Adsorption of Rare Bases on Transition Metal Doped γ-Graphyne Nanosheets: A DFT study

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Table S1 The structural characteristics of TM-GY.

System	Fe-GY	E_{ads}/eV	d/Å	Co-GY	E_{ads}/eV	d/Å	Ni-GY	E_{ads}/eV	d/Å
	-PP	-1.01	2.905	-PP	-1.08	3.241	-PP	-0.92	3.236
	-CO	-1.45	2.006	-CO	-0.68	2.958	-CO	-0.73	3.055
Cyt	=N	-1.22	2.008	=N	-1.24	2.220	=N	-0.58	2.841
	-NH	-0.80	2.951	-NH	-0.84	2.166	-NH	-0.54	2.971
	$-NH_2$	-0.54	3.163	$-NH_2$	-0.71	3.207	$-NH_2$	-0.54	3.133
	-PP	-1.14	2.882	-PP	-1.22	3.280	-PP	-1.06	3.249
	-CO	-0.87	1.929	-CO	-0.72	2.957	-CO	-0.75	3.049
5-meCyt	=N	-0.95	2.184	=N	-1.29	2.218	=N	-0.73	2.171
	-NH	-0.88	2.955	-NH	-0.89	2.167	-NH	-0.56	2.970
	$-NH_2$	-0.60	3.160	$-NH_2$	-0.80	3.130	$-NH_2$	-0.62	3.109
	-PP	-0.57	3.038	-PP	-1.25	3.240	-PP	-1.14	3.262
	-CO	-0.46	2.051	-CO	-0.71	2.906	-CO	-0.74	3.044
5-hmCyt	=N	-1.28	2.000	=N	-1.26	2.225	=N	-0.55	2.960
	-NH	-0.66	2.673	-NH	-0.89	2.167	-NH	-0.61	2.781
	$-NH_2$	-0.64	3.108	$-NH_2$	-0.80	3.115	$-NH_2$	-0.63	3.089
	-OH	-0.50	2.032	-OH	-0.89	2.187	-OH	-0.57	2.965
	-PP	-0.36	3.035	-PP	-1.13	3.270	-PP	-1.02	3.263
	-CO	-0.33	2.051	-CO	-0.66	2.968	-CO	-0.50	2.989
5-caCyt	=N	-1.19	2.006	=N	-1.19	2.246	=N	-0.69	3.104
	-NH	-0.03	2.721	-NH	-0.81	2.431	-NH	-0.60	2.670
	$-NH_2$	-0.56	3.171	$-NH_2$	-0.77	3.140	$-NH_2$	-0.59	3.131
	-COOH	-0.69	2.973	-COOH	-0.75	3.012	-COOH	-0.60	3.558
	-PP	-0.97	3.051	-PP	-1.14	3.250	-PP	-0.96	3.272
	-CO	-0.99	2.608	-CO	-0.64	2.980	-CO	-0.48	2.990
5-fCyt	=N	-1.20	1.996	=N	-1.28	2.224	=N	-0.78	2.989
	-NH	-0.02	2.719	-NH	-1.24	2.090	-NH	-0.56	2.730
	$-NH_2$	-0.55	3.150	$-NH_2$	-0.73	3.150	$-NH_2$	-0.56	3.129
	-CHO	-1.13	2.018	-CHO	-0.70	3.011	-CHO	-0.49	2.992

Table S2 Abbreviations and Corresponding terminology

Abbreviations	Corresponding terminology
RBs	Rare Bases
γ-G	γ-Graphyne
TM-GY	Transition metal-doped γ-graphyne
Cyt	Cytosine
5-meCyt	5-methylcytosine
5-hmCyt	5-hydroxymethylcytosine
5-caCyt	5-carboxycytosine
5-fCyt	5-formylcytosine
2D	Two-dimensional
GDY	Graphiyne
GDYNP	Graphiyne-based nanopore
PDOS	Partial density of states
CDD	Charge differential density
DFT	Density functional theory
GGA	Generalized gradient approximation
PBE	Perdew-Burke-Ernzerhof
DNP	Polarized double numerical
BSSE	Basis Set Superposition Error
XRD	X-ray Diffraction
STM	Scanning tunnel microscope
ESP	Electrostatic potential isosurface

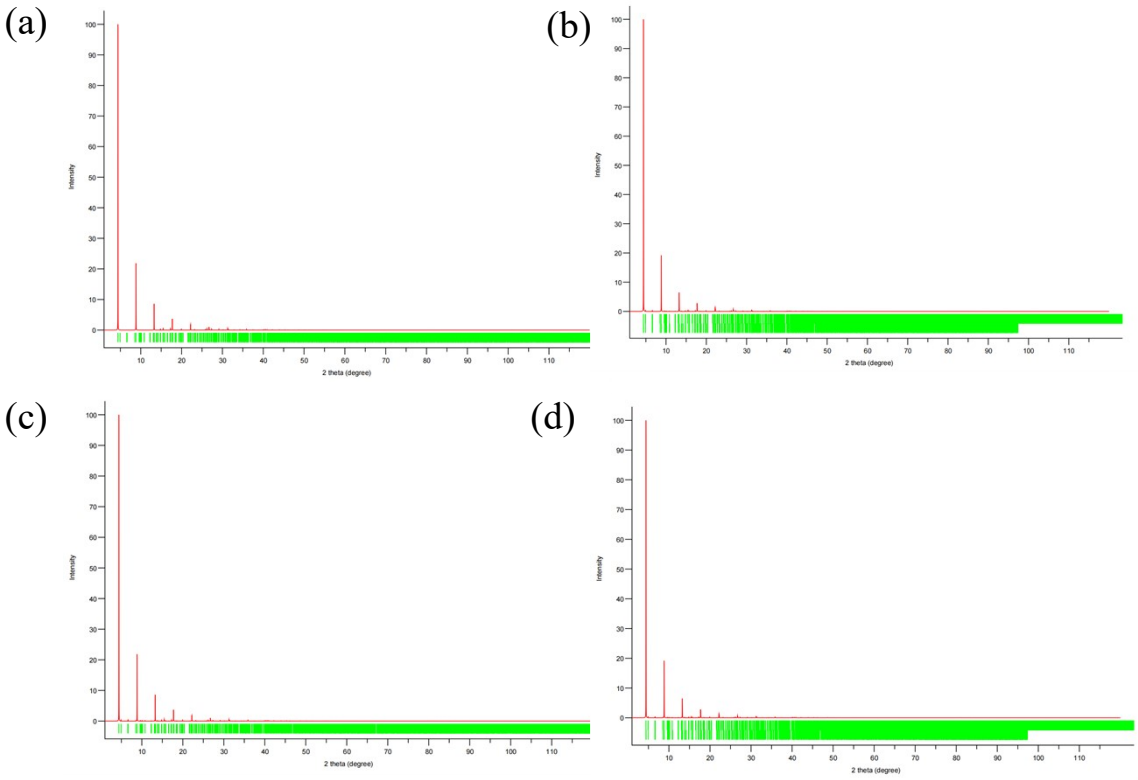


Fig. S1 The XRD of (a) γ-GY, (b) Fe-GY, (c) Co-GY, and (d) Ni-GY.

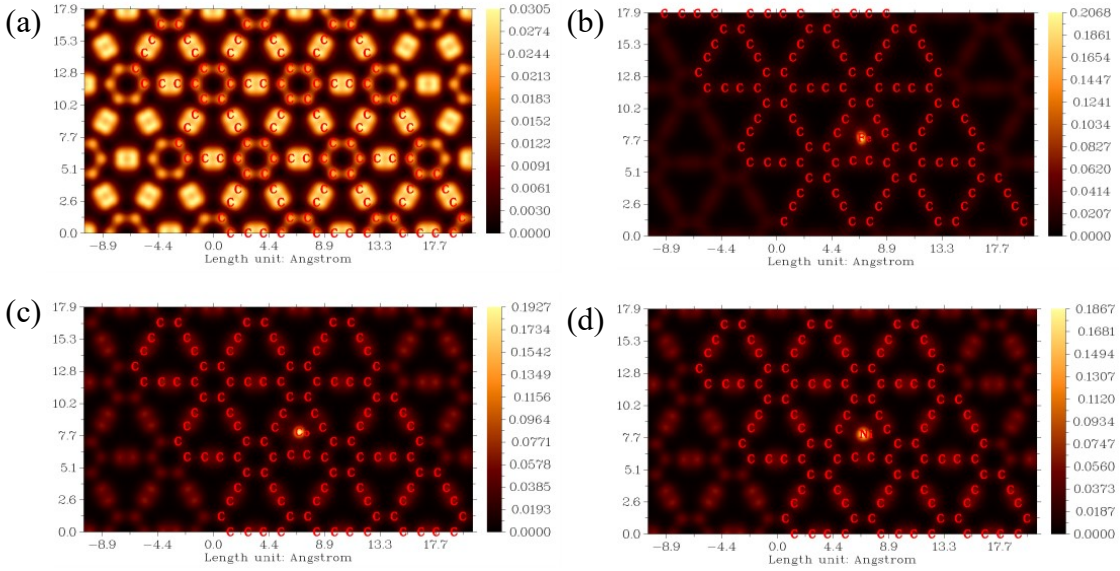


Fig. S2 The STM of (a) γ-GY, (b) Fe-GY, (c) Co-GY, and (d) Ni-GY.

