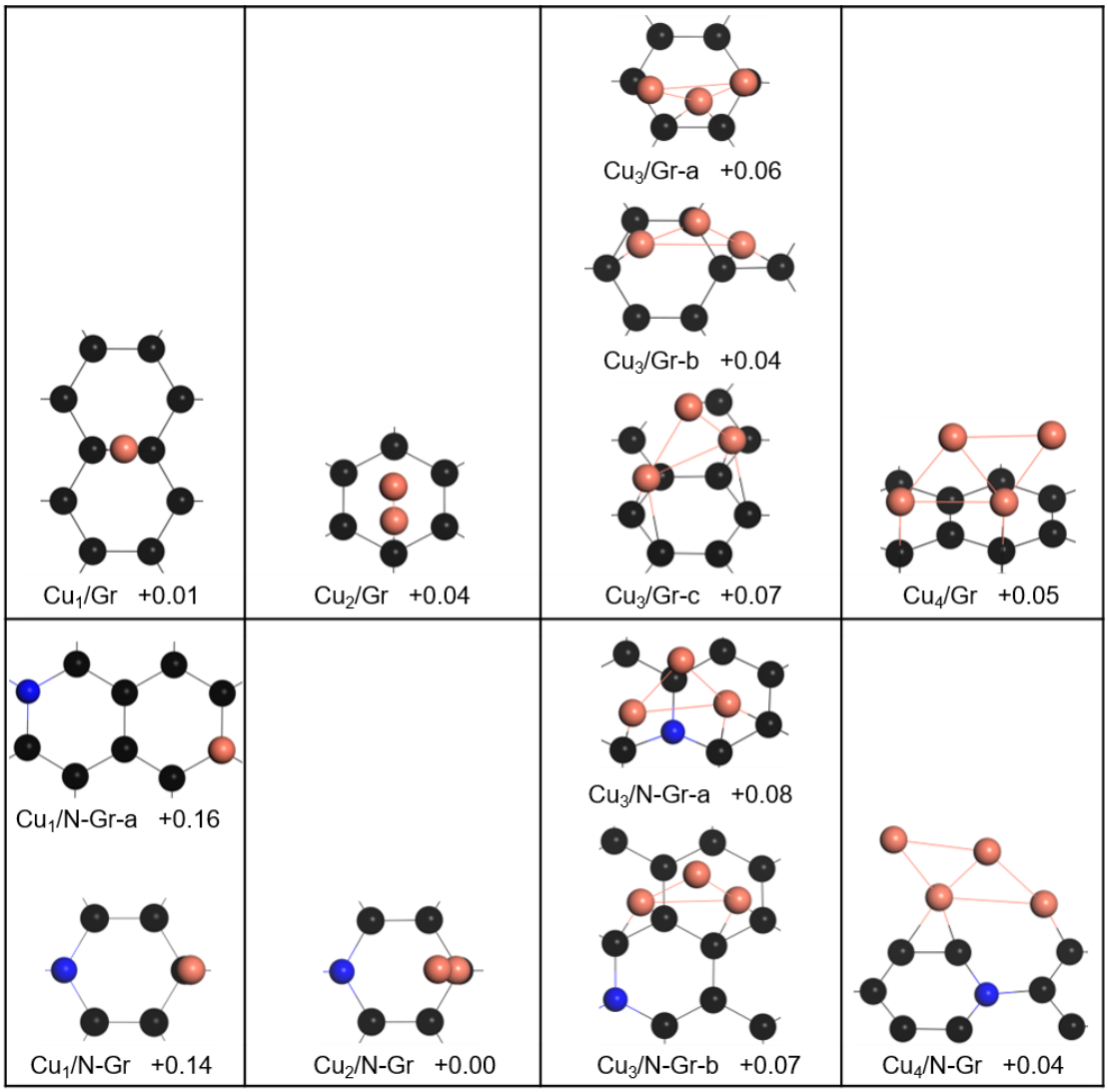

Figure S18. The sub-stable structures of Cu_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

