Electronic Supporting Information

Tunning Na adsorption on the edge of graphitic nanopore by incorporating functionalized-ligand and single-heteroatom dopant

Nenni[1], Adhitya G. Saputro[1,2,3,*], Ganes Shukri[1,2,3,**], Nadhratun Naiim Mobarak[4], Fine Dwinita Aprilyanti[2], Ahmad Nuruddin[1,2,3], and Hermawan K. Dipojono[1,2,3]

[1]Graduate Program of Engineering Physics, Faculty of Industrial Technology, Institut Teknologi Bandung, Bandung, West Java 40132, Indonesia

[2]Advanced Functional Materials Research Group, Faculty of Industrial Technology, Institut Teknologi Bandung, Bandung, West Java 40132, Indonesia

[3]Research Center for Nanoscience and Nanotechnology, Institut Teknologi Bandung, Bandung, West Java 40132, Indonesia

[4]Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, Bangi 43600, Selangor, Malaysia

Table S1. Adsorption energy of functional groups on X-ZGNR and X-AGNR systems.

Functional Group	Adsorption energy of functional group $E_{ads}^{functional}$ (eV)				
	ZGNR	B-ZGNR	N-ZNGR	S-ZGNR	P-ZGNR
H	-21.32	-21.19	-19.96	-18.88	-19.13
O	-24.54	-24.35	-22.78	-21.37	-22.35
HO	-24.86	-26.45	-23.48	-21.22	-23.40
HOOC	-28.35	-28.60	-27.40	-25.85	-26.18
	AGNR	B-AGNR	N-AGNR	S-AGNR	P-AGNR
H	-17.17	-16.84	-15.62	-13.63	-15.03
O	-17.93	-18.58	-18.35	-15.36	-18.14
HO	-20.24	-21.69	-18.95	-17.55	-18.95
HOOC	-23.98	-24.19	-22.65	-20.90	-22.03

Table S2. Relative adsorption energy of functional groups on X-ZGNR and X-AGNR systems. The values are relative to the HX-GNR systems.

Functional Group	Relative adsorption energy of functional group $\Delta E_{ads}^{functional}$ (eV)				
	ZGNR	B-ZGNR	N-ZNGR	S-ZGNR	P-ZGNR
O	-3.22	-3.16	-2.82	-2.49	-3.22
HO	-3.55	-5.26	-3.51	-2.33	-4.27
HOOC	-7.03	-7.41	-7.44	-6.97	-7.05
	AGNR	B-AGNR	N-AGNR	S-AGNR	P-AGNR
O	-0.76	-1.74	-2.73	-1.73	-3.10
HO	-3.07	-4.84	-3.33	-3.93	-3.91
HOOC	-6.81	-7.35	-7.04	-7.27	-7.00

Table S3. Formation energy for ZGNR and AGNR systems.

Functional Group	Formation energy E_{form} (eV)				
	ZGNR	B-ZGNR	N-ZNGR	S-ZGNR	P-ZGNR
H	1.81	2.10	1.03	2.36	2.67
O	-1.41	-1.10	-1.79	-0.13	-0.55
HO	-1.74	-3.16	-2.48	0.03	-1.60
HOOC	-5.22	-5.31	-6.41	-4.60	-4.39
	AGNR	B-AGNR	N-AGNR	S-AGNR	P-AGNR
H	0.66	2.10	0.97	3.13	2.65
O	-0.10	0.37	-1.76	1.40	-0.45
HO	-2.41	-2.74	-2.36	-0.80	-1.26
HOOC	-6.15	-5.24	-6.06	-4.15	-4.35

