Supporting Information

Structural and Electronic Properties of Bilayer Graphene Functionalized with Half-Sandwiched Transition Metal-Cyclopentadienyl Complexes

Xiaojing Yao[a], *Xiuyun Zhang*[b,*], Xiaoshan Ye[b] *and Jinlan Wang*[a,c,*]

[a] Department of Physics, Southeast University, Nanjing 211189, China

[b] Department of Physics, Yangzhou University, Yangzhou 225009, China

[c]Synergetic Innovation Center for Quantum Effects and Applications (SICQEA), Hunan Normal University, Changsha 410081, China

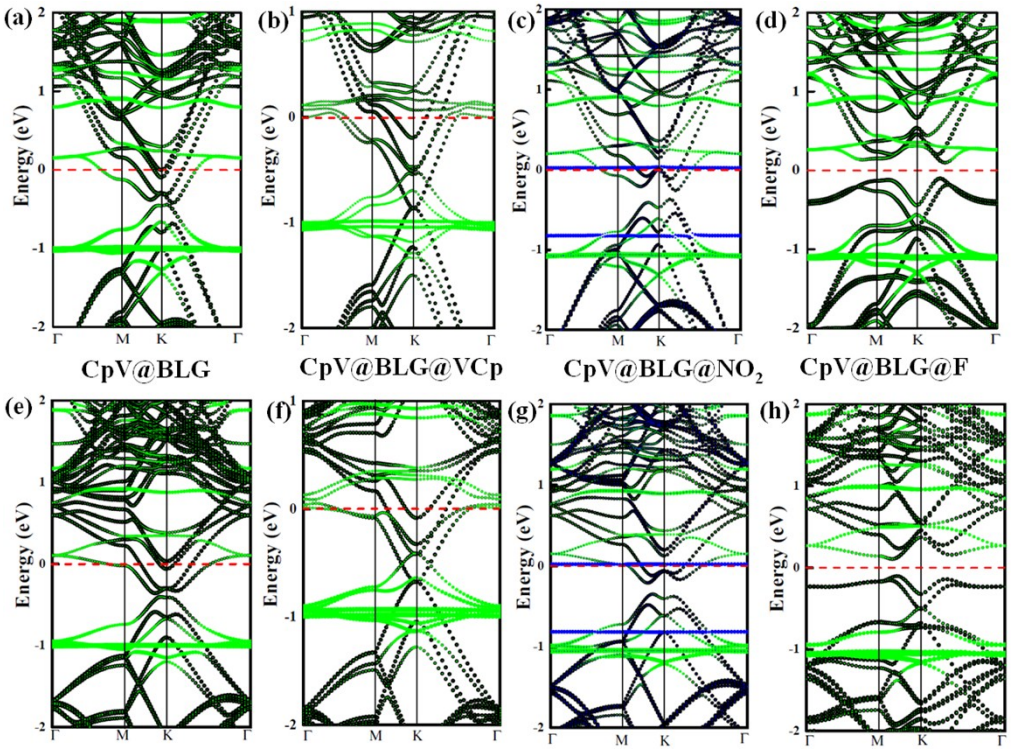

Figure S1. Band structures of CpC@BLG, CpV@BLG@VCp, CpV@BLG@NO_2 and CpV@BLG@F for different coverage rate (the effect of the supercell used on the band gaps). (a)-(d) used the BLG supercell of 4×4, (e-h) used the BLG supercell of 5×5.

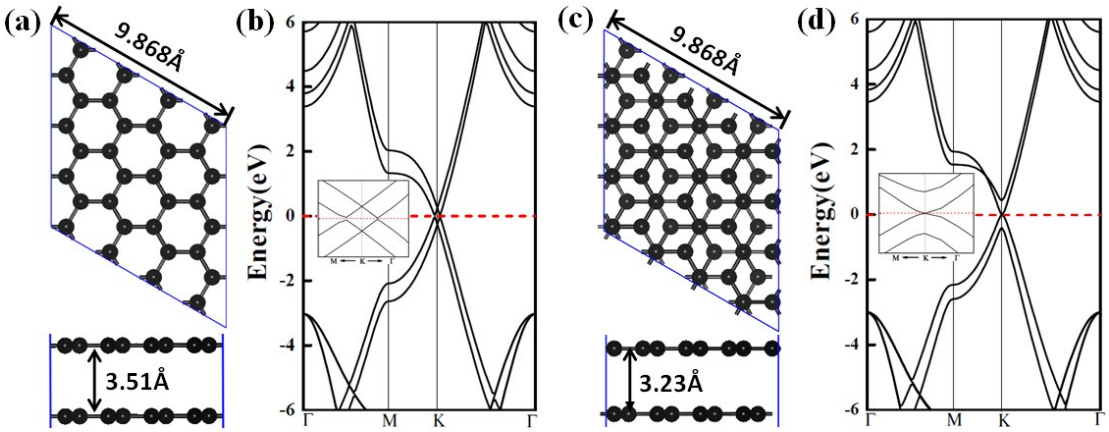

Figure S2. Optimized structures and band structures of (a,b) AA- and (c,d) AB-stacked BLG.