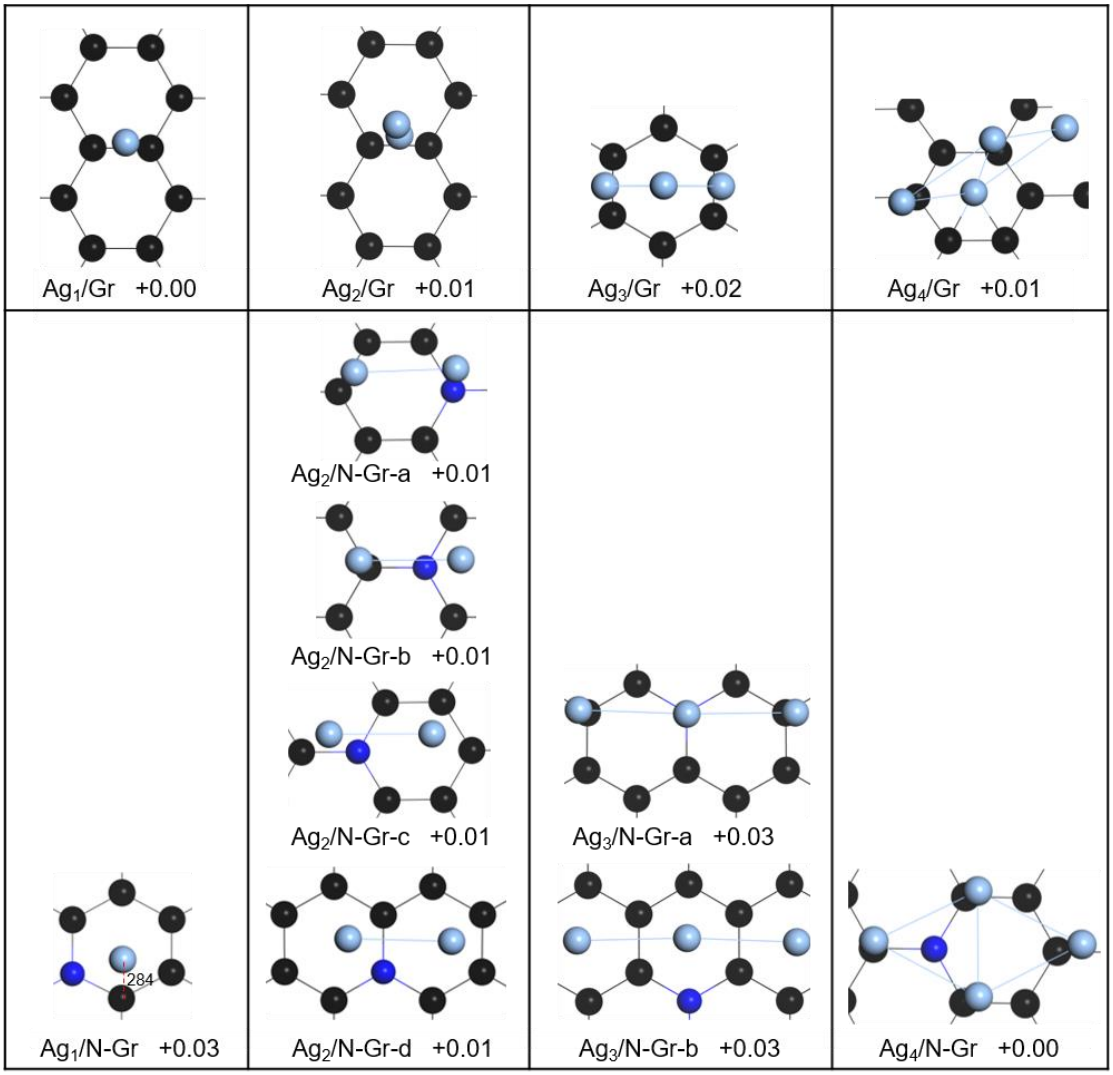

Figure S19. The sub-stable structures of Ag_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