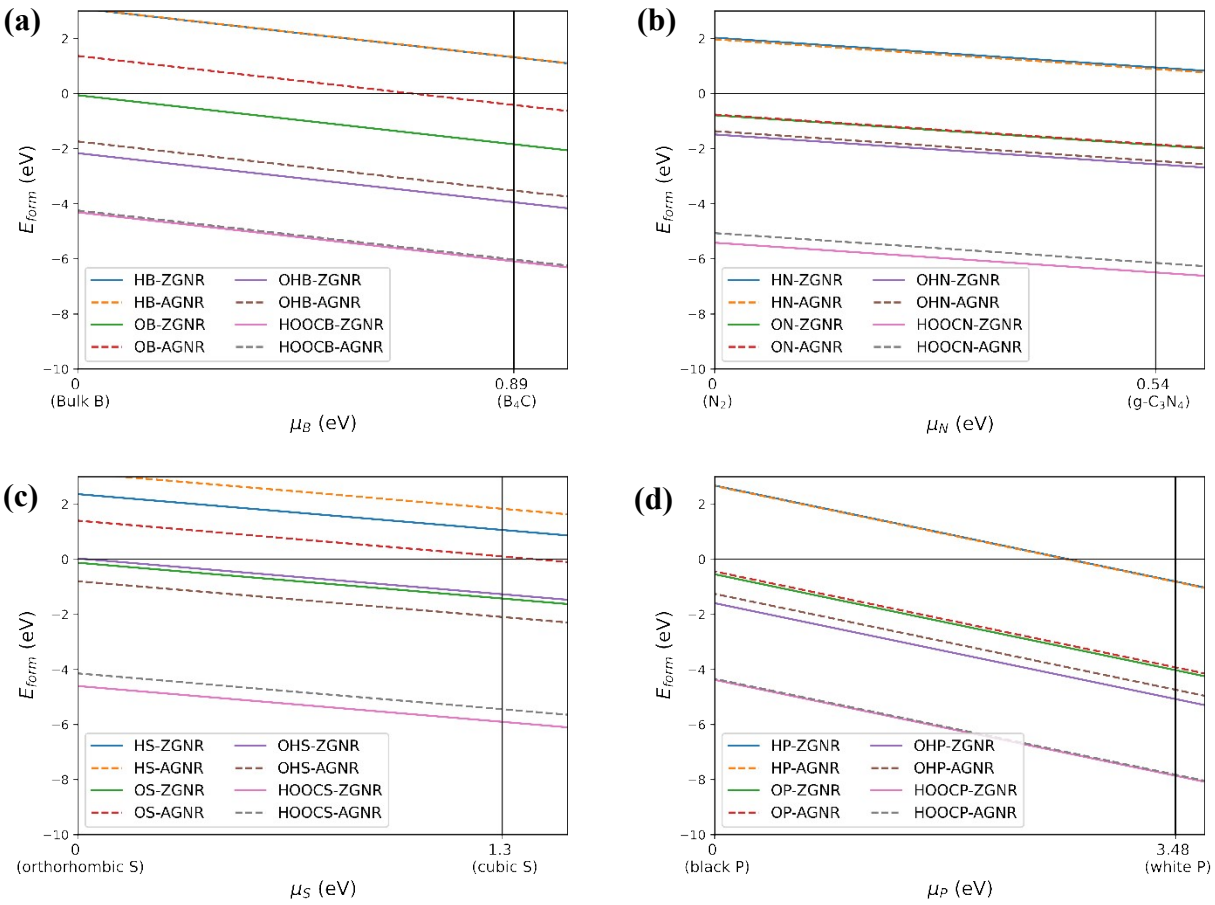


Figure S1. (a)-(d) Heteroatom dopant incorporation energy (B, N, P, S) on the edge of ZGNR & AGNR as a function of the dopant chemical potential.

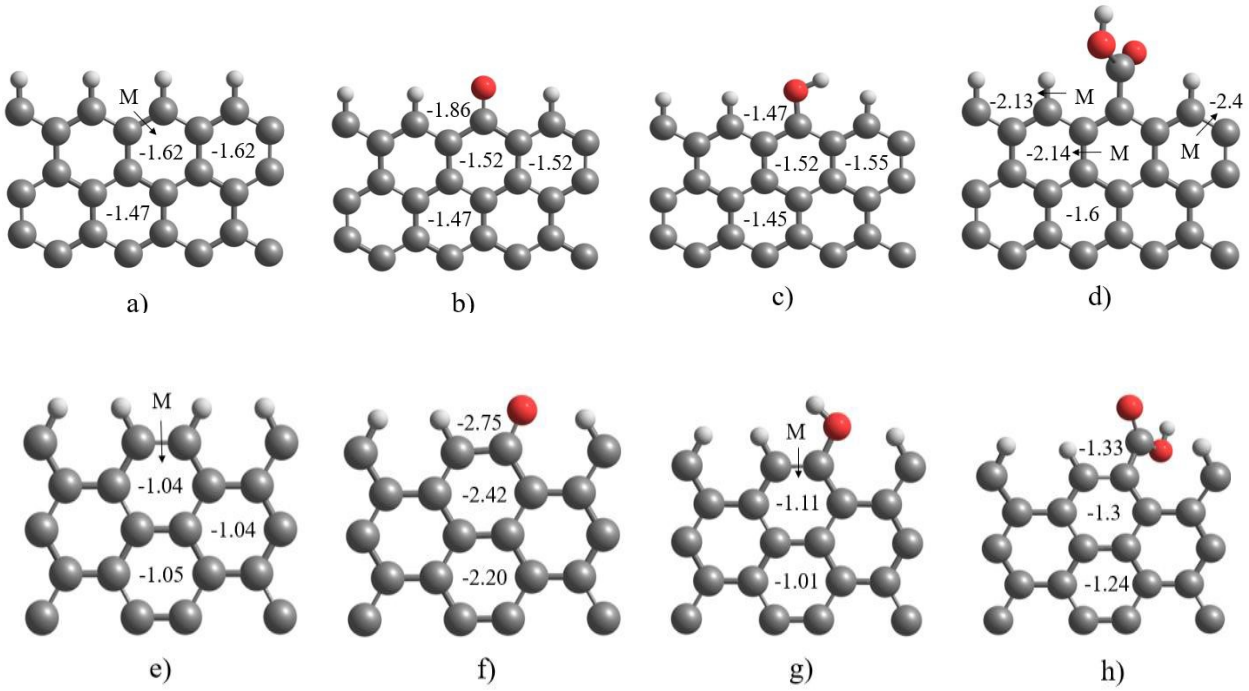


Figure S2. Na adsorption energy on (a) H-ZGNR, (b) O-ZGNR, (c) HO-ZGNR, (d) HOOC-ZGNR, (e) H-AGNR, (f) O-AGNR, (g) HO-AGNR, (h) HOOC-AGNR at different sites. Hydrogen atoms are indicated in white, carbon atoms in grey, oxygen in red.