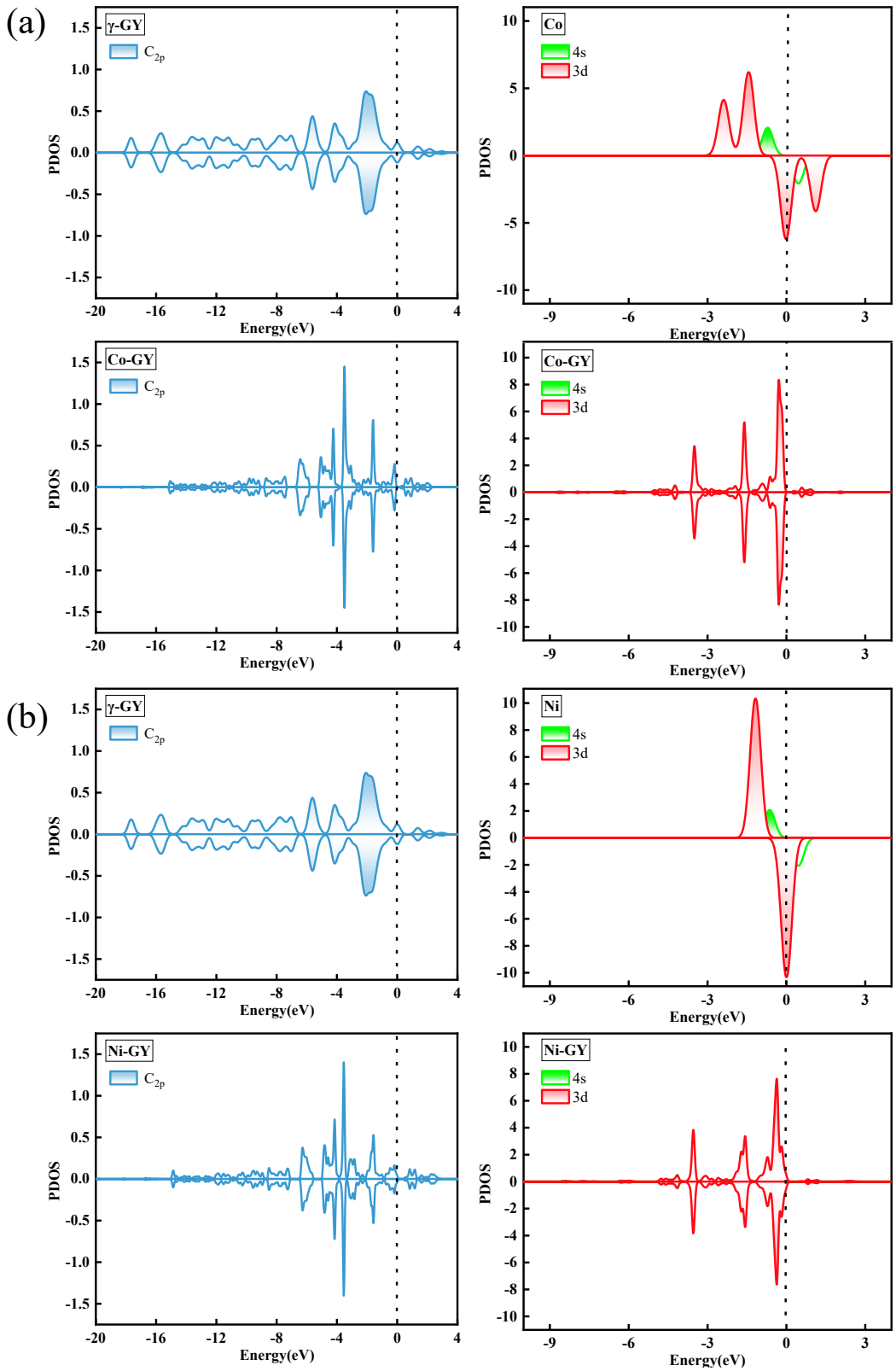


Fig. S3 PDOS plots: (a) the comparison of the C_{2p} orbitals between γ-GY and Co-GY in the left panel, the comparison of the Co valence orbitals of the standalone Co atom with those within the Co-GY system in the right panel, (b) the comparison of the C_{2p} orbitals between γ-GY and Ni-GY in the left panel, the comparison of the Ni valence orbitals of the standalone Ni atom with those within the Ni-GY system in the right panel.

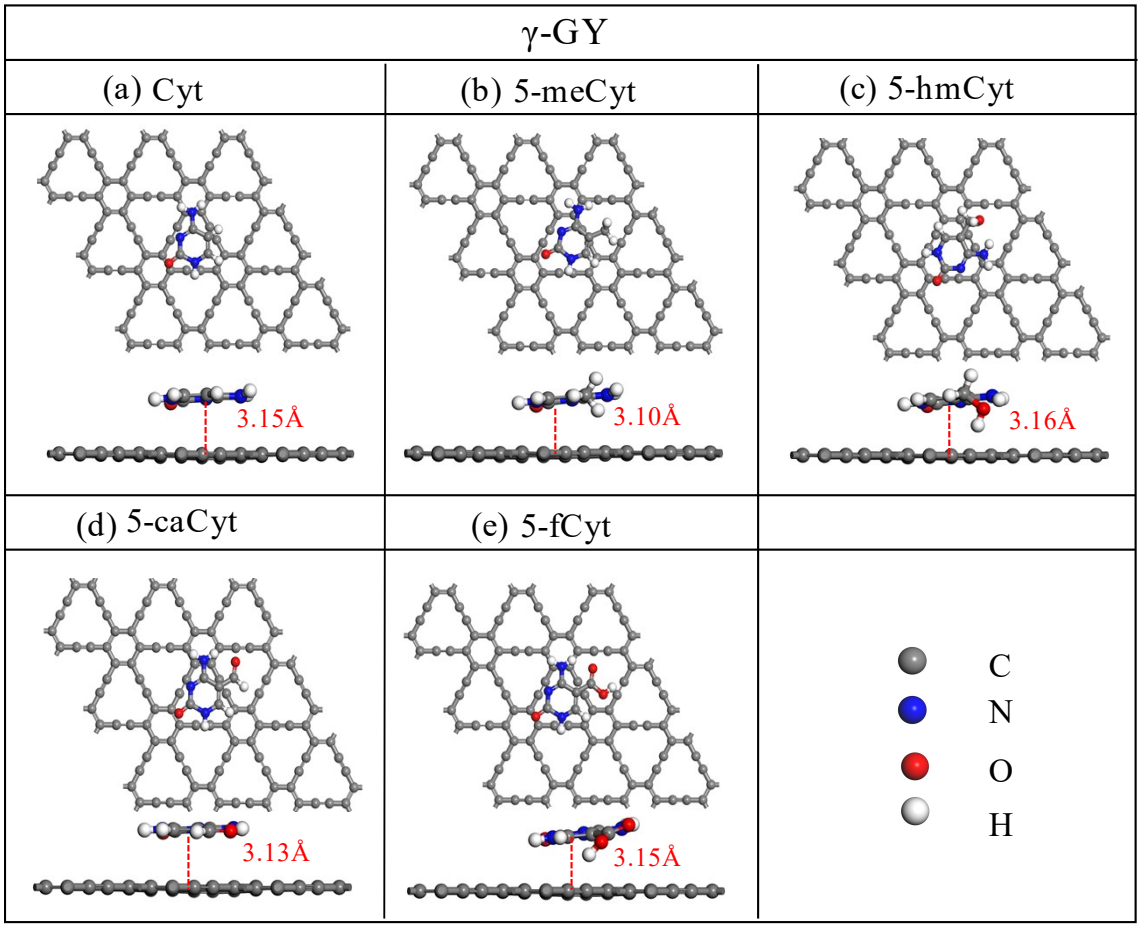


Fig. S4 Optimized geometries of (a) Cyt, (b) 5-meCyt, (c) 5-hmCyt, (d) 5-caCyt, and (e) 5-fCyt absorbed on γ-GY system (top and side perspective).