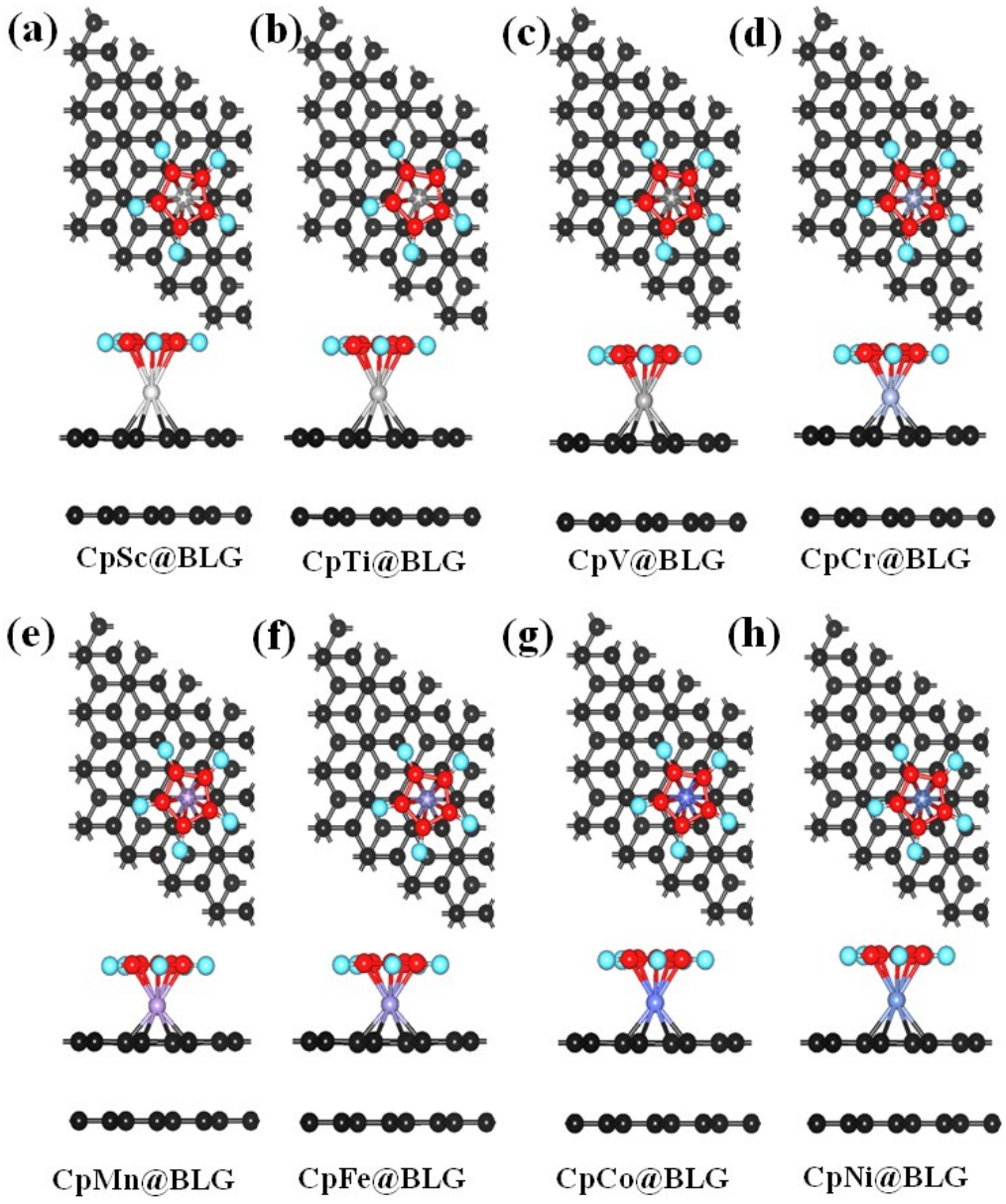

Figure S3. The optimized structures of CpTM@BLG (TM=Sc-Ni).

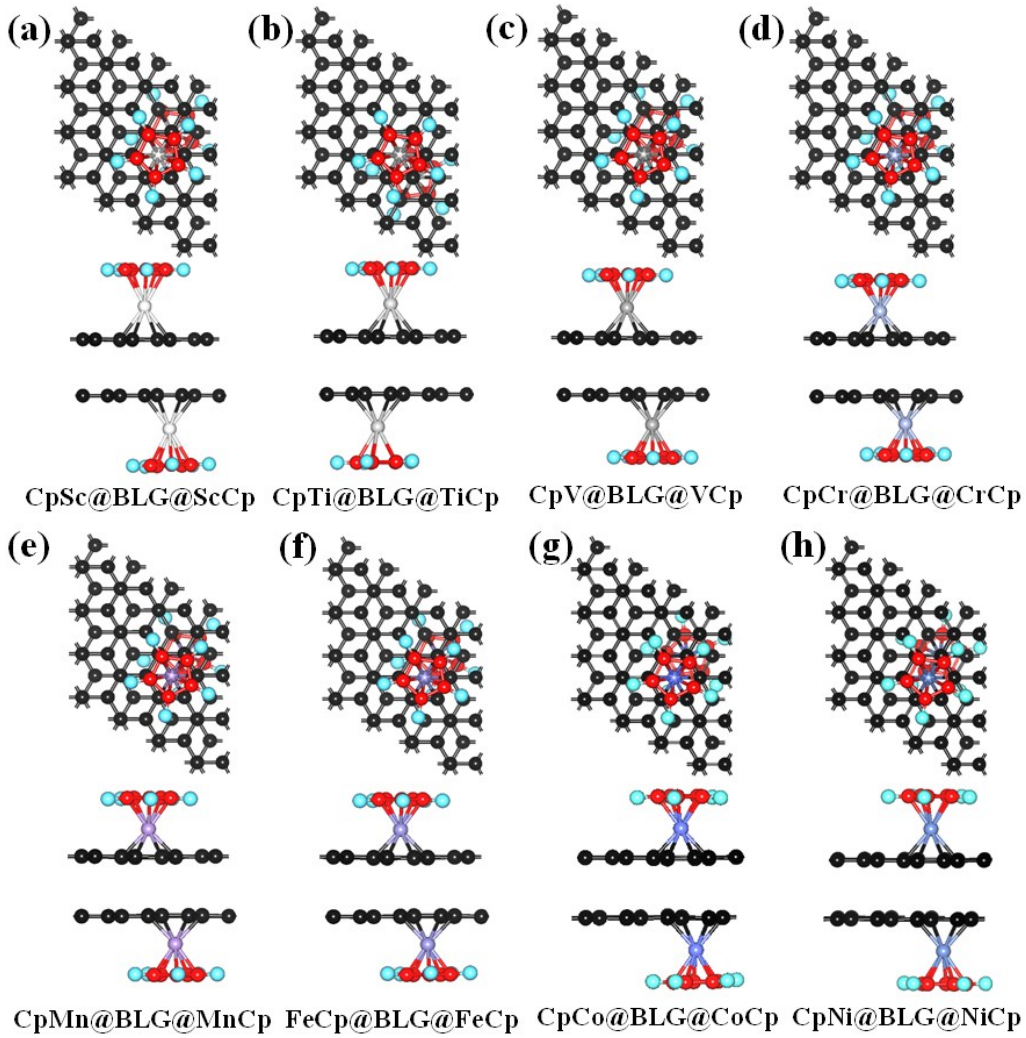

Figure S4. The optimized structures of CpTM@BLG@TMCp (TM=Sc-Ni).

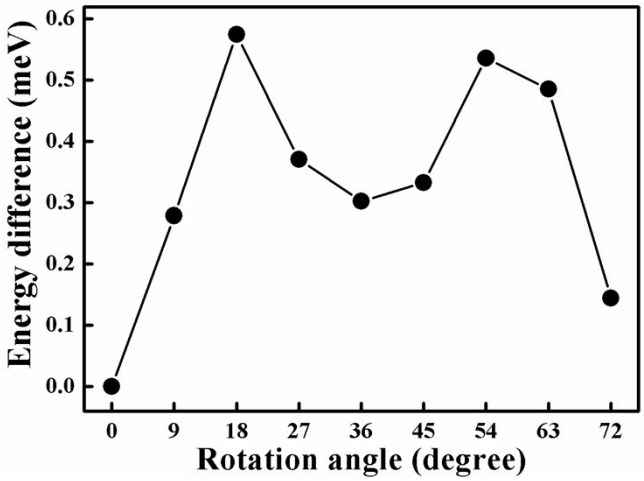

Figure S5. The energy profile vs. the rotation angle θ (0-72^0) of the cyclopentane.