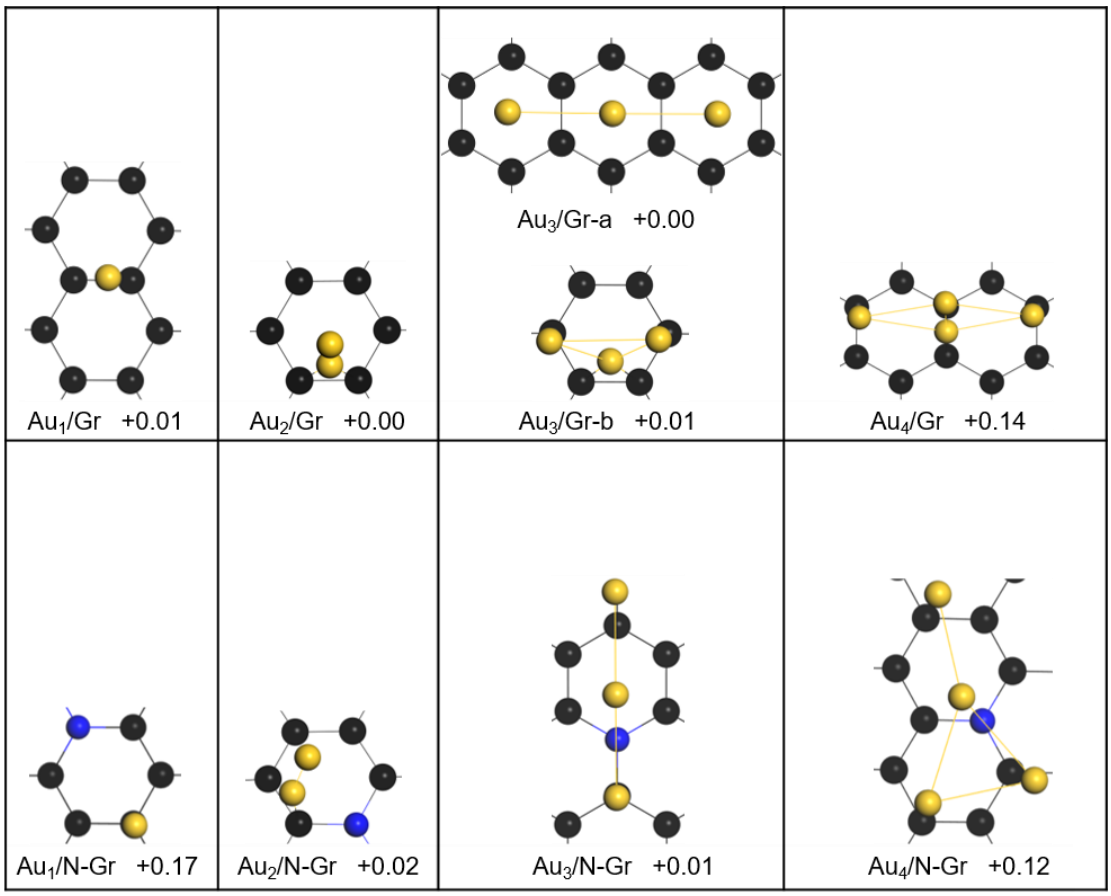

Figure S20. The sub-stable structures of Au_n (n=1–4) adsorption on Gr and N-Gr surfaces with relative energies ΔE (eV).

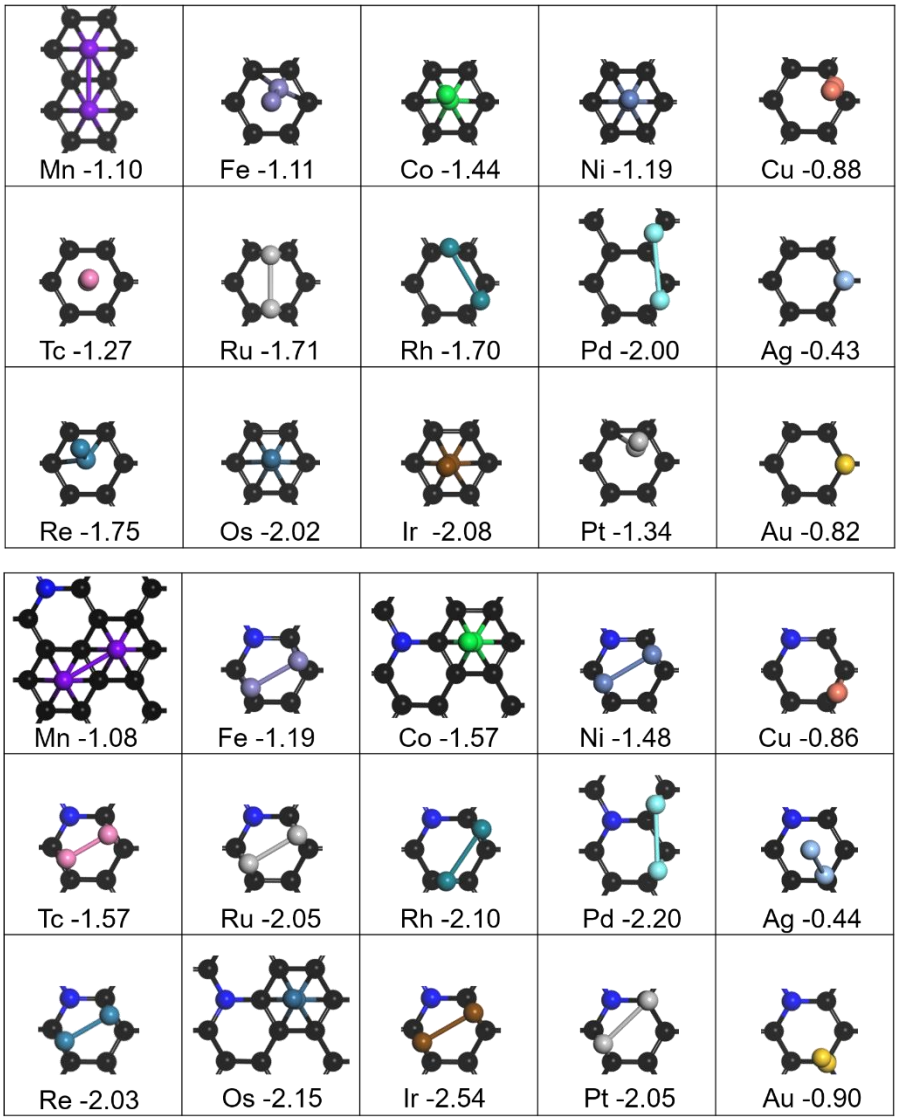

Figure S21. Summary for the adsorption of TM dimers on Gr (the top) and N-Gr (the bottom) surfaces with associated E_{ads} (eV).

