Supporting Information
for
Influence of graphene on the electronic and magnetic properties of an iron(III) porphyrin chloride complex

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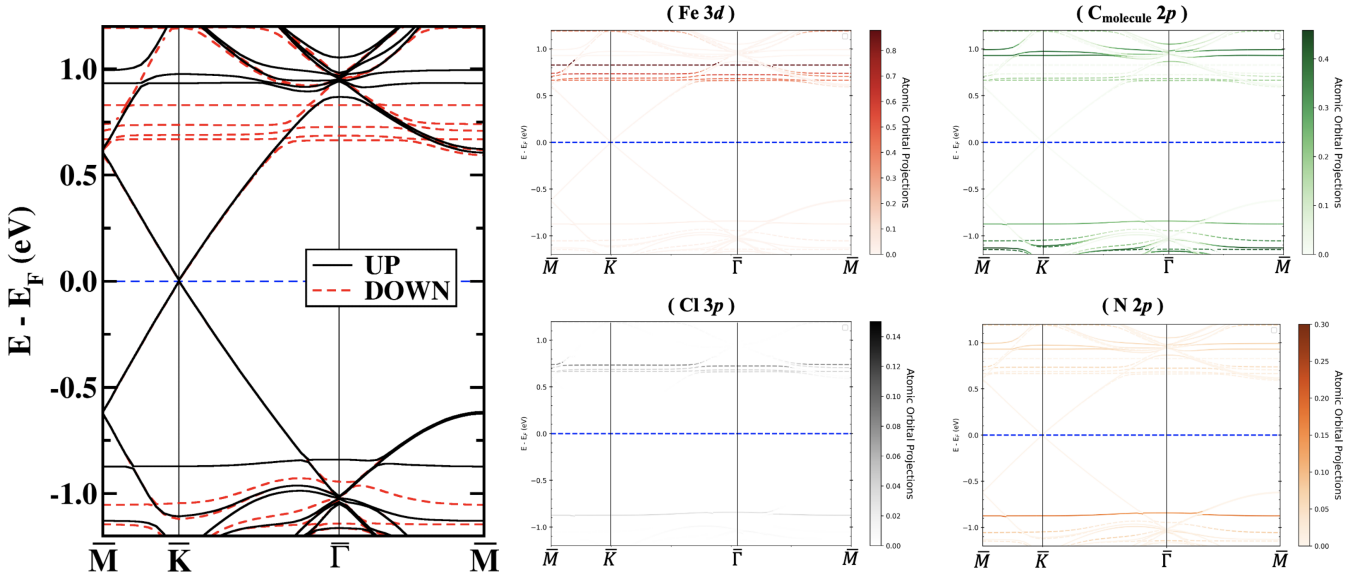

FIG. 1. (Left) Spin-resolved and (middle and right) both spin- and orbital-resolved band structures in [Fe^{III}(P)(Cl)] absorbed on a graphene sheet (8×8) within GGA + U (4 eV). In all plots, solid (dashed) lines represent spin-up (spin-down) bands. The main contribution to forming the Dirac point at the Fermi level stems from C(graphene) 2p, which is shown in the main text.

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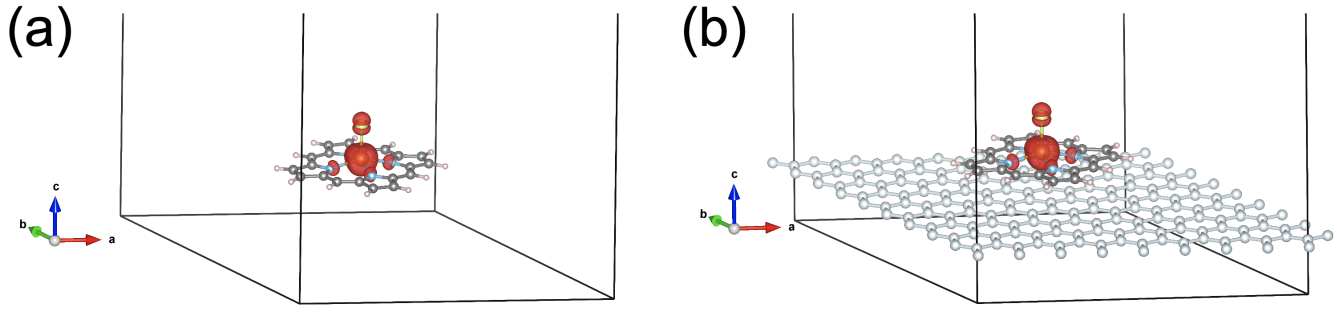

FIG. 2. Spin density plot ($\rho_\uparrow - \rho_\downarrow$) of (a) [$Fe^{III}$(P)(Cl)] and (b) [$Fe^{III}$(P)(Cl)] absorbed on a graphene sheet (8×8) within GGA + U (4 eV) with an isovalue of 0.067 e/Å. The spin density plots of both cases are almost similar independent of the existence of graphene, indicating a minimal role of graphene.