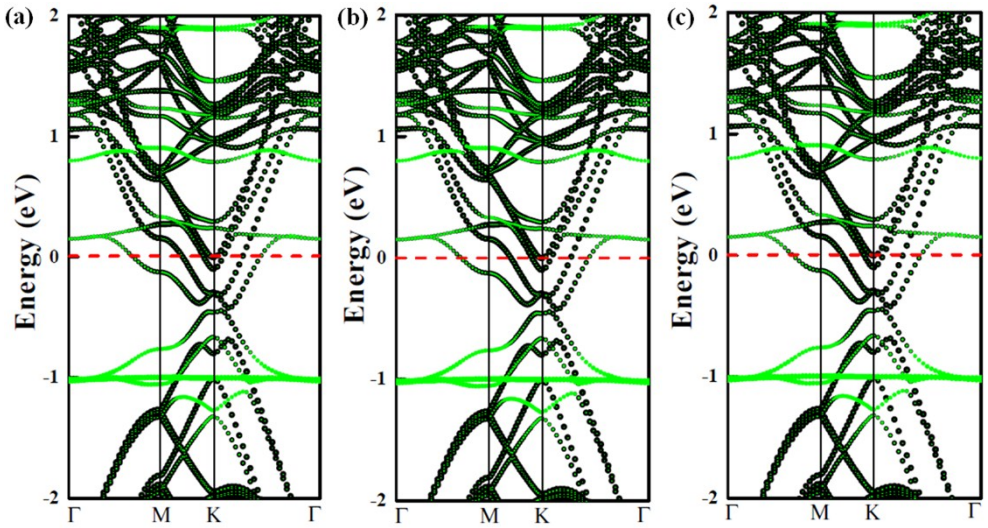

Figure S6. Band structures of CpTM@BLG systems with different rotation angle θ of the cyclopentane. (a) θ=18^0; (b) θ=36^0; (c) θ=54^0. The green and black circles represent the *d* orbitals of TMs and *p* orbitals of C in bilayer graphene and the size of the circles in each band denotes the contributions from different states.

TM	CpTM@BLG				CpTM@BLG@TMCp			
	d(TM-Cp)	d(TM-BLG)	$d_{c\text{-}c}$ (Cp)	$d_{c\text{-}c}$ (BLG)	d(TM-Cp)	d(TM-BLG)	$d_{c\text{-}c}$ (Cp)	$d_{c\text{-}c}$ (BLG)
Sc	2.088	1.938	1.422-1.428	1.434-1.444	2.095-2.096	1.932-1.935	1.423-1.427	1.435-1.443
Ti	1.977	1.857	1.426	1.435	1.979	1.852-1.853	1.426	1.435
V	1.872	1.755	1.428	1.435-1.436	1.867-1.870	1.741-1.744	1.428-1.429	1.435-1.438
Cr	1.745	1.580	1.433-1.434	1.437-1.438	1.744-1.745	1.579-1.580	1.434	1.437-1.438
Mn	1.678	1.546	1.433	1.433	1.679-1.682	1.549-1.552	1.432-1.433	1.432-1.433
Fe	1.638	1.563	1.434	1.434	1.639-1.640	1.563-1.565	1.434	1.434
Co	1.744	1.649	1.430-1.431	1.434	1.745-1.746	1.649-1.650	1.430-1.431	1.434
Ni	1.794	1.749	1.430	1.434	1.795-1.796	1.748-1.749	1.429-1.431	1.434-1.435

TM	CpTM@BLG@F					CpTM@BLG@NO_2				
	$d_{TM\text{-}Cp}$	$d_{TM\text{-}BLG}$	$d_{c\text{-}c(Cp)}$	$d_{c\text{-}c(BLG)}$	$d_{F\text{-}BLG}$	$d_{TM\text{-}Cp}$	$d_{TM\text{-}BLG}$	$d_{c\text{-}c(Cp)}$	$d_{c\text{-}c(BLG)}$	$d_{N\text{-}BLG}$
Sc	2.085	1.964	1.421-1.428	1.431-1.441	1.598	2.086	1.952	1.422-1.427	1.432-1.440	3.404
Ti	1.973	1.855	1.426	1.436	1.584	1.972	1.856	1.426-1.427	1.435-1.436	3.289
V	1.876	1.815	1.427	1.435	1.596	1.874	1.781	1.427	1.435	3.333
Cr	1.753	1.600	1.433	1.437-1.438	1.586	1.749	1.591	1.433	1.437-1.438	3.264
Mn	1.679	1.547	1.432-1.433	1.433-1.434	1.571	1.681	1.550	1.432	1.433	3.393
Fe	1.627	1.563	1.433-1.434	1.434	1.602	1.632	1.562	1.433-1.434	1.434	3.339
Co	1.730	1.646	1.431	1.434-1.435	1.595	1.727	1.642	1.430-1.431	1.434	3.449
Ni	1.778	1.743	1.430-1.431	1.435	1.588	1.784	1.743	1.430	1.434-1.435	3.287

Table S1. Geometry Parameters of CpTM@BLG, CpTM@BLG@TMCp, CpTM@BLG@NO_2 and CpTM@BLG@F (TM=Sc-Ni). *d*(TM-Cp), *d*(TM-BLG), and d-BLG are the distances of TM atoms to the center of Cp ring, the bonded carbon ring in BLG and the distances between the two layers, respectively. *d*c-c (Cp) and *d*c-c (BLG) are the C-C bond lengths in Cp and the TM-bonded carbon ring in BLG. *d*(F-BLG)/ *d*(N-BLG)is the distance between the F/N atoms and the bonded C atom/bottom layer of graphene. The unit of distance is angstrom (Å).