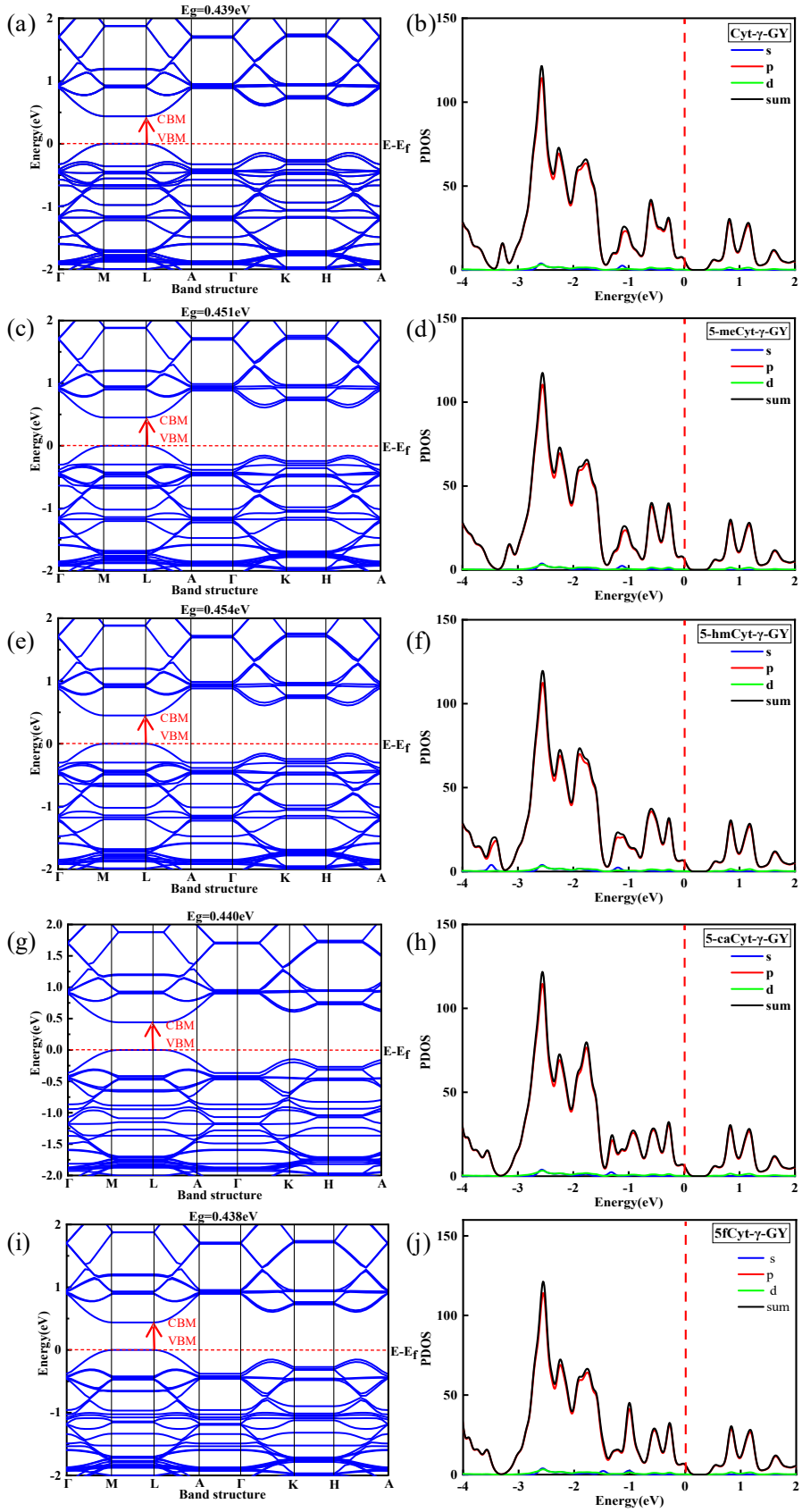


Fig. S5 Band structure (the left) of (a) Cyt, (c) 5-meCyt, (e) 5-hmCyt, (g) 5-caCyt and (i) 5-fCyt absorbed on γ-GY nanosheets, DOS plot (the right) of (b) Cyt, (d) 5-meCyt, (f) 5-hmCyt, (h) 5-caCyt and (j) 5-fCyt absorbed on γ-GY nanosheets. The Fermi level is set to zero.

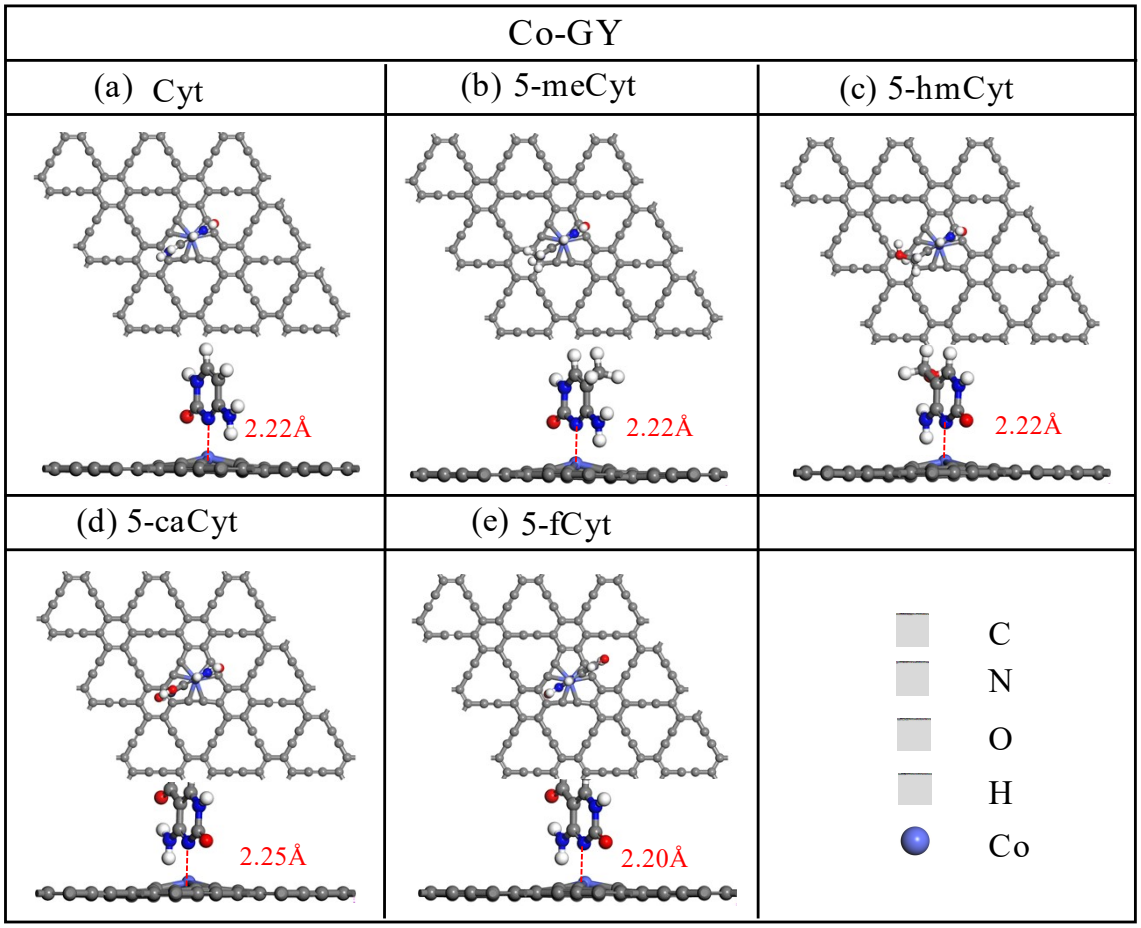


Fig. S6 Optimized geometries of (a) Cyt, (b) 5-meCyt, (c) 5-hmCyt, (d) 5-caCyt, and (e) 5-fCyt absorbed on Co-GY system (top and side perspective).