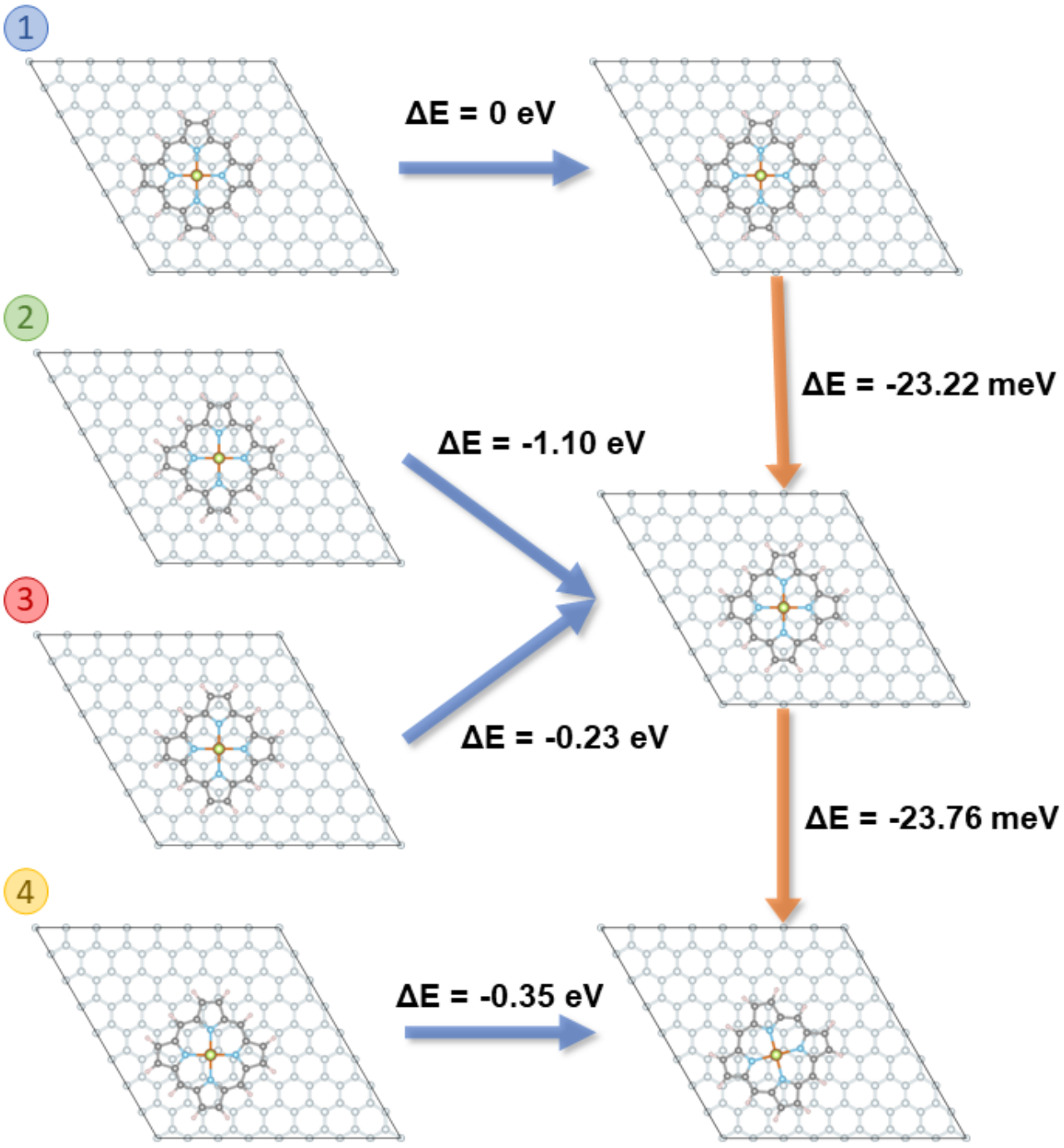

FIG. 3. Structures before (in the left column) and after (in the right column) relaxation with VASP. Blue arrows highlight variations in total energy between the unrelaxed and relaxed structures, while orange arrows denote differences in total energy between two relaxed structures. As a result, the case04 (named bridge2 in the main text) is found to be energetically the most stable.