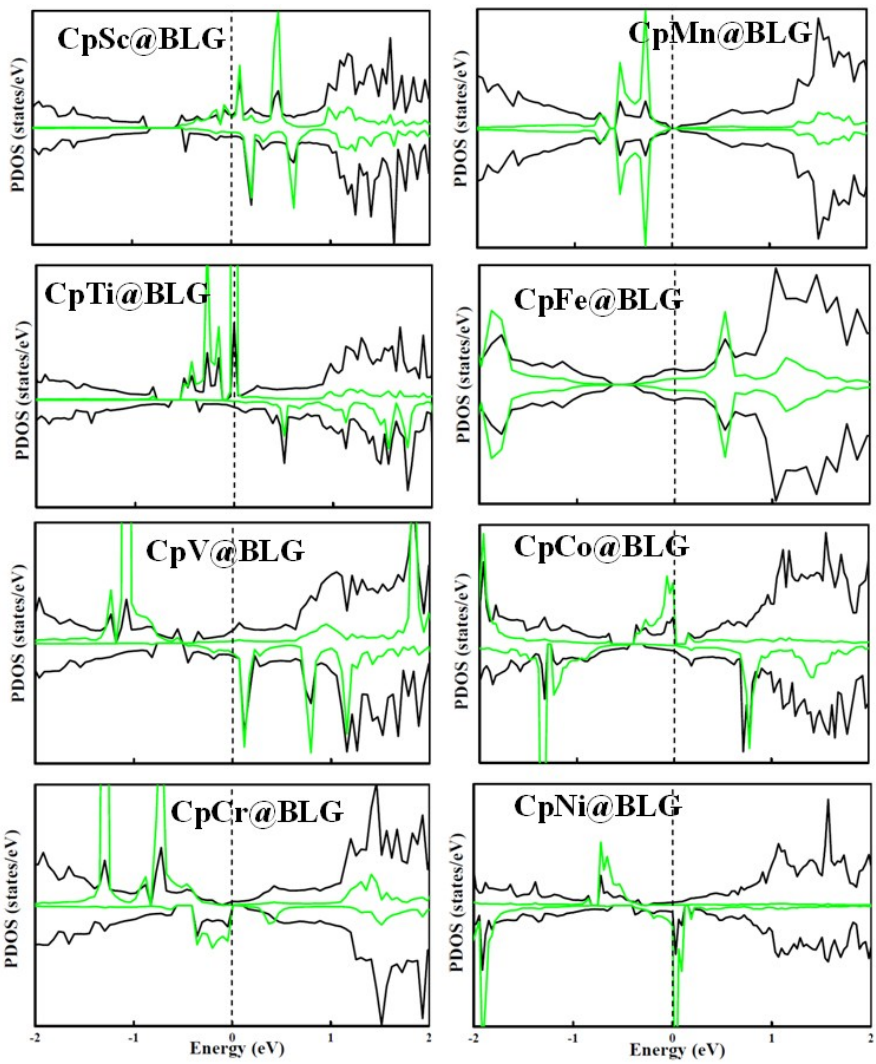

Figure S7. Calculated projected-DOS (PDOS) for CpTM@BLG systems. Black and green curves represent projected BLG-*p* and TM-*d* states, respectively. The Fermi level (dashed line) is shifted to 0 eV.

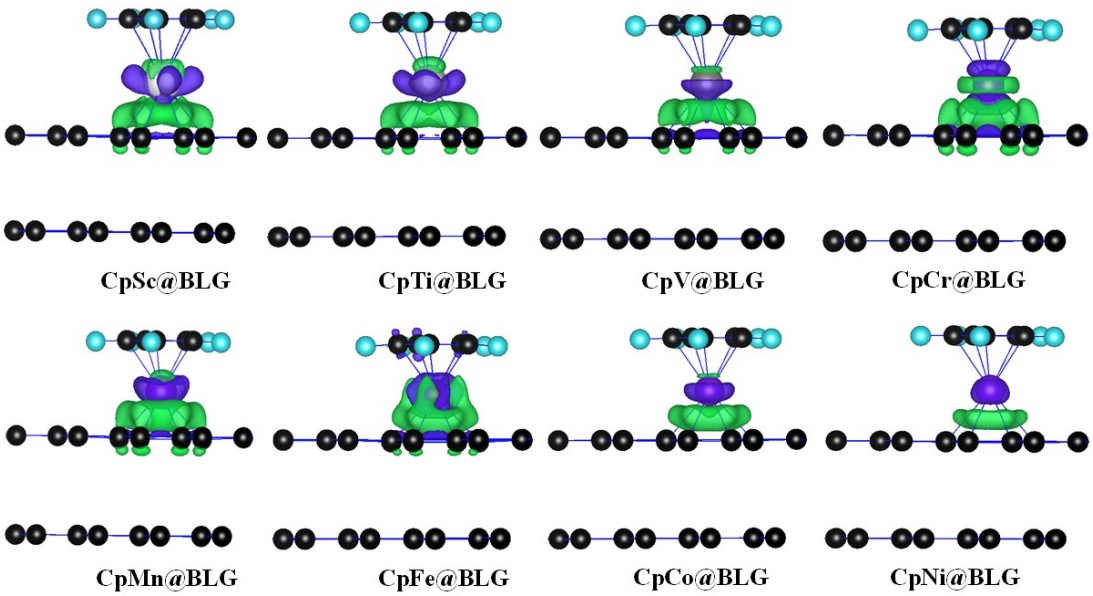

Figure S8. Iso-surfaces of electron charge density difference for CpTM@BLG. The isovalue is 0.04 e/Å^3. Green and violet zones indicate the accumulation and depletion of electrons.

Adsorption	e-up	e-down	Adsorption	e-up	e-down
CpSc	0.7786	0.1286	CpSc-ScCp	0.8655	0.9103
CpTi	0.6664	0.0782	CpTi-TiCp	0.7098	0.7651
CpV	0.6635	0.0818	CpV-VCp	0.7052	0.7578
CpCr	0.6513	0.0554	CpCr-CrCp	0.6761	0.71574
CpMn	0.4932	0.0262	CpMn-MnCp	0.5114	0.5167
CpFe	0.4852	0.1173	CpFe-FeCp	0.5537	0.6038
CpCo	0.3838	0.0401	CpCo-CoCp	0.4133	0.4152
CpNi	0.3253	0.0513	CpNi-NiCp	0.3728	0.3411
Adsorption	e-up	e-down	Adsorption	e-up	e-down
CpSc-NO_2	0.5997	-0.2597	CpSc-F	0.6852	-0.0663
CpTi-NO_2	0.5774	-0.3515	CpTi-F	0.6198	-0.0984
CpV-NO_2	0.4902	-0.2786	CpV-F	0.5087	-0.0401
CpCr-NO_2	0.5436	-0.3759	CpCr-F	0.5898	-0.1012
CpMn-NO_2	0.4352	-0.4602	CpMn-F	0.4703	-0.1275
CpFe-NO_2	0.2916	-0.2221	CpFe-F	0.4079	-0.0791
CpCo-NO_2	0.2390	-0.3562	CpCo-F	0.2731	-0.1102
CpNi-NO_2	0.1750	-0.3077	CpNi-F	0.2082	-0.0492

Table S2. Summary of results for CpTM@BLG, CpTM@BLG@TMCp, CpTM@BLG@NO_2 and CpTM@BLG@F systems, e-up and e-down are the excess electrons on the two sub-layer graphene, respectively.