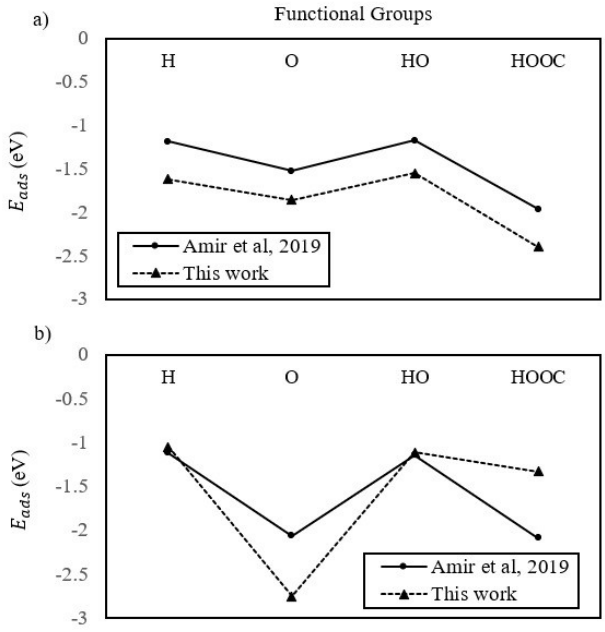
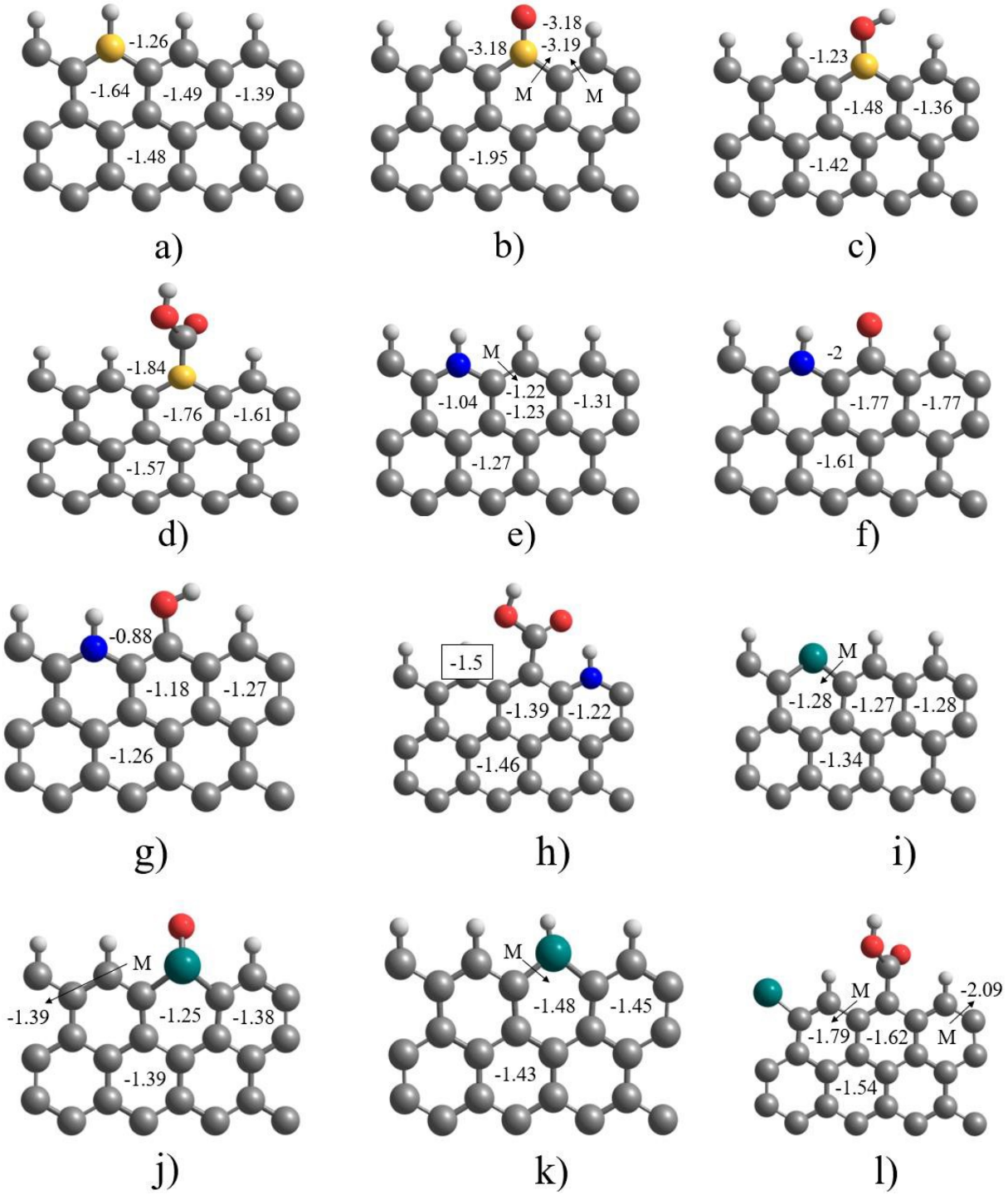


Figure S3. The comparison [1] of Na adsorption energy on the edge functionalized groups of (a) ZGNR and (b) AGNR.