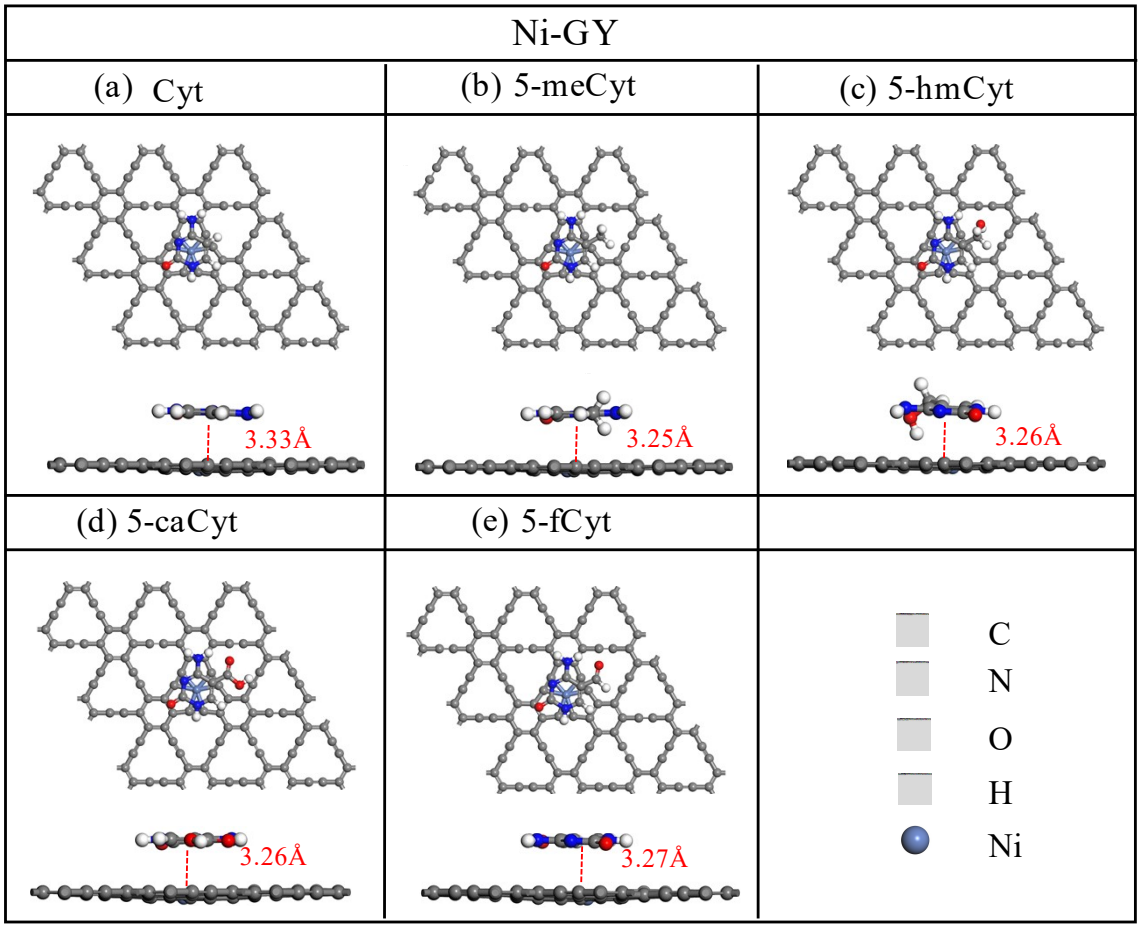


Fig. S7 Optimized geometries of (a) Cyt, (b) 5-meCyt, (c) 5-hmCyt, (d) 5-caCyt, and (e) 5-fCyt absorbed on Fe-GY system (top and side perspective).

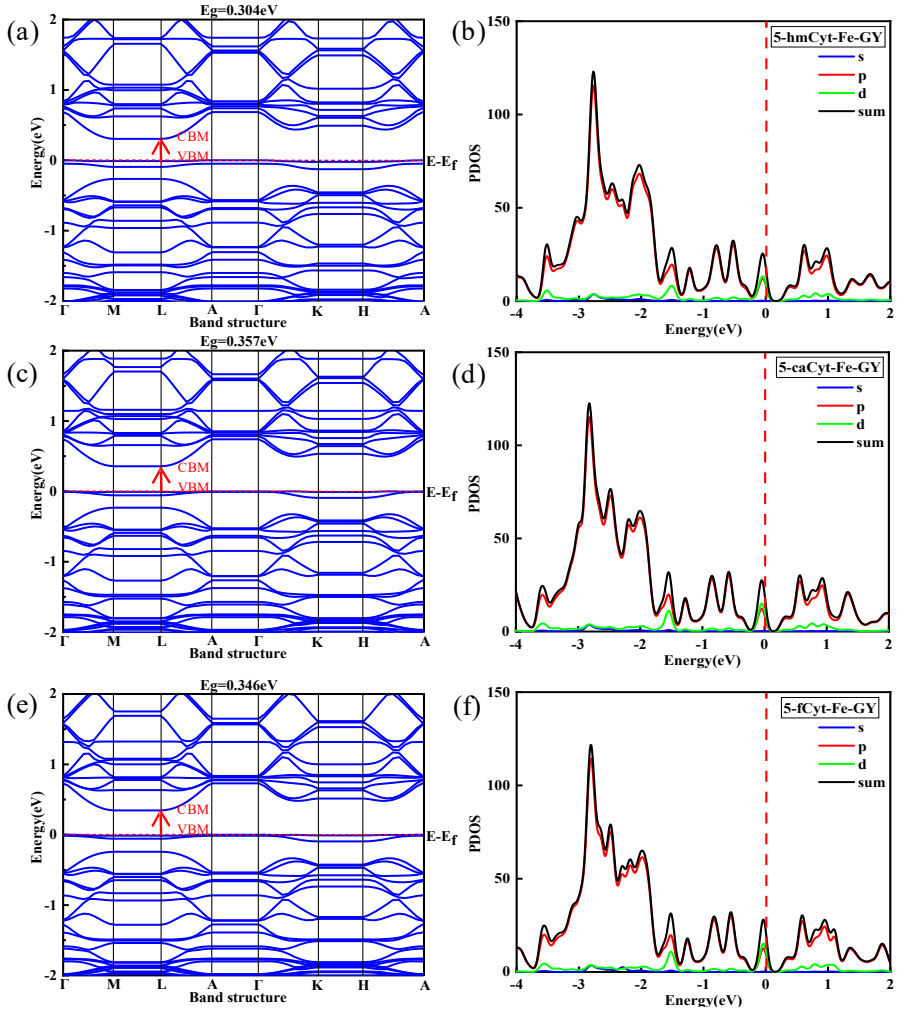


Fig.S8 Band structure (the left) of (a) 5-hmCyt, (c) 5-caCyt and (e) 5-fCyt absorbed on Fe-GY nanosheets, DOS plot(the right) of (b) 5-hmCyt, (d) 5-caCyt and (f) 5-fCyt absorbed on Fe-GY nanosheets. The Fermi level is set to zero.

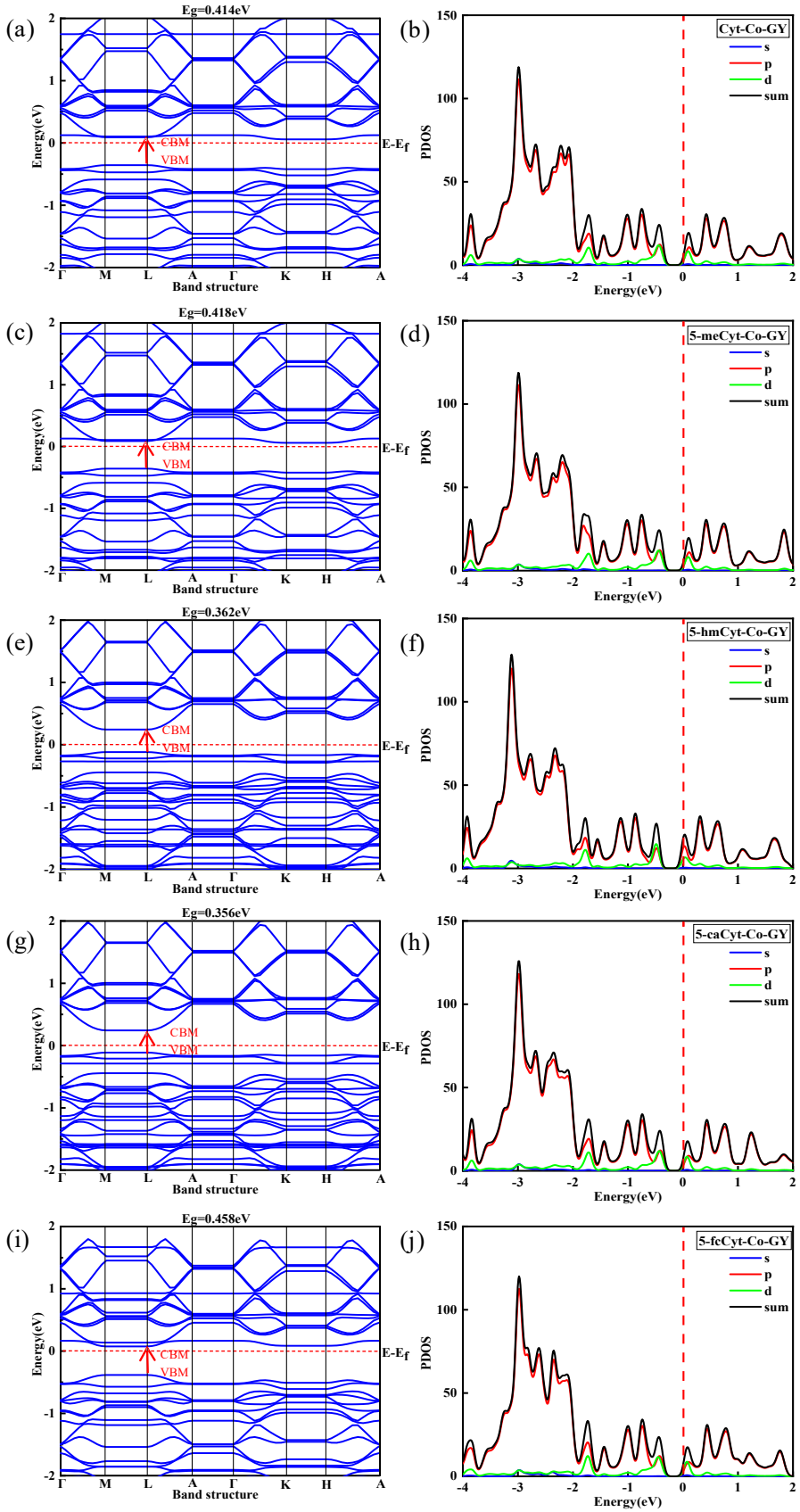


Fig. S9 Band structure (the left) of (a) Cyt, (c) 5-meCyt, (e) 5-hmCyt, (g) 5-caCyt and (i) 5-fCyt absorbed on Co-GY nanosheets, DOS plot(the right) of (b) Cyt, (d) 5-meCyt, (f) 5-hmCyt, (h) 5-caCyt and (j) 5-fCyt absorbed on Co-GY nanosheets. The Fermi level is set to zero.