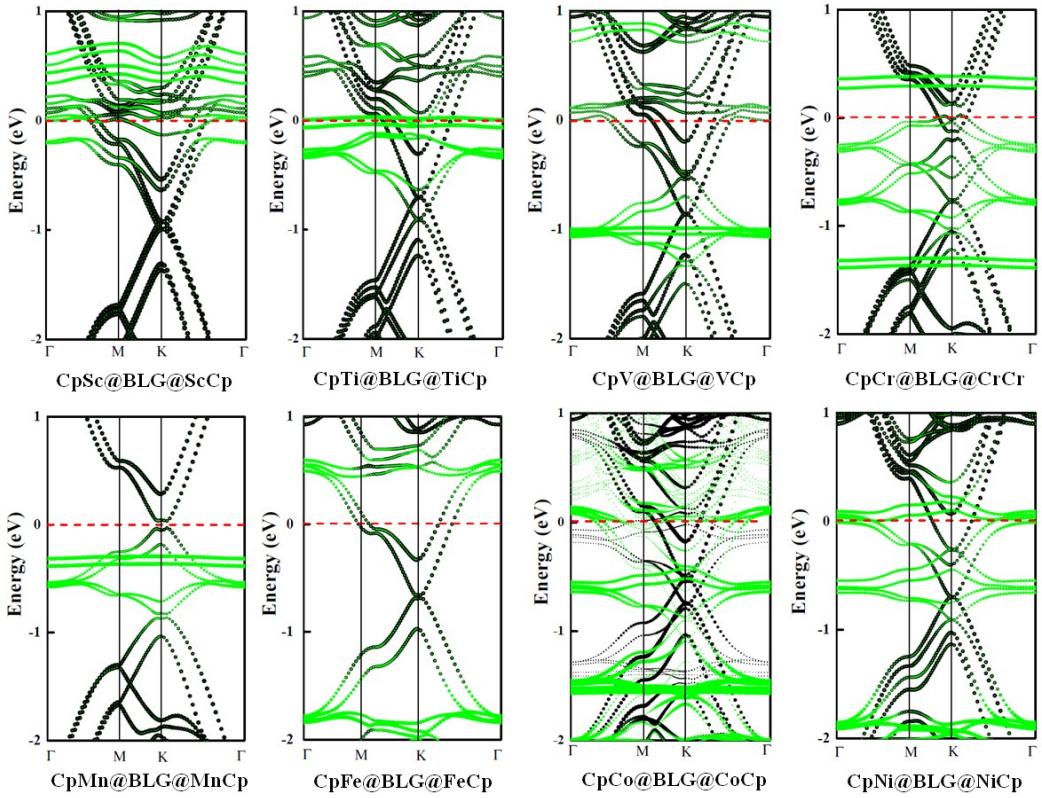

Figure S8. Band structures (a-h) of double sides adsorption of CpTM@BLG@TMCp.

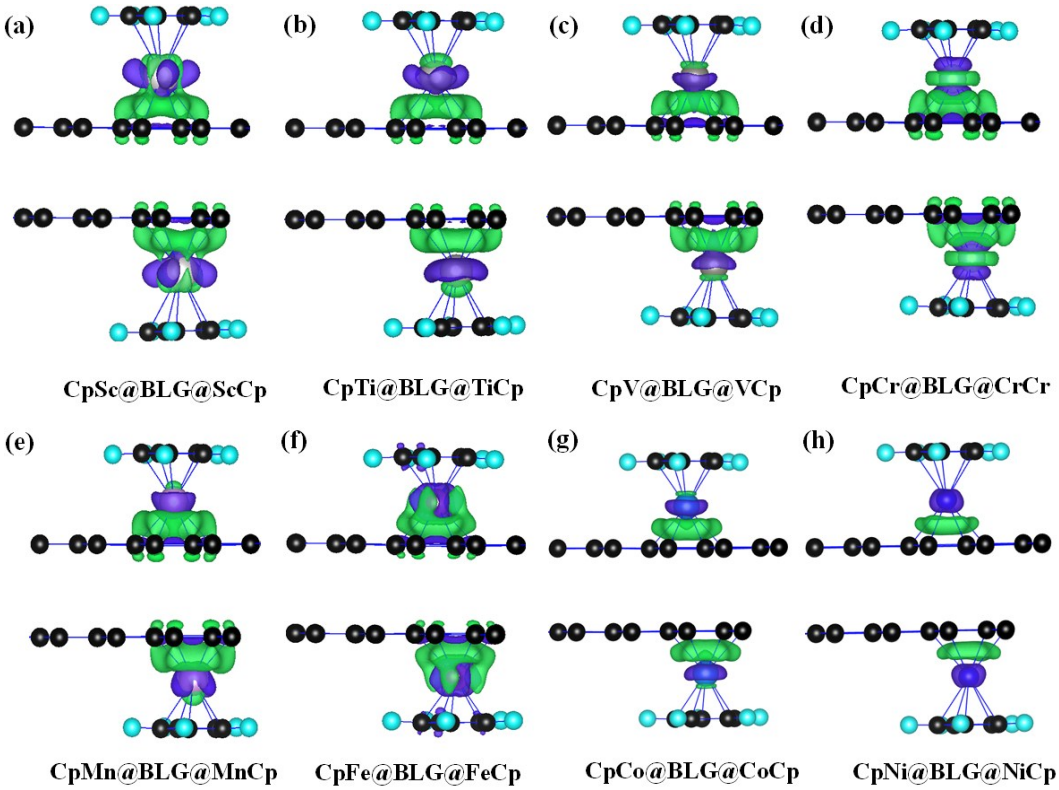

Figure S9. Iso-surfaces of electron charge density difference for CpTM@BLG@TMCp. The isovalue is 0.04 e/Å^3. Green and violet zones indicate the accumulation and depletion of electrons.