-1.26
-1.64
-1.49
-1.39
-1.48
a)
-3.18
-3.18
-3.19
M
M
-1.95
b)
-1.23
-1.48
-1.36
-1.42
c)
-1.84
-1.76
-1.61
-1.57
d)
M
-1.04
-1.22
-1.23
-1.31
-1.27
e)
-2
-1.77
-1.77
-1.61
f)
-0.88
-1.18
-1.27
-1.26
g)
-1.5
-1.39
-1.22
-1.46
h)
M
-1.28
-1.27
-1.28
-1.34
i)
M
-1.39
-1.25
-1.38
-1.39
j)
M
-1.48
-1.45
-1.43
k)
M
-2.09
-1.79
-1.62
M
-1.54
l)

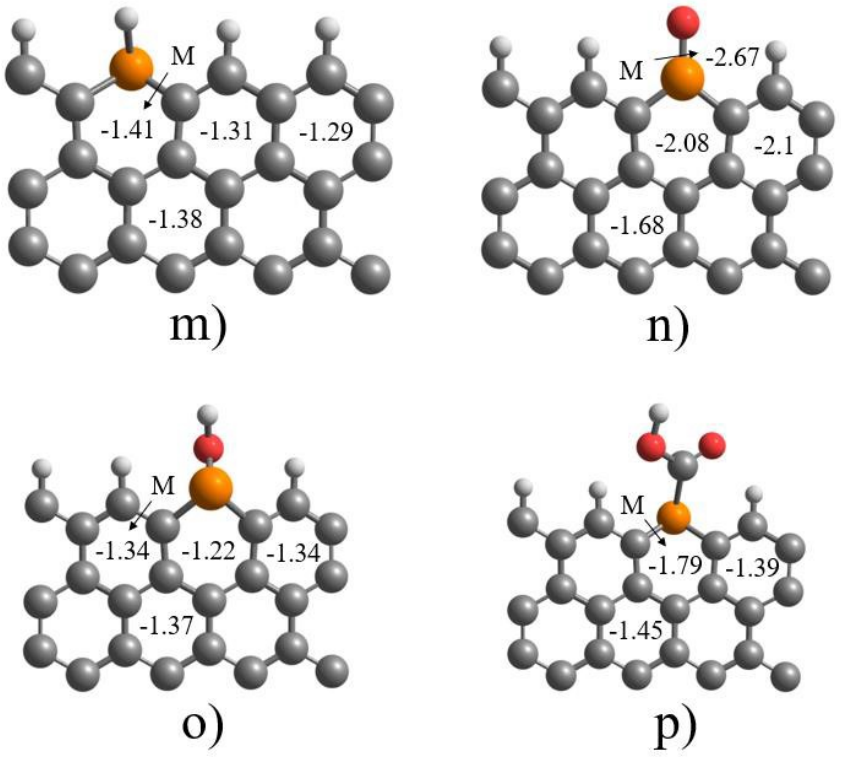
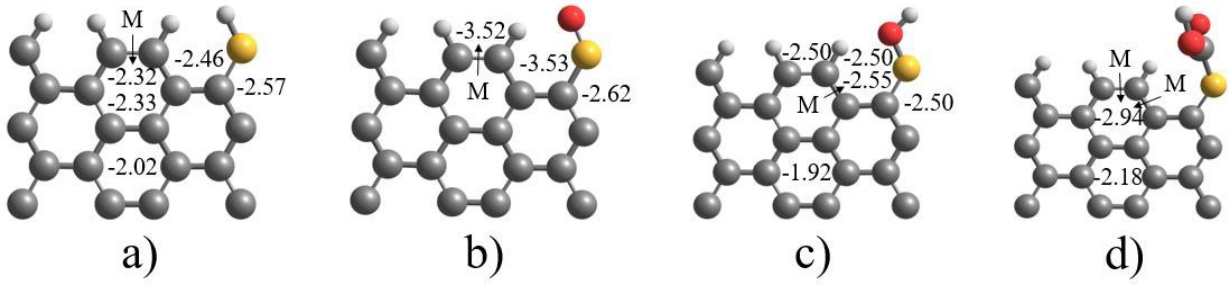


Figure S4. Na adsorption energy (in eV) on (a) HB (b) OB, (c) HOB, (d) HOOCB, (e) HN, (f) ON, (g) HON, (h) HOOCN, (i) HS, (j) OS, (k) HOS, (l) HOOCS, (m) HP, (n) OP, (o) HOP, and (p) HOOCP-ZGNR. White, grey, red, yellow, blue, green, orange, purple represent hydrogen, carbon, oxygen, boron, nitrogen, sulphur, phosphorus, and Na atoms, respectively. The notation "M" indicates that the Na moved from the initial site (to the site signed by the black arrow) upon relaxation.