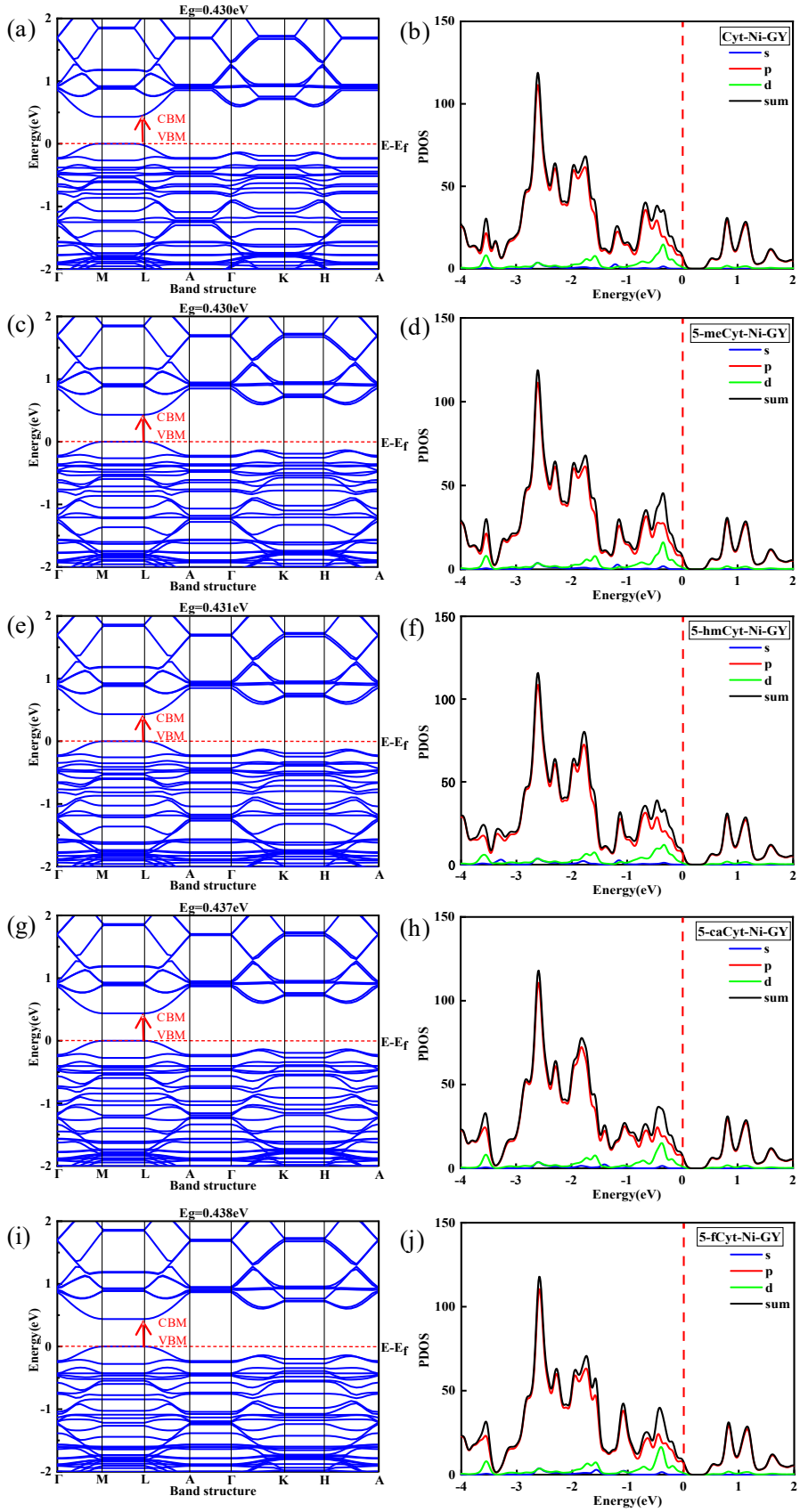
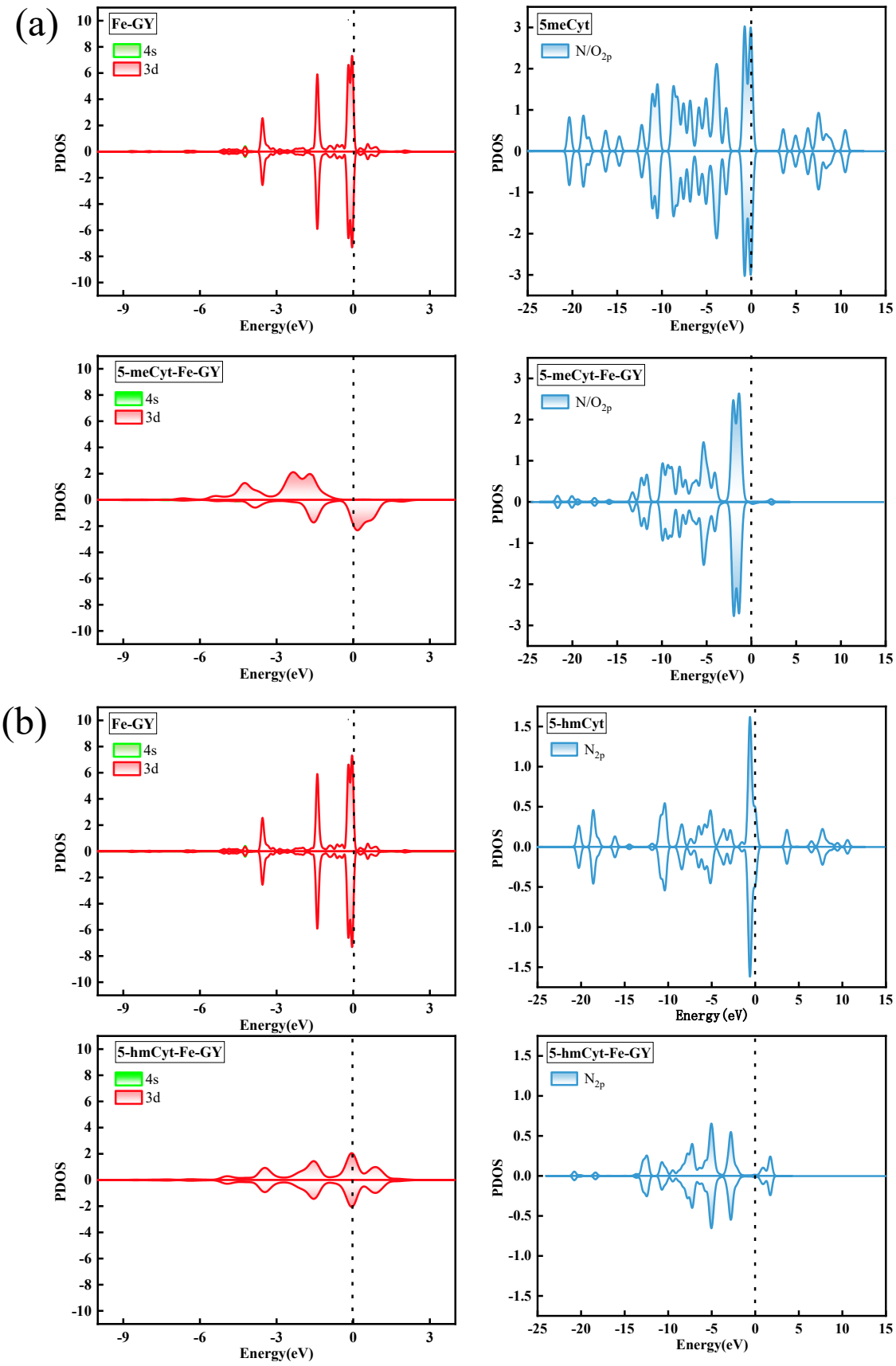


Fig. S10 Band structure (the left) of (a) Cyt, (c) 5-meCyt, (e) 5-hmCyt, (g) 5-caCyt and (i) 5-fCyt absorbed on Ni-GY nanosheets, DOS plot(the right) of (b) Cyt, (d) 5-meCyt, (f) 5-hmCyt, (h) 5-caCyt and (j) 5-fCyt absorbed on Ni-GY nanosheets. The Fermi level is set to zero.