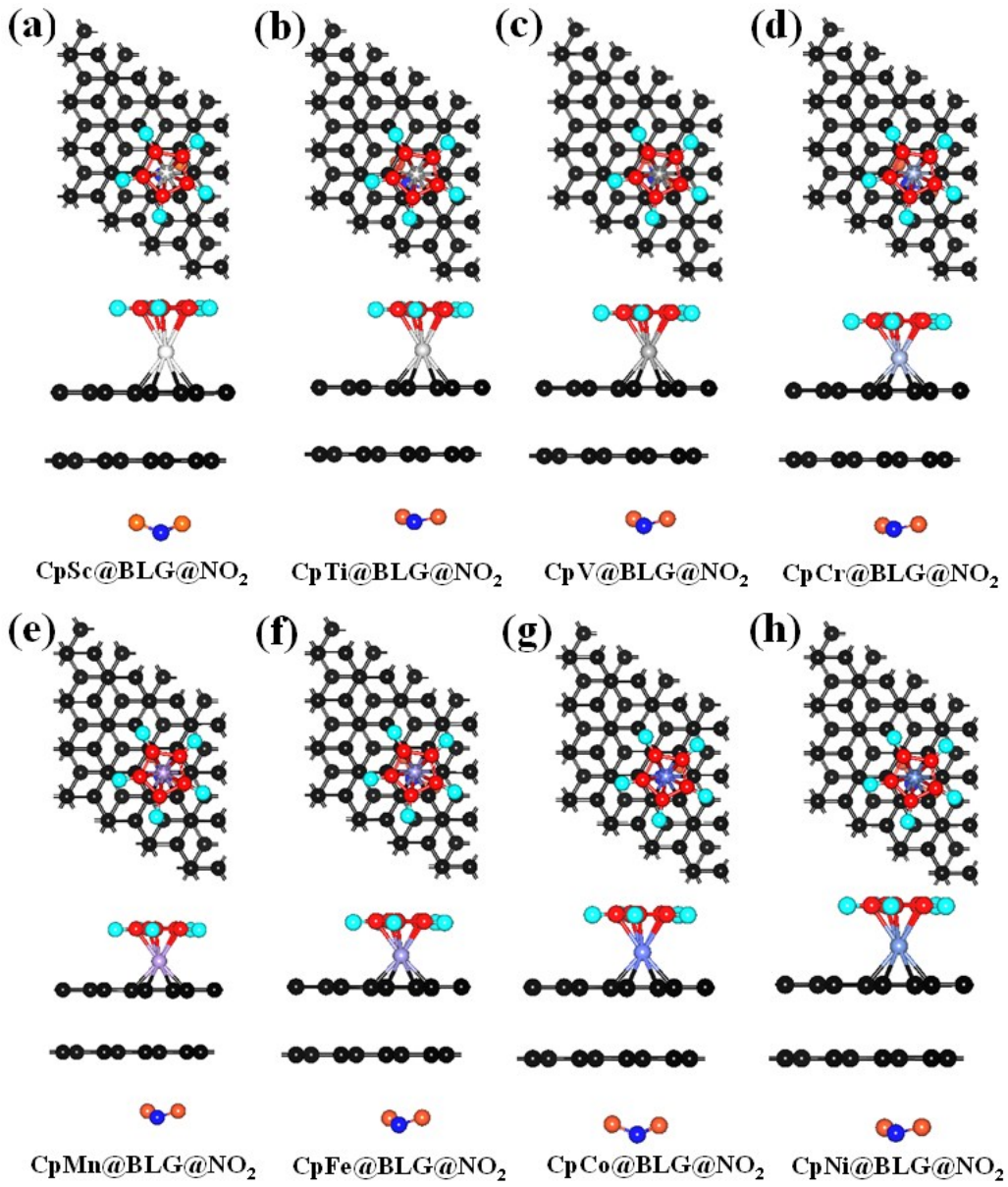

Figure S10. The optimized structures of CpTM@BLG@NO_2 (TM=Sc-Ni).

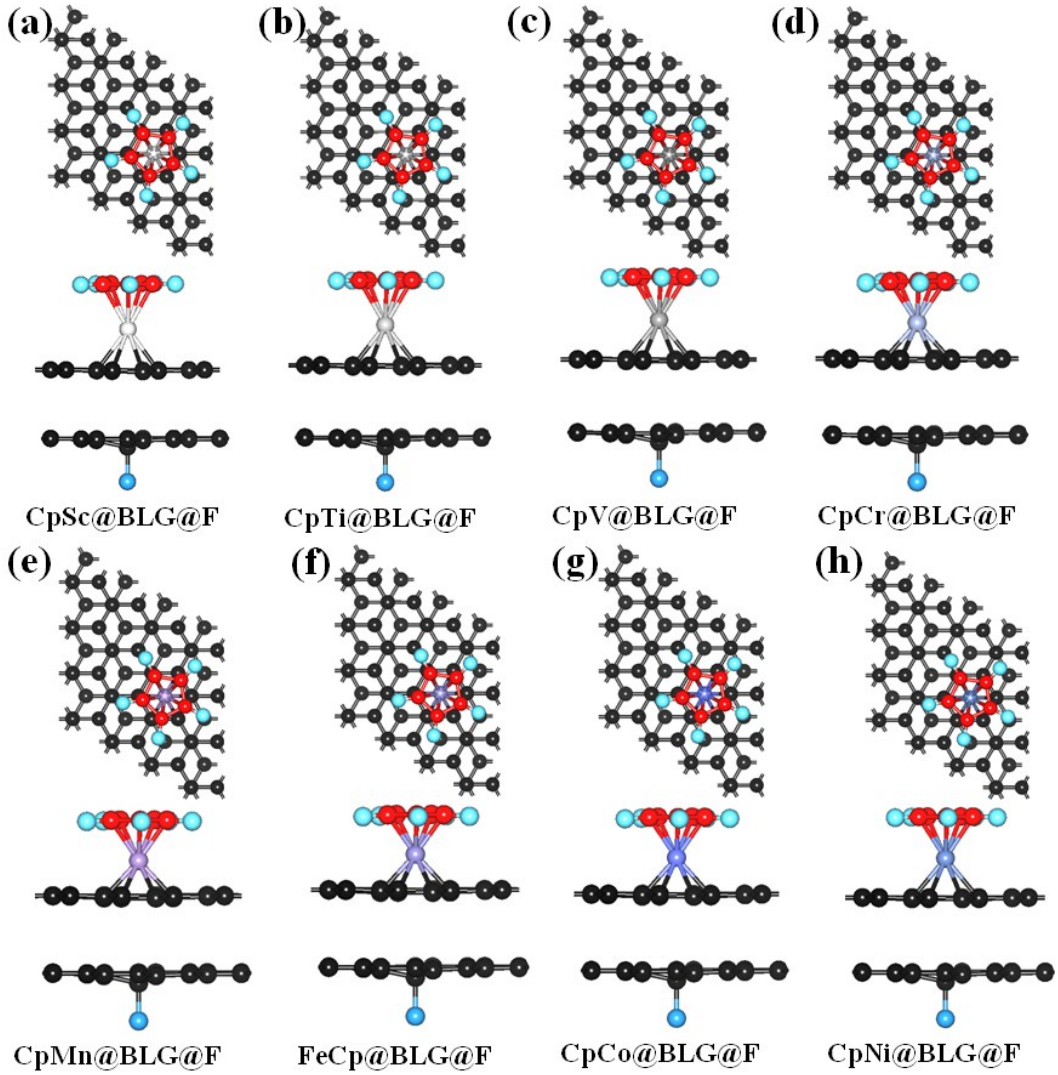

Figure S11. The optimized structures of CpTM@BLG@F (TM=Sc-Ni).

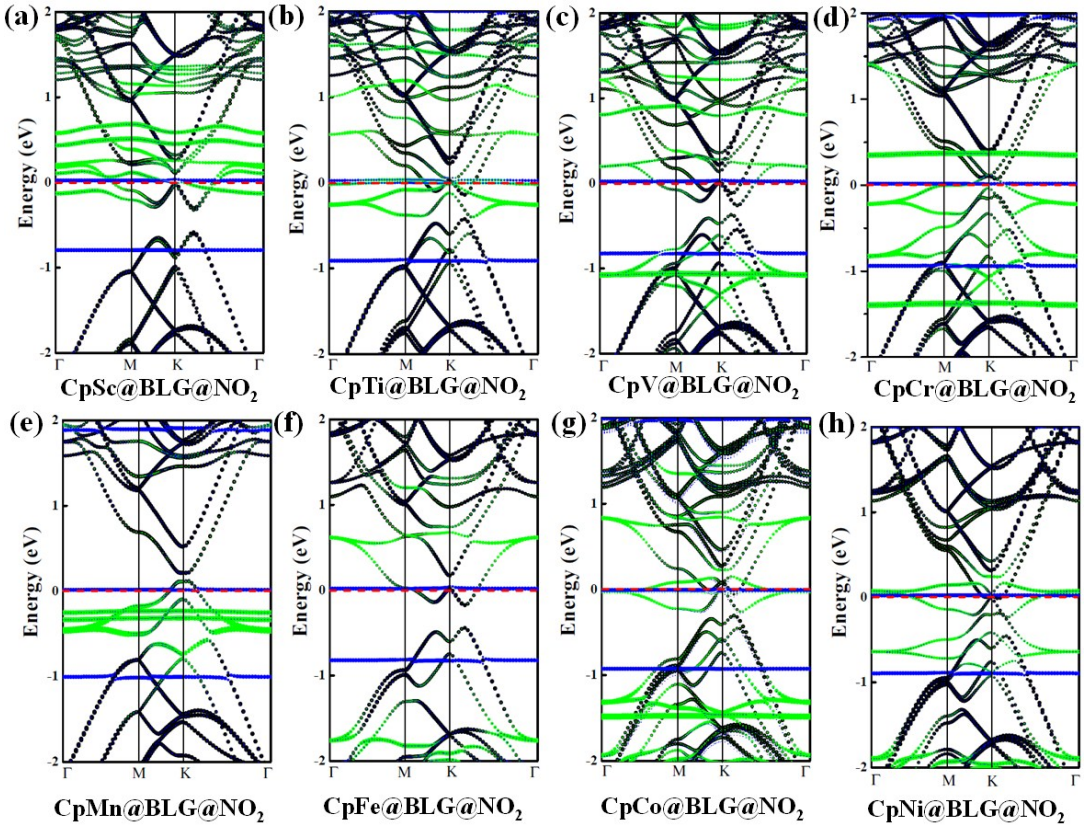

Figure S12. Band structures (a-h) of CpTM@BLG@NO_2.