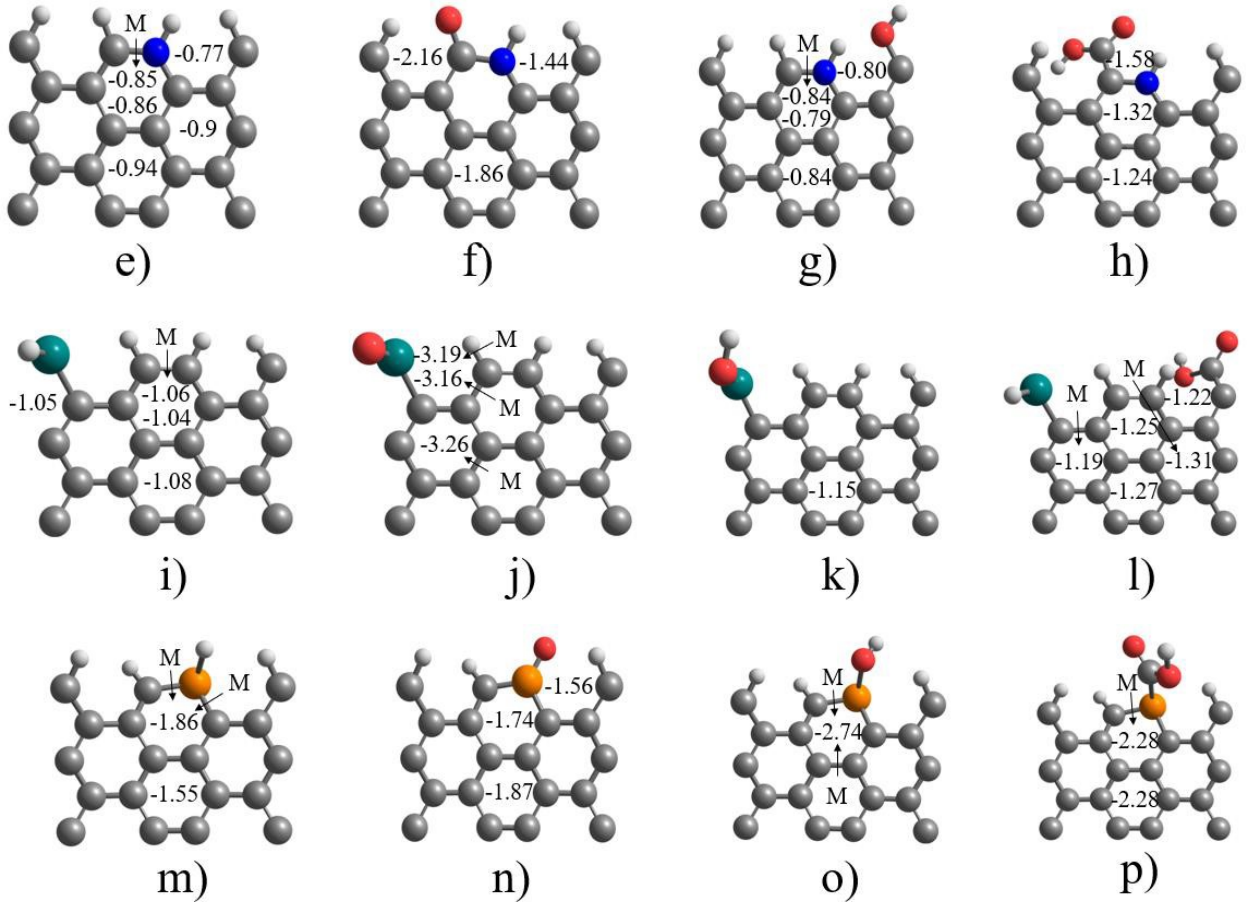
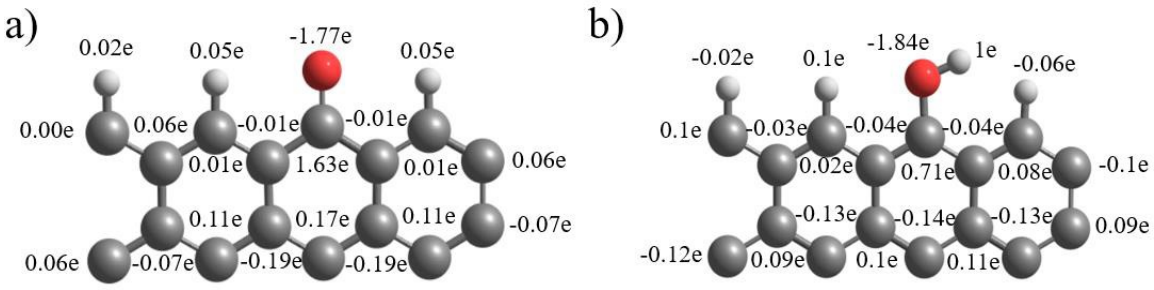


Figure S5. Na adsorption energy (in eV) on (a) HB (b) OB, (c) HOB, (d) HOOCB, (e) HN, (f) ON, (g) HON, (h) HOOCN, (i) HS, (j) OS, (k) HOS, (l) HOOCS, (m) HP, (n) OP, (o) HOP, (p) HOOCP-AGNR. White, grey, red, yellow, blue, green, orange, purple represent hydrogen, carbon, oxygen, boron, nitrogen, sulphur, phosphorus, and Na atoms, respectively.

Table S4. Calculated formation energies (E_{form}) and strongest adsorption energies (E_{ads}) of Na on heteroatom doped Z/AGNR terminated with H and oxygen-functional groups edge.

System	ZGNR		AGNR	
	E_{form} (eV)	E_{ads} (eV)	E_{form} (eV)	E_{ads} (eV)
HB	2.1	-1.64	2.1	-2.57
OB	-1.1	-3.19	0.37	-3.53
HOB	-3.16	-1.48	-2.74	-2.55
HOOCB	-5.31	-1.84	-5.24	-2.94
HN	1.03	-1.31	0.97	0.94
ON	-1.79	-2.00	-1.76	-2.16
HON	-2.48	-1.27	-2.36	-0.84
HOOCN	-6.41	-1.50	-6.06	-1.58
HS	2.36	-1.34	3.13	-1.08
OS	-0.13	-1.39	1.40	-3.26
HOS	0.03	-1.48	-0.8	-1.15
HOOCS	-4.60	-2.09	-4.15	-1.31
HP	2.67	-1.41	2.65	-1.86
OP	-0.55	-2.67	-0.45	-1.87
HOP	-1.60	-1.37	-1.26	-2.74
HOOCP	-4.39	-1.79	-4.35	-2.28