(a)
Fe-GY
4s
3d
PDOS
Energy(eV)
5meCyt
N/O2p
5-meCyt-Fe-GY
(b)
5-hmCyt
N2p
Energy (eV)
5-hmCyt-Fe-GY

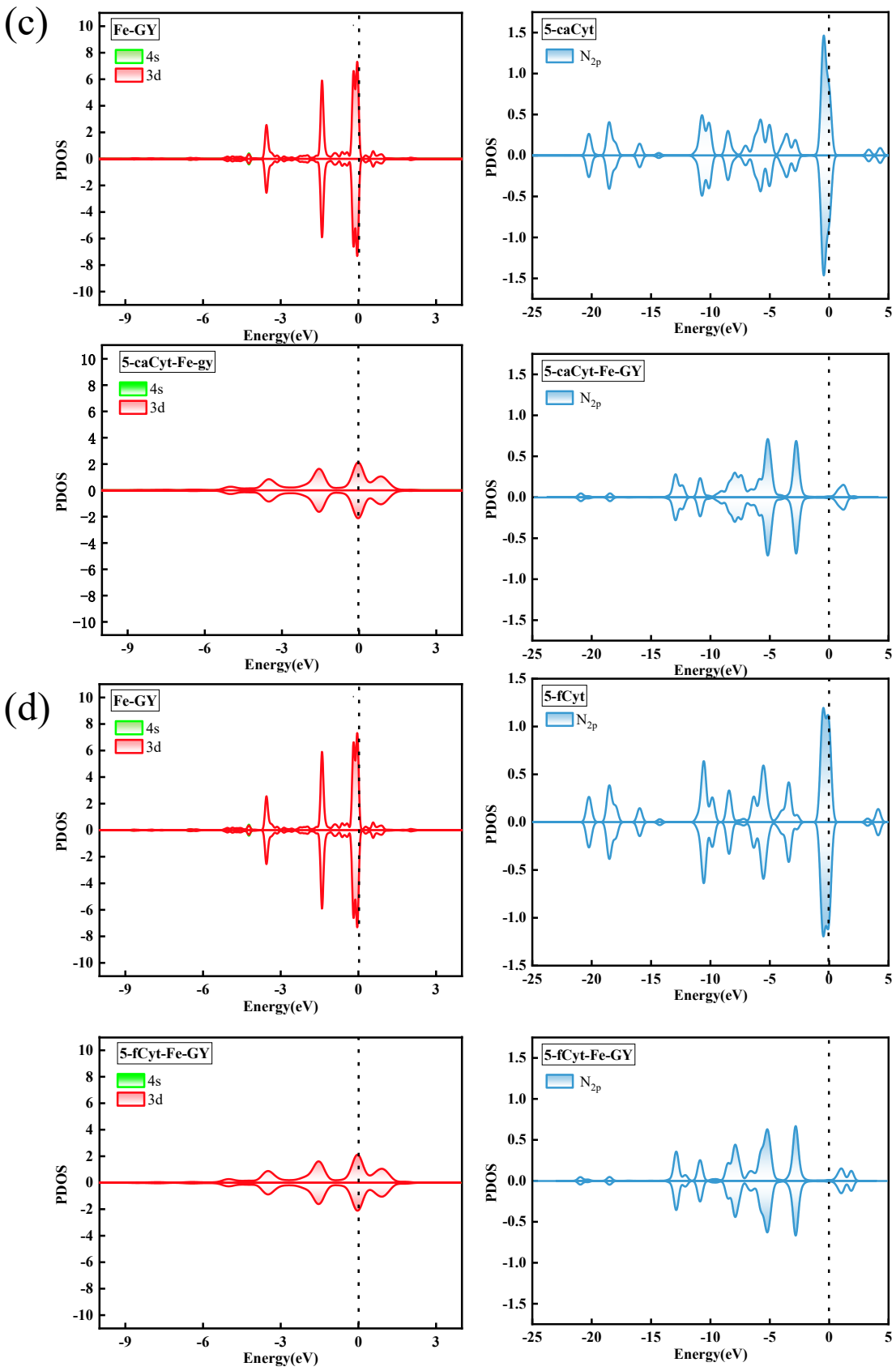
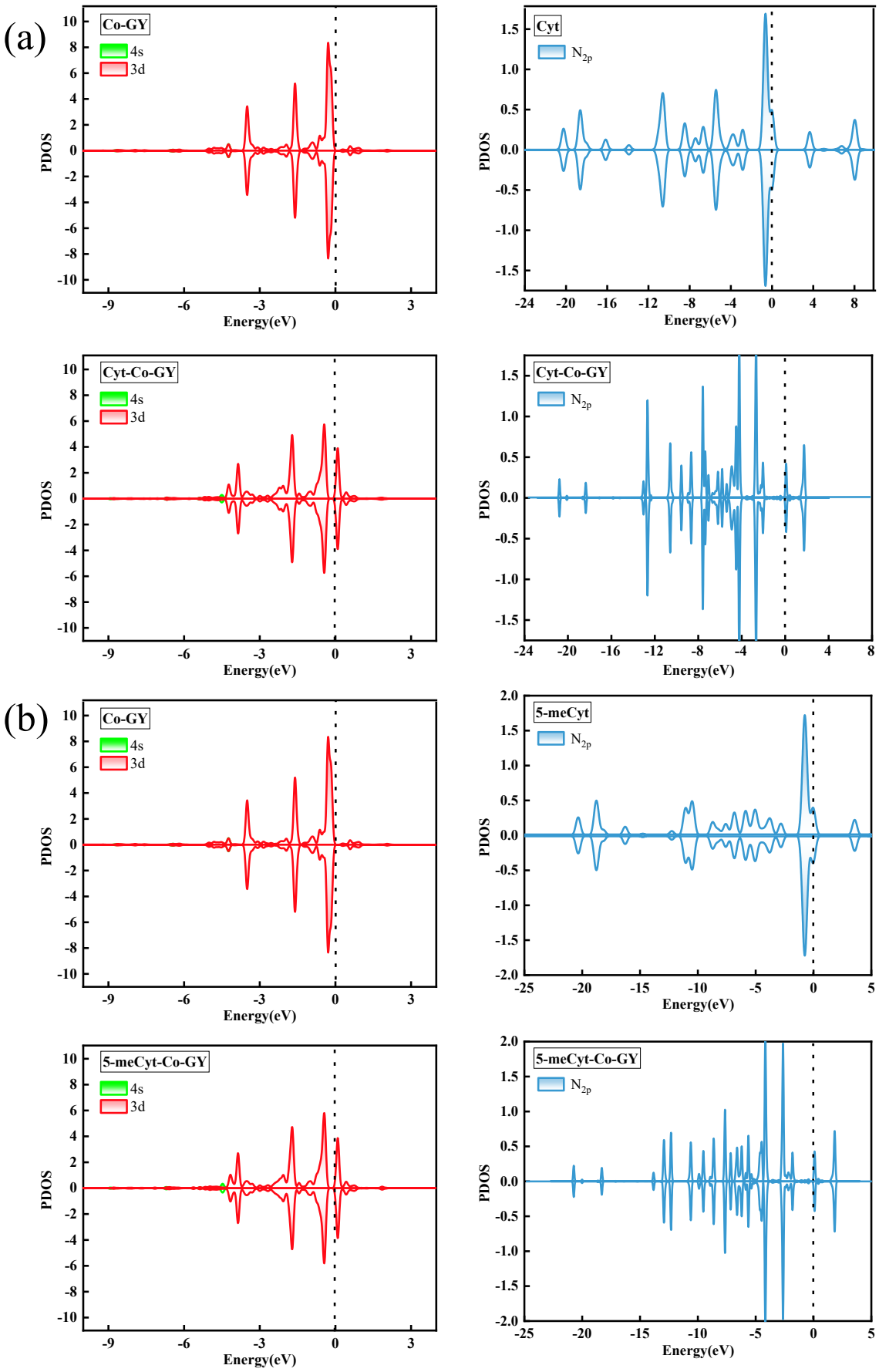
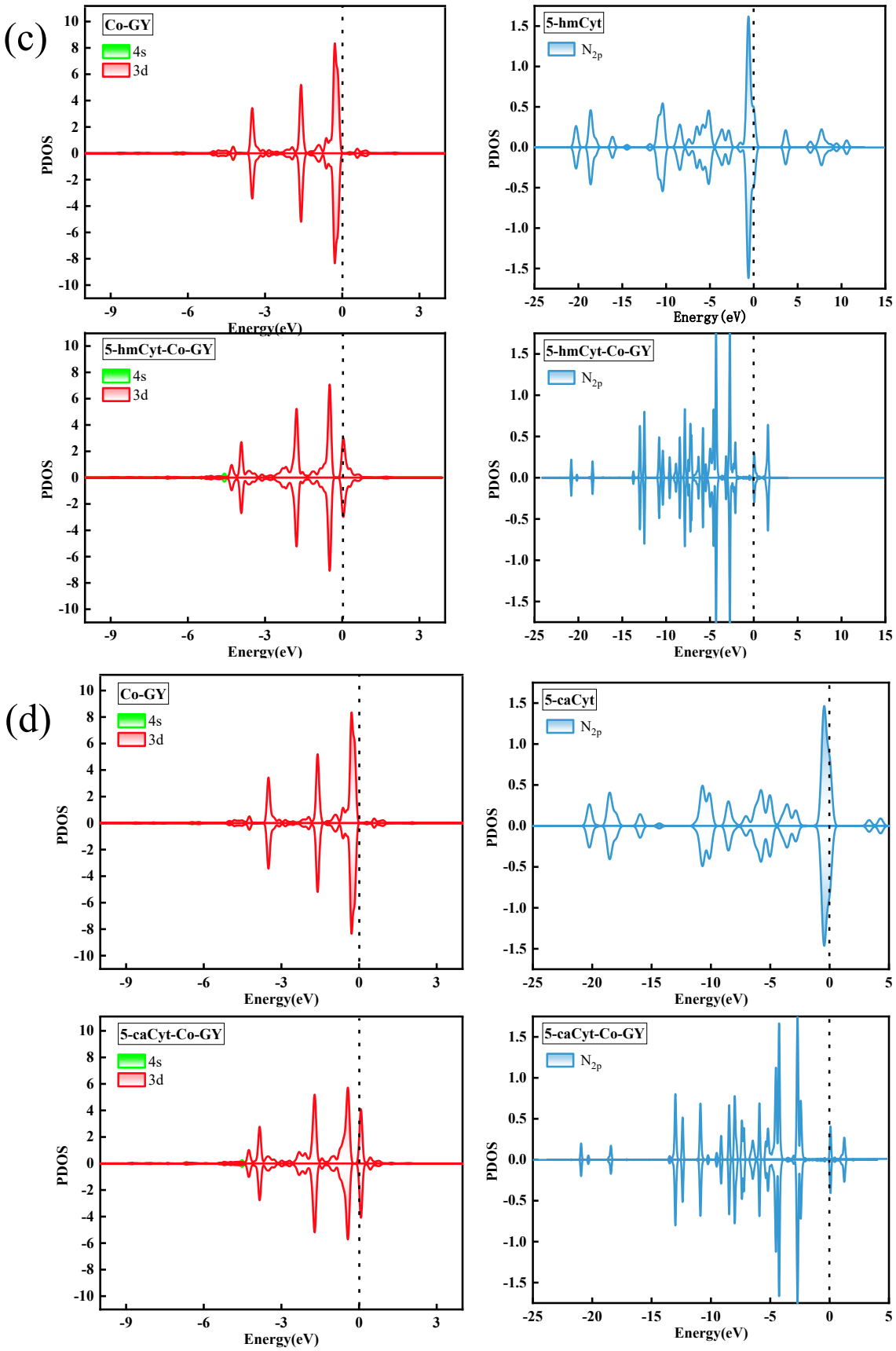