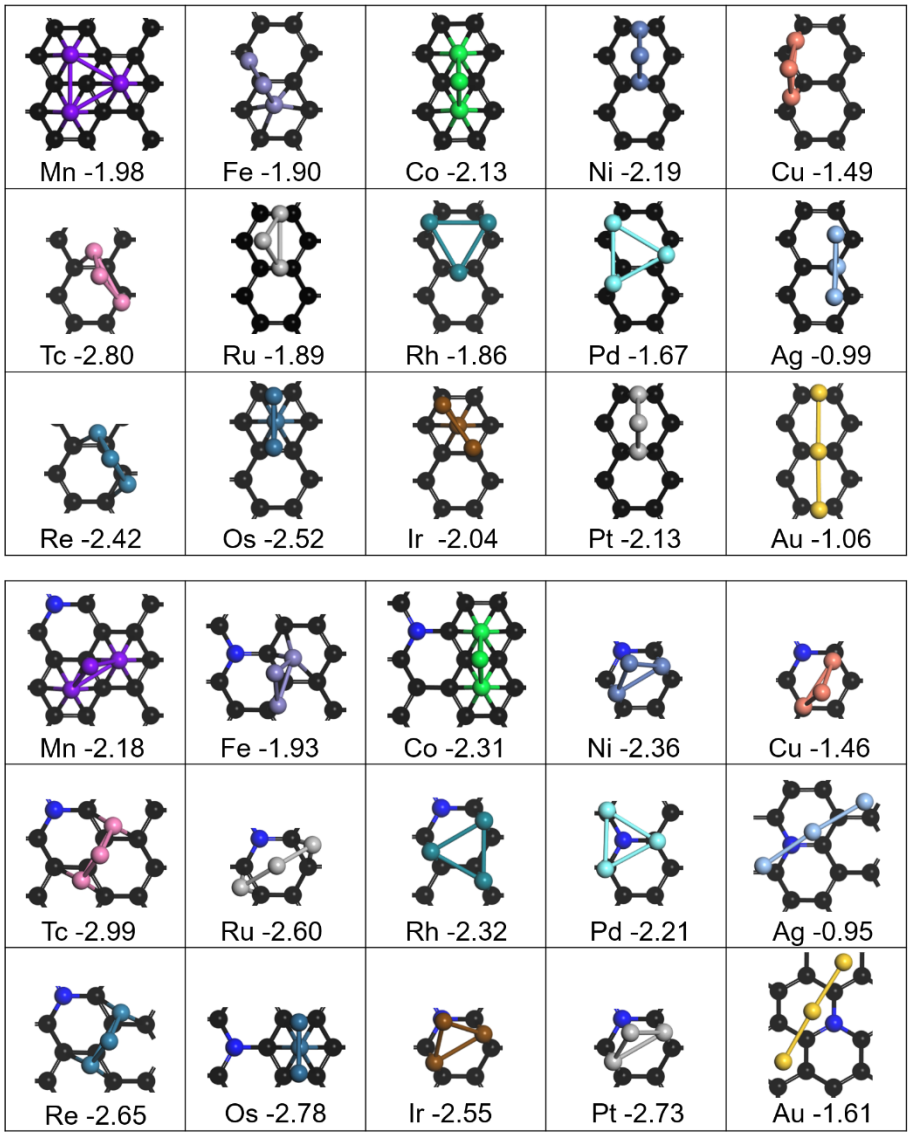

Figure S22. Summary for the adsorption of TM trimers on Gr (the top) and N-Gr (the bottom) surfaces with associated E_{ads} (eV).