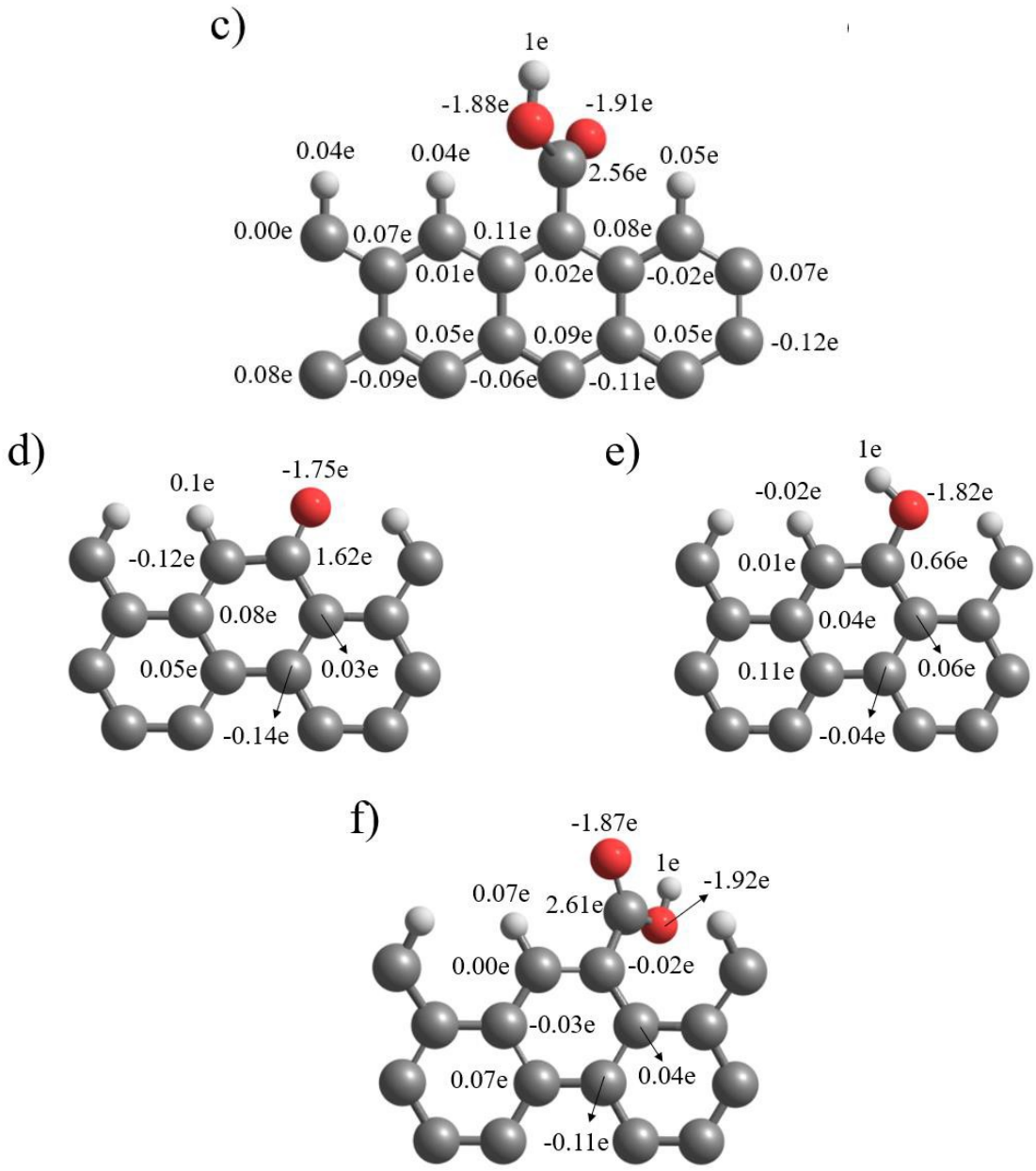


Figure S6. Bader charge distribution (before Na adsorption) of (a) O, (b) HO, (c) HOOC-ZGNR and (d) O, (e) HO, (f) HOOC-AGNR.