Fig. S11 PDOS plots: (a) the comparison of the Fe valence orbitals between Fe-GY and 5-meCyt-Fe-GY in the left panel, the comparison of the O_{2p}/N_{2p} of the standalone 5-meCyt with those within the 5-meCyt-Fe-GY system in the right panel; (b) the comparison of the Fe valence orbitals between Fe-GY and 5-hmCyt-Fe-GY in the left panel,

the comparison of the N_{2p} of the standalone 5-hmCyt with those within the 5-hmCyt-Fe-GY system in the right panel; (c) the comparison of the Fe valence orbitals between Fe-GY and 5-caCyt-Fe-GY in the left panel, the comparison of the N_{2p} of the standalone 5-caCyt with those within the 5-caCyt-Fe-GY system in the right panel; (d) the comparison of the Fe valence orbitals between Fe-GY and 5-fCyt-Fe-GY in the left panel, the comparison of the N_{2p} of the standalone 5-fCyt with those within the 5-fCyt-Fe-GY system in the right panel.


(a)
Co-GY
4s
3d
PDOS
Energy(eV)
Cyt
N2p
Cyt-Co-GY
(b)
5-meCyt
5-meCyt-Co-GY


(c)
Co-GY
4s
3d
PDOS
Energy(eV)
5-hmCyt
N2p
Energy (eV)
5-hmCyt-Co-GY
(d)
Co-GY
5-caCyt
5-caCyt-Co-GY

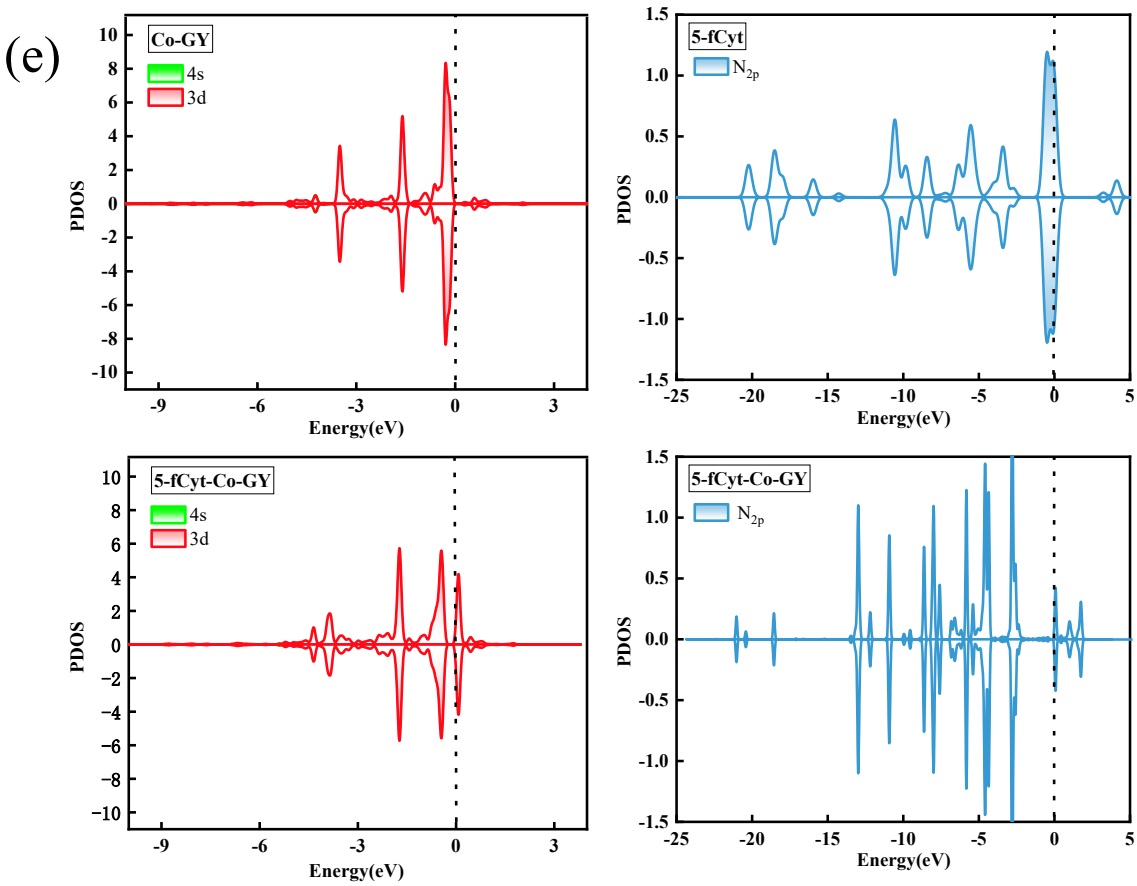


Fig. S12 PDOS plots: (a) the comparison of the Co valence orbitals between Co-GY and Cyt-Co-GY in the left panel, the comparison of theO_{2p}/N_{2p} of the standalone Cyt with those within the Cyt-Co-GY system in the right panel; (b) the comparison of the Co valence orbitals between Co-GY and 5-meCyt-Co-GY in the left panel, the comparison of the O_{2p}/N_{2p} of the standalone 5-meCyt with those within the 5-meCyt-Co-GY system in the right panel; (c) the comparison of the Co valence orbitals between Co-GY and 5-hmCyt-Co-GY in the left panel, the comparison of the O_{2p}/N_{2p} of the standalone 5-hmCyt with those within the 5-hmCyt-Co-GY system in the right panel; (d) the comparison of the Co valence orbitals between Co-GY and 5-caCyt-Co-GY in the left panel, the comparison of the O_{2p}/N_{2p} of the standalone 5-caCyt with those within the 5-caCyt-Co-GY system in the right panel; (e) the comparison of the Co valence orbitals between Co-GY and 5-fCyt-Co-GY in the left panel, the comparison of the O_{2p}/N_{2p} of the standalone 5-fCyt with those within the 5-fCyt-Co-GY system in the right panel.