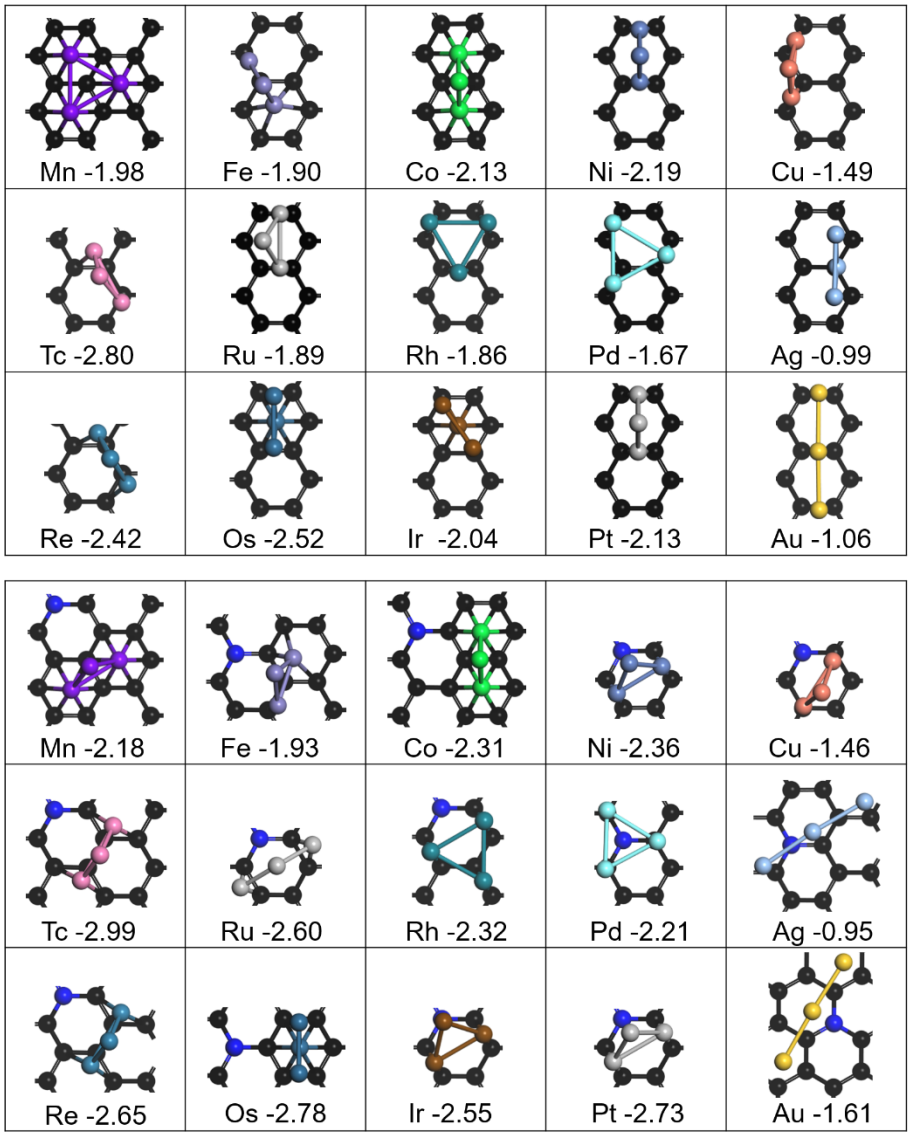

Figure S23. Summary for the adsorption of TM tetramers on Gr (the top) and N-Gr (the bottom) surfaces with associated E_{ads} (eV).

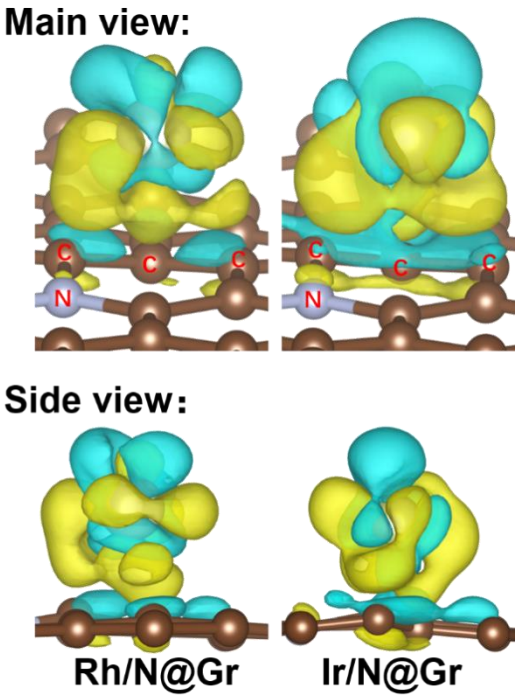

Figure S24. The main and side view of the 3D charge density difference plots for Rh_1/N-Gr and Ir_1/N-Gr, respectively, where the isosurface value is set to be 0.005 e/bohr^3.