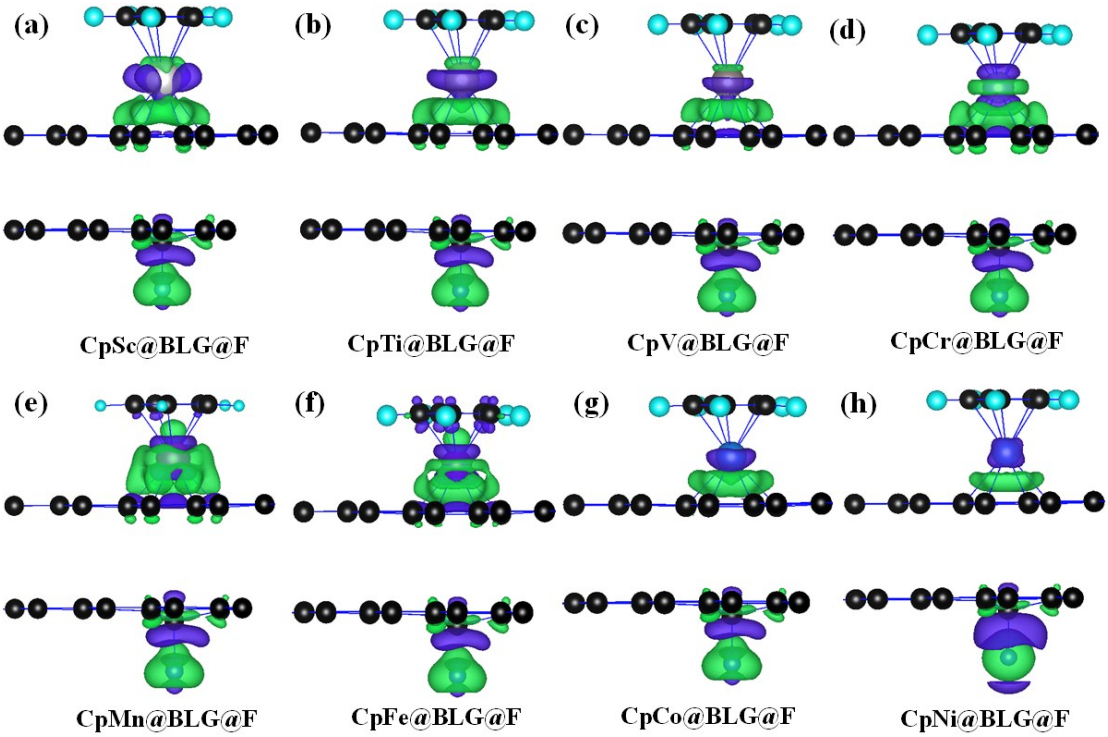

Figure S13. Iso-surfaces of electron charge density difference for CpTM@BLG@F. The isovalue is 0.04 e/Å^3. Green and violet zones indicate the accumulation and depletion of electrons.

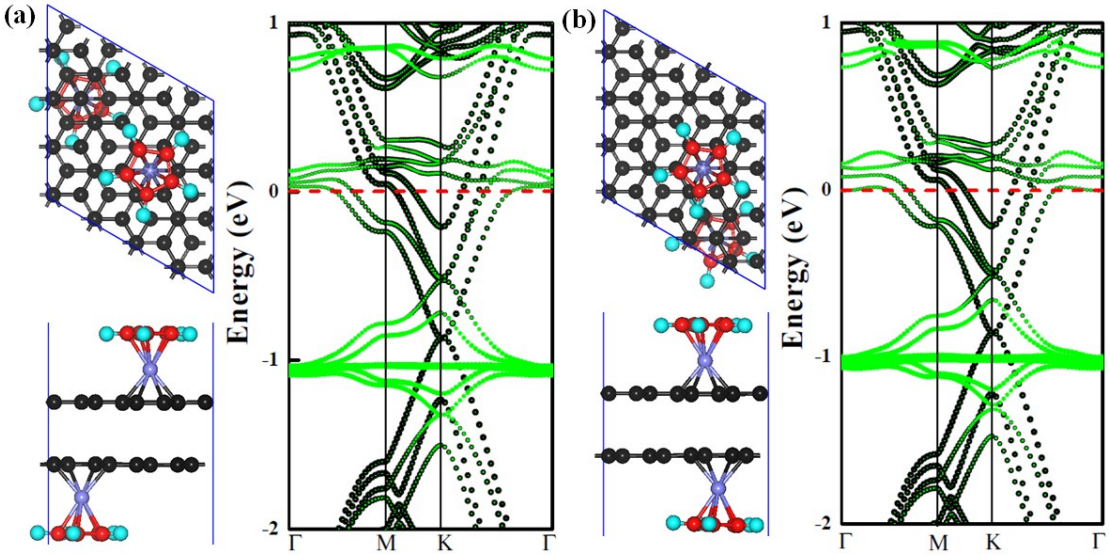

Figure S14. (a) and (b) are another two geometric structures and the corresponding band structures for CpV@BLG@VCp.