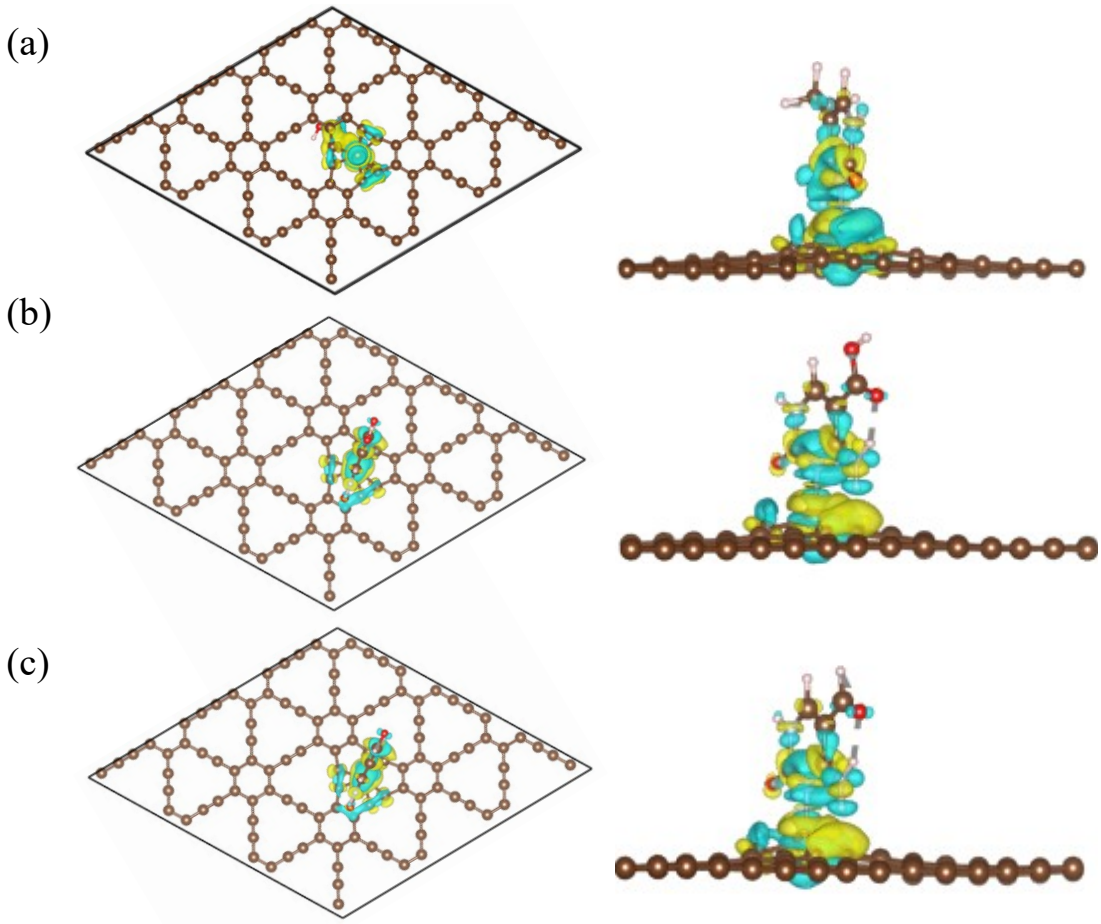


Fig. S13 The CDD of (a) 5-hmCyt-Fe-GY, (b) 5-caCyt-Fe-GY, (c) 5-fCyt-Fe-GY (top and side view). The yellow and blue are the charge accumulation and depletion, respectively.

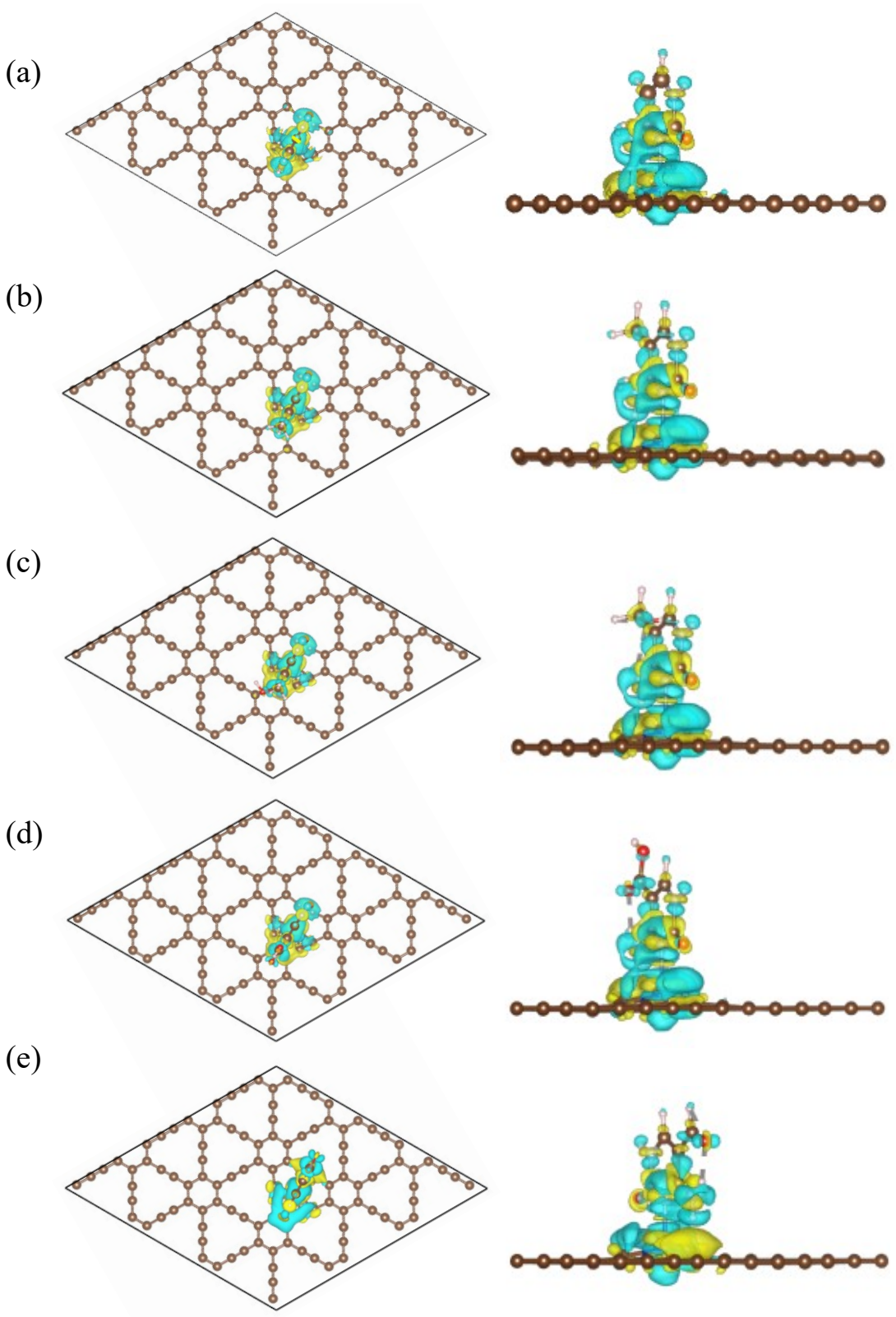


Fig. S14 The CDD of (a) Cyt-Co-GY, (b) 5-meCyt-Co-GY(c) 5-hmCyt-Co-GY, (d) 5-caCyt-Co-GY, (e) 5-fCyt-Co-GY (top and side view). The yellow and blue are the charge accumulation and depletion, respectively.

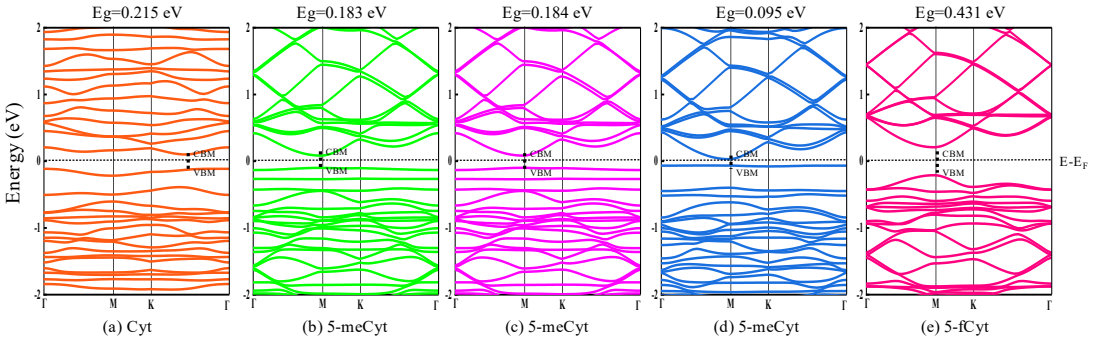


Fig. S15 Band structure of (a) Cyt, (b) 5-meCyt, (c) 5-hmCyt, (d) 5-caCyt and (e) 5-fCyt absorbed on Ni-GY nanosheets (0.2 V/Å electric fields). The Fermi level is set to zero.