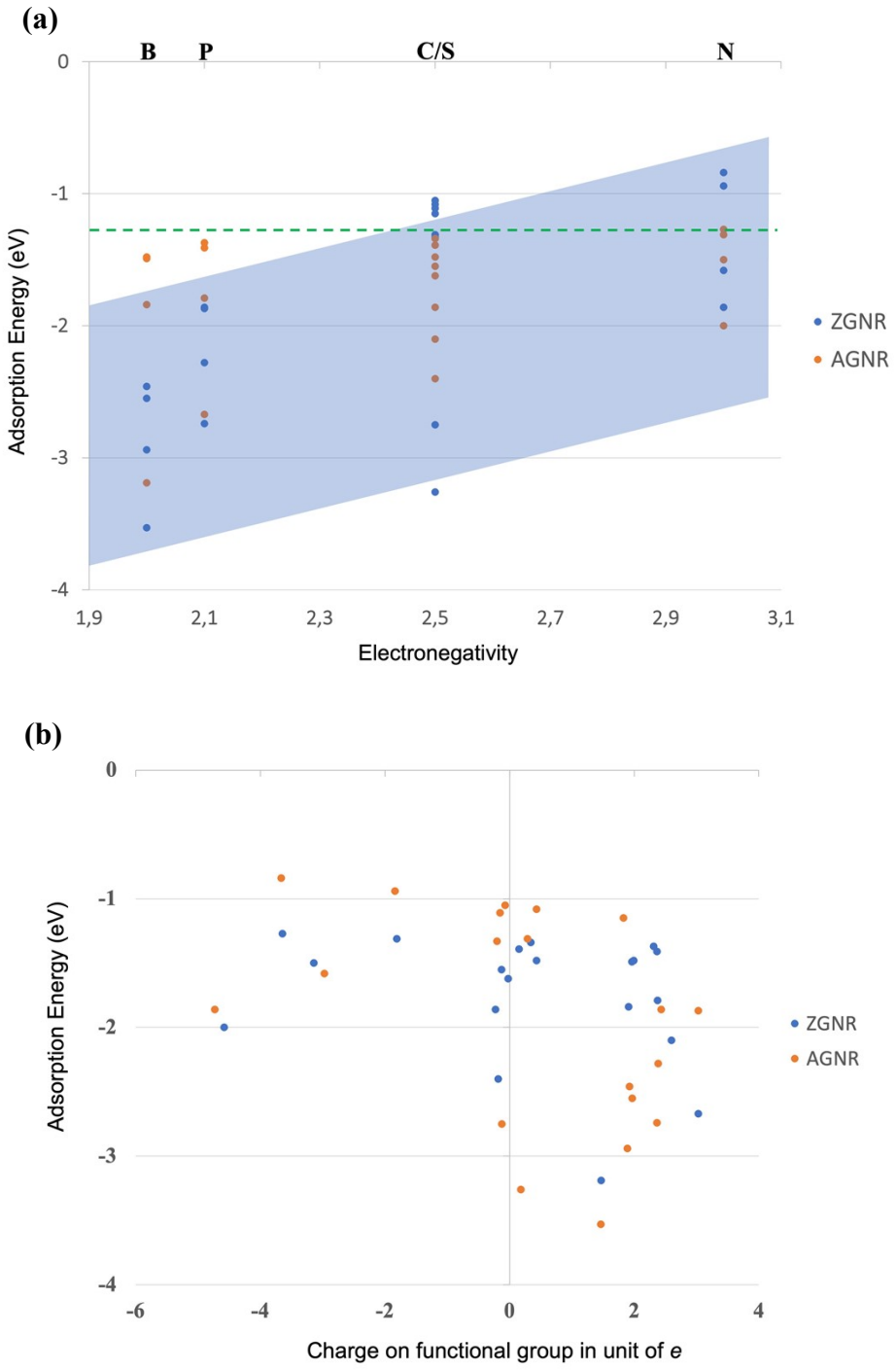
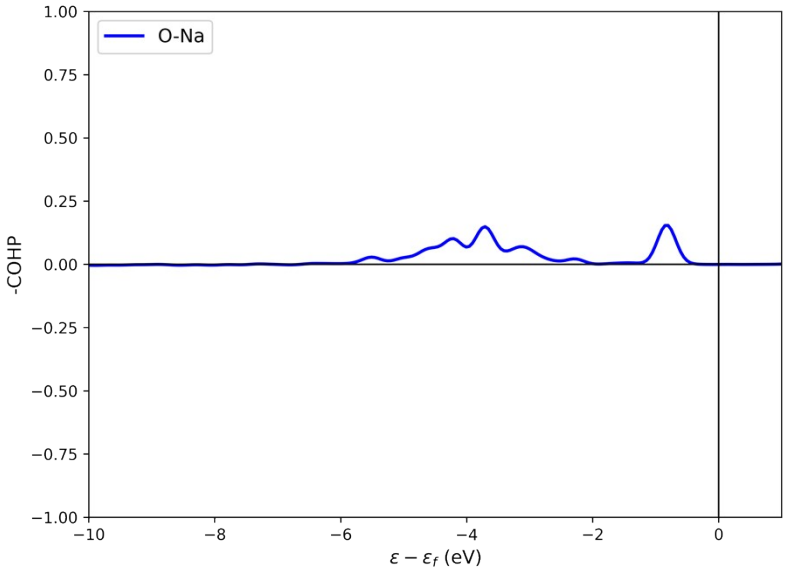
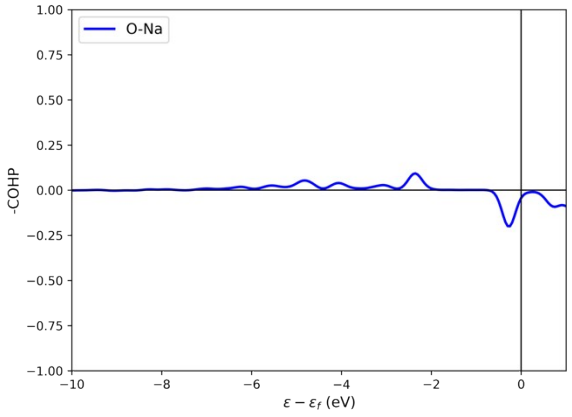


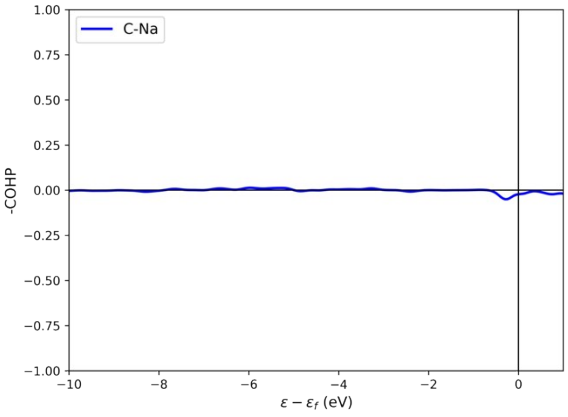
Figure S7. (a) Adsorption energies of single Na atom in the vicinity of single heteroatom dopant *versus* the electronegativity of the considered heteroatom dopant. (b) Adsorption energies of single Na atom on nearby sites of functionalized ligands – heteroatom dopant. The green dashed line in (a) corresponds to the cohesive energy of Na.