Table S4. Electronegativity and IP (eV) for each TM elements, and associated charge transfer ($\Delta q/e$) (positive values represent clusters getting electron)

	electron egativity	IP/eV	Δq /e							
			Gr			N-Gr				
Mn	1.55	7.43	–0.58	–0.98	–1.47	–0.69	–0.49	–0.96	–0.97	–0.62
Tc	1.90	7.28	–0.60	–0.44	–0.72	–1.00	–0.54	–0.53	–0.72	–1.06
Re	1.90	7.88	–0.53	–0.55	–0.81	–0.58	–0.44	–0.56	–0.78	–1.12
Fe	1.83	7.88	–0.69	–0.42	–0.75	–0.99	–0.61	–0.62	–0.70	–0.93
Ru	2.20	7.37	–0.45	–0.44	–0.44	–0.70	–0.38	–0.39	–0.46	–0.78
Os	2.20	8.73	–0.37	–0.36	–0.38	–0.38	–0.25	–0.28	–0.28	–0.57
Co	1.88	7.86	–0.62	–0.35	–0.75	–0.83	–0.51	–0.29	–0.67	–0.73
Rh	2.28	7.46	–0.30	–0.33	–0.44	–0.42	–0.16	–0.24	–0.35	–0.38
Ir	2.20	9.22	–0.08	–0.12	–0.23	–0.30	–0.06	–0.10	–0.24	–0.41
Ni	1.91	7.64	–0.49	–0.22	–0.45	–0.70	–0.24	–0.32	–0.35	–0.56
Pd	2.20	8.33	–0.19	–0.27	–0.32	–0.18	–0.12	–0.16	–0.16	–0.13
Pt	2.28	8.96	–0.00	+0.06	–0.08	–0.16	+0.08	+0.05	+0.03	–0.06
Cu	1.90	7.73	–0.25	–0.12	–0.49	–0.38	–0.12	–0.09	–0.30	–0.18
Ag	1.93	7.58	–0.11	–0.02	–0.34	–0.19	+0.06	–0.02	+0.21	–0.06
Au	2.54	9.22	+0.13	+0.08	+0.32	+0.08	+0.18	+0.10	+0.46	+0.17