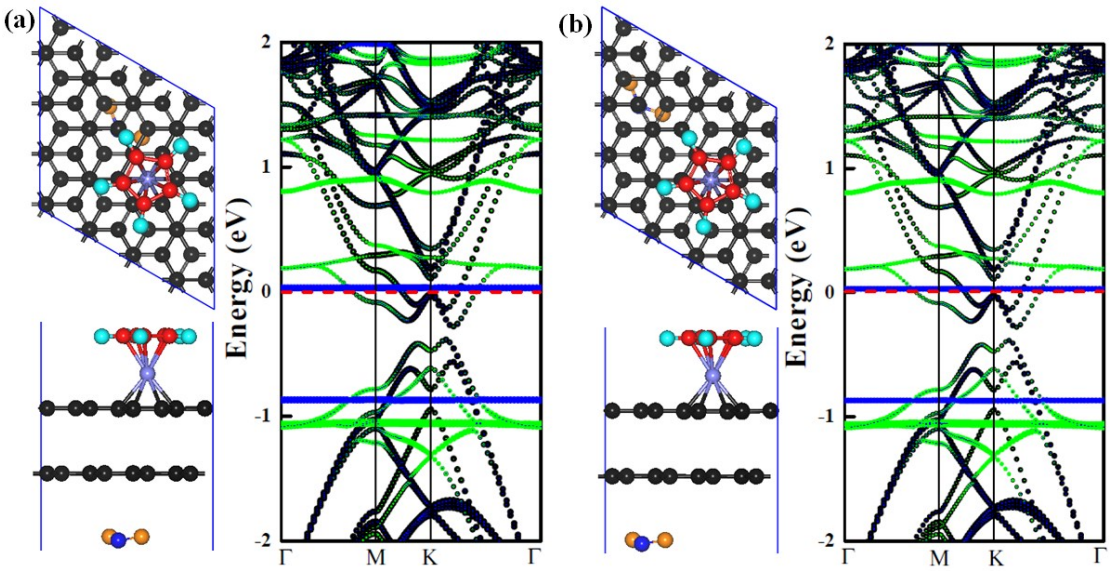

Figure S15. (a) and (b) are another two geometric structures and the corresponding band structures for CpV@BLG@NO_2.

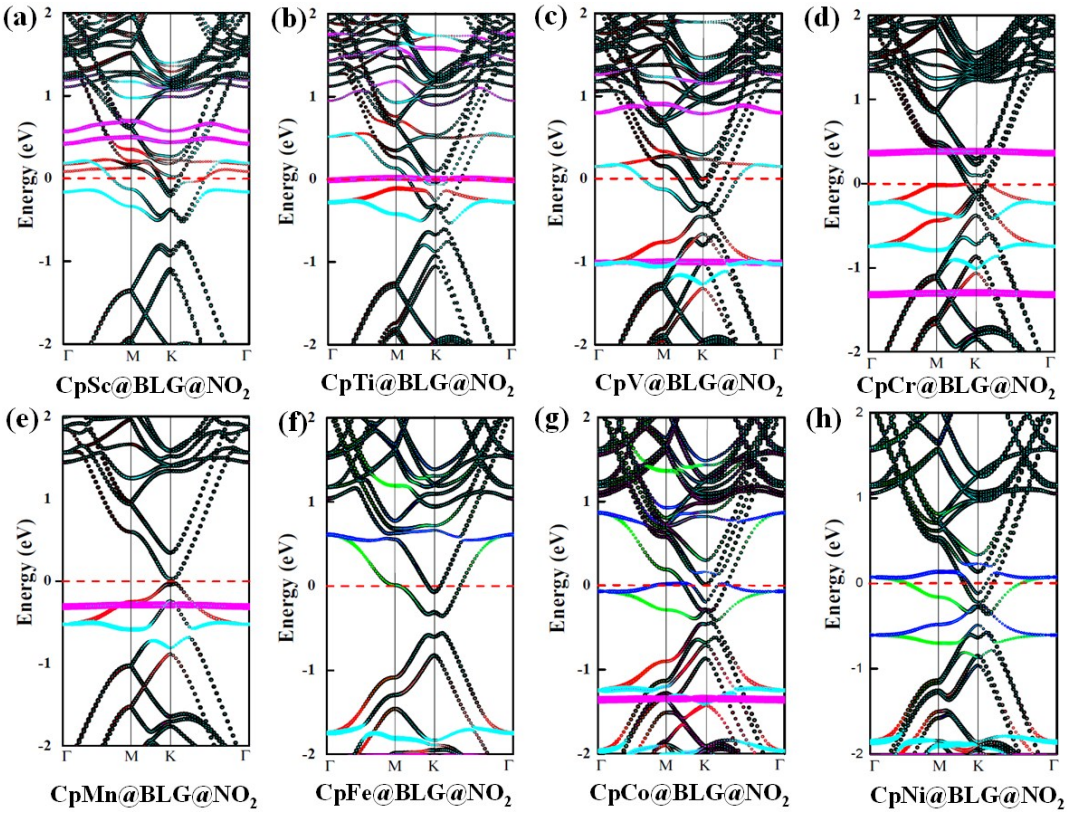

Figure S16. Analysis of band structures for d orbital of metal atom of CpTM@BLG. Red, green, blue, magenta, cyan and black dots represent d_{xy}, d_{yz}, d_{xz}, d_{z2}, and d_{x2-y2} for TM and *p* orbitals for C on graphene.

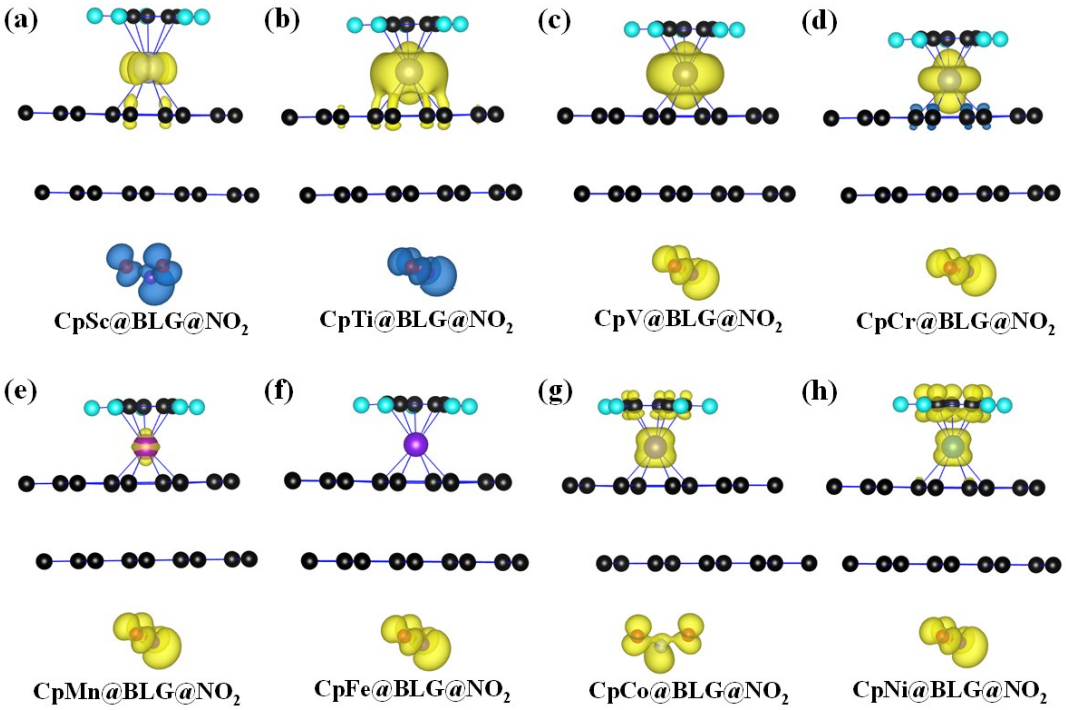

Figure S17. Spin densities of CpTM@BLG@NO_2 (TM=Sc-Ni). Yellow and blue represent spin up and spin down density, respectively.