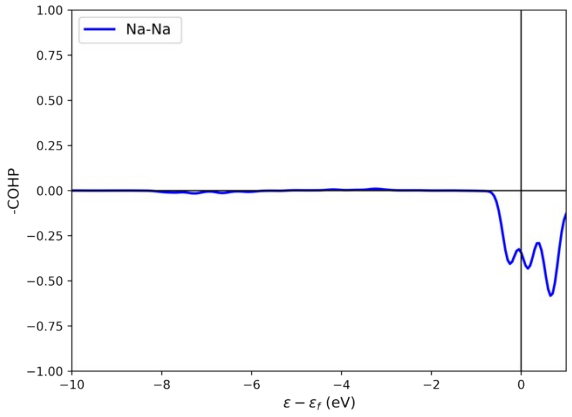
(a)


O-Na
-COHP
$\varepsilon - \varepsilon_f$ (eV)

(b)


O-Na
-COHP
$\varepsilon - \varepsilon_f$ (eV)


C-Na
-COHP
$\varepsilon - \varepsilon_f$ (eV)


Na-Na
-COHP
$\varepsilon - \varepsilon_f$ (eV)

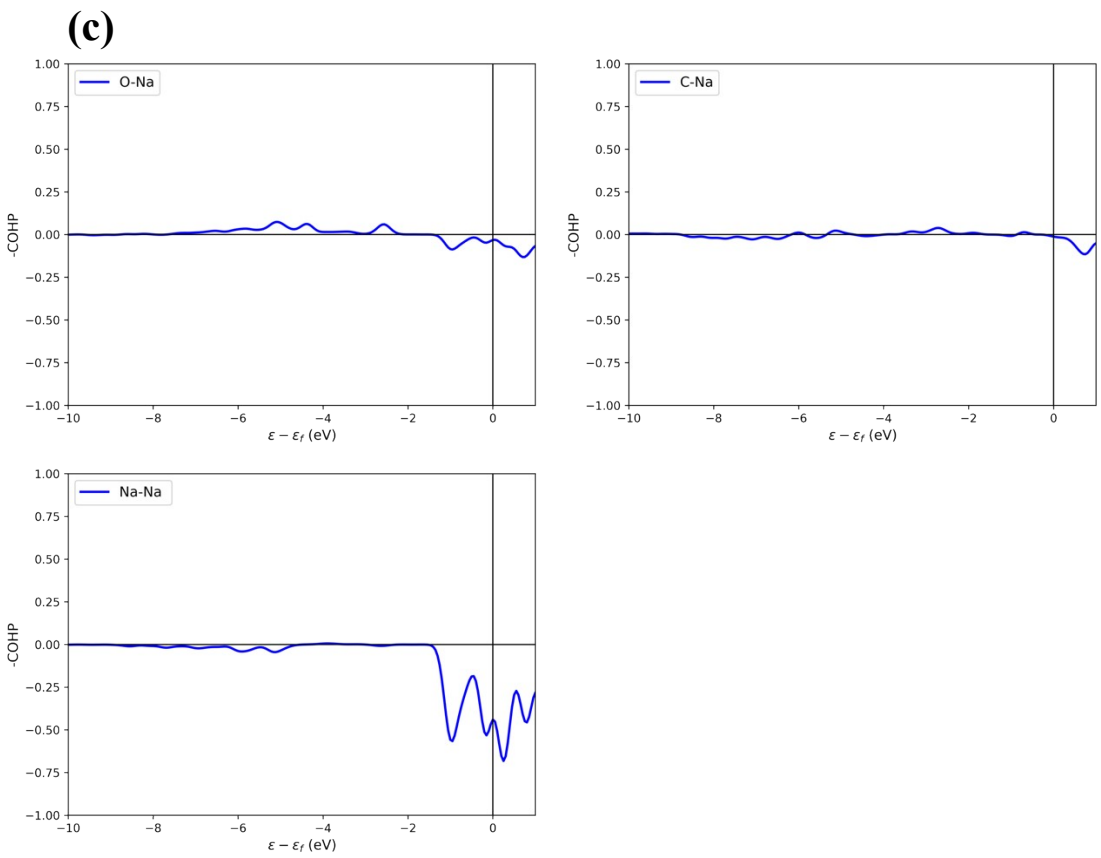


Figure S8. COHP plot of: (a) The closest pair of Na-O for 1 adsorbed Na, (b) the closest pairs of Na-O, Na-C and Na-Na for 6 adsorbed Na and (c) the closest pairs of Na-O, Na-C and Na-Na for 10 adsorbed Na. All COHPs were calculated for Na adsorb on the OB-ZGNR.

References

[1] A. H. Farokh Niaei, T. Roman, T. Hussain, and D. J. Searles, "Computational Study on the Adsorption of Sodium and Calcium on Edge-Functionalized Graphene Nanoribbons," *J. Phys. Chem. C*, vol. 123, no. 24, pp. 14895–14908, 2019, doi: 10.1021/acs.jpcc.9b02003.