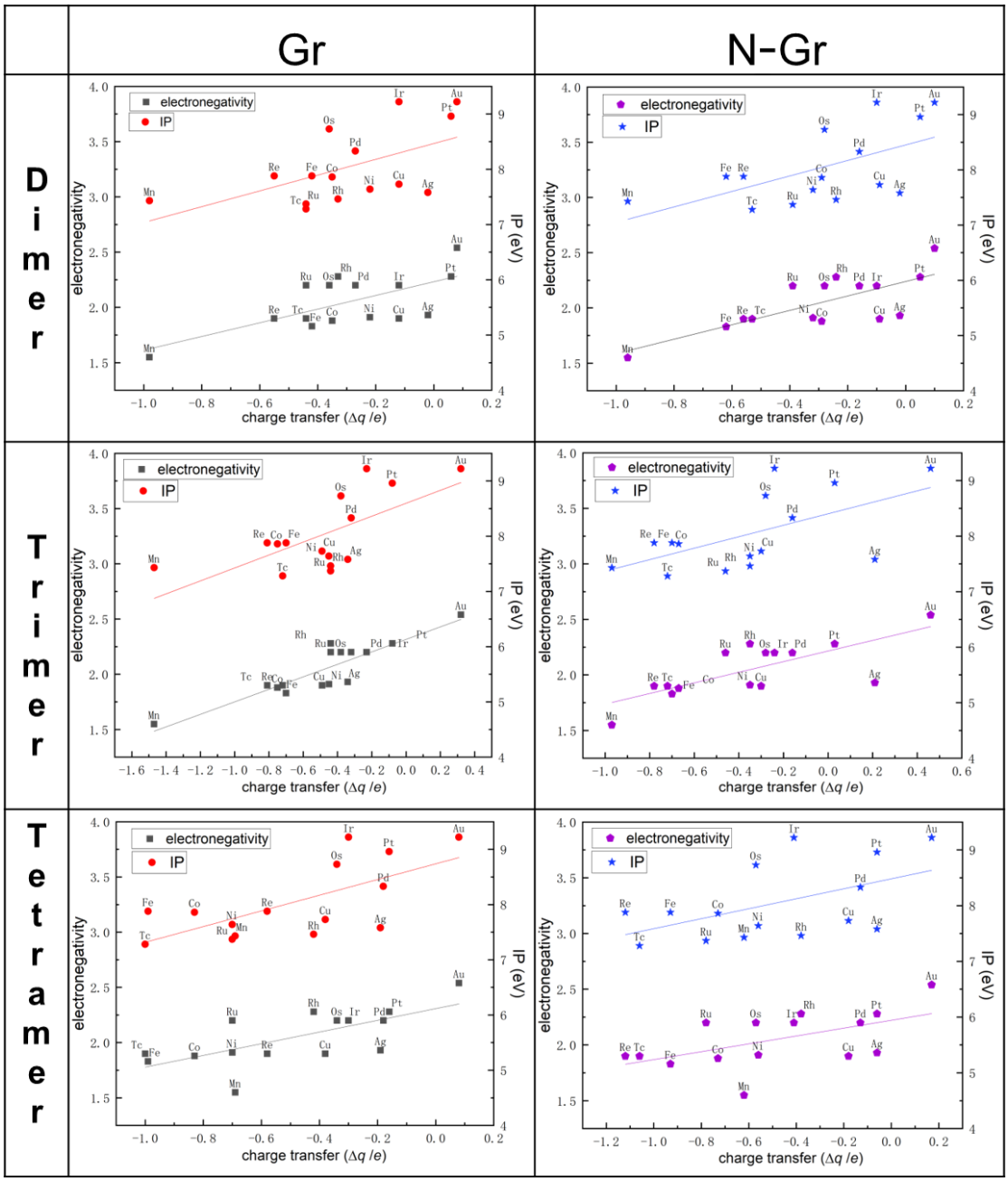

Figure S25. Plots of electronegativity and IP versus charge transfer for dimers, trimers, and tetramers on Gr (the left) and N-Gr (the right) surfaces.

Table S5. magnetic moment (μ/μ_B), z axis electric-dipole moment (p/D), and work function (Φ/eV) for the total system

Atom	n	$\mu(\mu_B)$	p(D)	Φ(eV)	$\mu(\mu_B)$	p(D)	Φ(eV)
			Gr			N-Gr	
Slab		0.00	0.00	4.27	0.00	0.00	3.39
Mn	1	5.44	0.13	4.31	4.65	–0.14	3.48
	2	8.45	0.10	3.37	7.58	–0.28	3.50
	3	11.44	0.68	3.44	2.26	0.79	3.27
	4	13.70	1.44	4.04	14.31	0.95	3.59
Tc	1	0.56	2.06	3.94	0.83	1.62	3.89
	2	1.90	–0.63	4.05	0.88	–0.25	3.99
	3	2.55	0.42	3.69	1.87	0.27	3.41
	4	2.33	0.57	3.66	0.99	0.01	4.03
Re	1	3.51	0.47	4.43	1.18	–0.29	3.82
	2	1.56	0.65	3.85	0.83	0.11	3.98
	3	2.56	0.45	3.72	2.19	–0.28	3.42
	4	0.42	–0.35	3.86	–0.13	–0.17	5.24
Fe	1	2.22	1.95	4.10	1.73	1.23	3.67
	2	6.42	0.60	4.10	5.44	0.05	3.68
	3	8.44	0.84	3.60	7.98	0.44	3.51
	4	10.44	1.03	3.34	9.46	0.66	3.28
Ru	1	1.56	1.37	4.02	1.20	1.03	3.71
	2	3.98	–0.46	4.04	3.24	–0.17	3.58
	3	6.00	–0.30	3.99	4.99	–0.91	3.89
	4	1.58	–0.38	3.73	3.63	–0.31	3.32
Os	1	1.66	0.51	3.98	1.87	–0.66	4.08
	2	2.43	0.16	3.79	2.29	–0.54	3.58
	3	3.91	0.20	4.00	4.36	–0.50	3.74
	4	2.43	–0.04	3.65	0.95	–0.31	3.86
Co	1	1.43	1.68	3.82	1.27	1.07	3.49
	2	4.01	–0.16	4.02	3.45	–0.55	3.51
	3	5.42	0.24	3.94	4.44	–0.23	3.62
	4	6.44	0.69	3.71	5.45	0.07	3.26
Rh	1	0.56	0.84	4.07	0.00	0.96	3.86
	2	1.79	1.26	4.05	0.99	0.92	3.73
	3	2.61	0.93	4.01	3.96	0.77	4.14
	4	3.52	–0.43	4.02	1.14	–0.07	4.00
Ir	1	0.95	0.30	4.19	0.00	0.35	3.93
	2	0.44	–1.33	4.42	0.97	–1.12	4.55
	3	1.92	–0.49	3.96	0.00	–0.95	4.93
	4	0.44	–0.20	3.92	1.23	–0.06	4.15
Ni	1	0.00	1.12	3.85	0.52	0.49	3.49
	2	2.02	–0.83	4.54	1.44	–0.39	3.94
	3	1.02	0.24	3.86	1.42	–0.15	3.99
	4	2.41	0.59	3.73	1.44	–0.17	3.52
Pd	1	0.00	1.25	4.11	0.00	0.61	3.39
	2	0.00	1.31	4.03	0.55	0.06	4.02
	3	0.01	0.75	3.92	0.00	–0.23	3.95
	4	1.60	–0.55	4.08	1.40	–0.86	3.94
Pt	1	0.00	0.27	4.09	0.55	–0.63	4.12
	2	1.57	–2.04	4.93	1.11	–1.20	4.82
	3	0.39	–1.40	4.57	1.18	–1.81	4.46
	4	1.92	–0.54	4.05	1.07	–0.84	4.78
Cu	1	0.63	0.03	4.04	0.00	–0.30	4.22
	2	0.00	–0.97	4.45	0.00	–1.25	3.73
	3	0.46	0.71	3.15	0.00	0.56	3.63

	4	0.00	–0.39	4.13	0.00	–0.78	3.58
Ag	1	0.90	–0.28	4.17	0.45	–1.34	3.87
	2	0.00	–1.19	4.36	0.00	–1.22	3.59
	3	0.56	1.57	3.90	0.00	–2.78	4.47
	4	0.00	0.20	4.02	0.00	–0.91	3.44
Au	1	0.80	–1.56	4.86	0.00	–1.65	4.77
	2	0.00	–1.83	4.71	0.00	–2.24	4.17
	3	0.00	–3.51	6.02	0.00	–4.29	5.93
	4	0.00	–1.74	4.71	0.00	–2.30	4.39

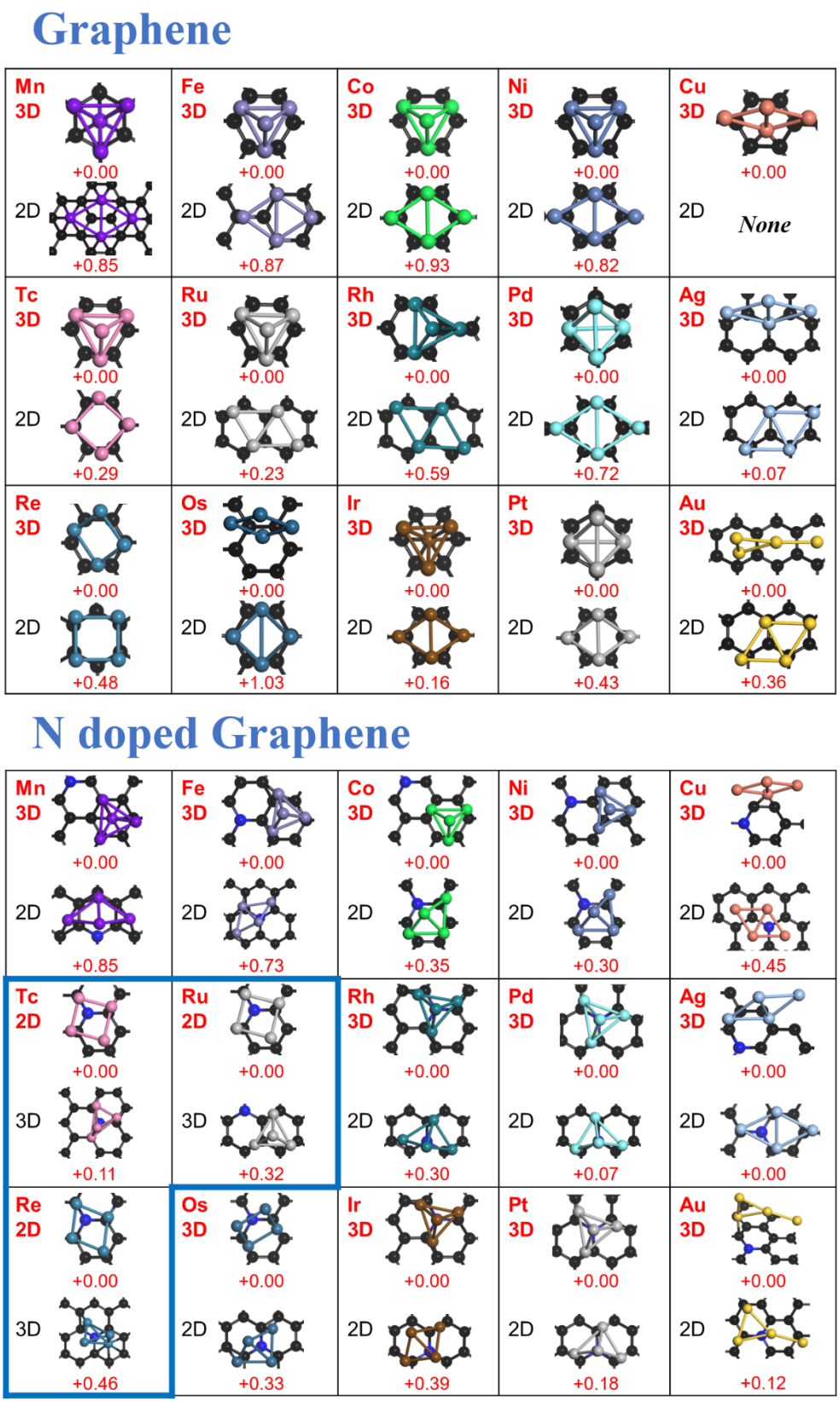

Figure S26. Comparison of 3D growth mode and 2D growth mode for tetramers on Gr and N-Gr surfaces with relative energies (eV).