Atom	x	y	z		Atom	x	y	z
Fe	-0.008727	-0.018712	-0.027386		H	-2.807025	4.920590	0.764329
N	2.039261	-0.038703	-0.423795		H	-2.918084	6.613482	0.199272
N	0.018645	-2.085525	-0.291067		H	-1.434104	6.035505	1.013858
N	-2.027350	-0.079449	-0.558443		H	1.142692	6.135294	1.054967
N	-0.006855	1.965865	-0.690620		H	2.695939	6.711881	0.380044
H	5.258322	2.520041	-0.103633		H	2.548809	5.036769	0.988904
H	6.329694	1.112051	-0.219948		C	2.866594	1.066465	-0.540529
H	5.285019	-2.436879	0.425613		C	4.261354	0.663259	-0.499534
H	6.341749	-1.072927	0.019912		C	5.436649	1.584783	-0.664586
H	3.230297	-3.218110	-0.085206		C	4.269658	-0.714215	-0.350769
H	1.136046	-6.341818	0.354381		C	5.454771	-1.637094	-0.317767
H	2.503704	-5.247820	0.628502		C	2.880382	-1.133481	-0.307521
H	-2.467761	-5.296082	0.427187		C	2.452553	-2.456629	-0.181559
H	-1.055603	-6.359770	0.295138		C	1.130690	-2.905653	-0.192492
H	-3.176103	-3.282842	-0.304438		C	0.729065	-4.298698	-0.112836
H	-6.303957	-1.247590	-0.918514		C	1.669406	-5.469322	-0.061595
H	-5.222178	-2.650110	-1.001224		C	-0.655328	-4.313684	-0.164380
H	-6.317108	0.939204	-1.144815		C	-1.569199	-5.506158	-0.180724
H	-5.252174	2.305824	-1.519959		C	-1.080201	-2.929031	-0.272717
H	-3.216763	3.093999	-0.948123		C	-2.408895	-2.505552	-0.344843
H	-2.482437	5.098214	-1.742792		C	-2.854273	-1.188370	-0.476548
H	-1.115283	6.199207	-1.493041		C	-4.248183	-0.790110	-0.564417
H	1.075649	6.207170	-1.470083		C	-5.424473	-1.717230	-0.444499
H	2.485743	5.135638	-1.547798		C	-4.256295	0.587876	-0.708390
H	3.189948	3.157312	-0.747055		C	-5.442666	1.506624	-0.781002
H	5.944713	1.012574	-2.718194		C	-2.867703	1.012174	-0.702502
H	6.594420	2.602857	-2.218403		C	-2.439769	2.335124	-0.827807
H	4.858113	2.425058	-2.607243		C	-1.117612	2.783421	-0.820540
H	4.889825	-2.867887	-2.044871		C	-0.714390	4.171741	-0.957215
H	6.624945	-2.949758	-1.620923		C	-1.652964	5.340886	-1.053909
H	5.970159	-1.503011	-2.444220		C	0.670115	4.186312	-0.912289
H	1.437054	-6.103705	-2.147584		C	1.586289	5.376204	-0.952695
H	2.930247	-6.697610	-1.362115		C	1.092877	2.806321	-0.748791
H	2.806520	-4.989608	-1.876075		C	2.421774	2.383066	-0.677298
H	-2.537881	-5.076433	-2.101214		C	5.725186	1.926615	-2.139326
H	-2.678426	-6.779208	-1.573367		C	5.751916	-2.277069	-1.687923
H	-1.128494	-6.166191	-2.223632		C	2.244333	-5.836192	-1.443668
H	-4.906452	-2.556939	1.514843		C	-2.004195	-5.905364	-1.604038
H	-6.627184	-2.747762	1.066698		C	-5.761194	-2.064504	1.018659
H	-6.007300	-1.153390	1.591422		C	-5.783396	2.147779	0.578480
H	-6.018392	1.373724	1.329746		C	-2.237331	5.751486	0.311763
H	-6.658364	2.814723	0.484857		C	2.019075	5.842390	0.450813
H	-4.935479	2.744545	0.958776		Cl	-0.097459	0.204579	2.223812

TABLE I. Cartesian coordinates (Å) of the relaxed [Fe^{III}(OEP)(Cl)] complex in the high spin state at the TPSS/def2-TZVP:def2-SVP level of theory.

Atom	x	y	z		Atom	x	y	z
Fe	-0.007323	-0.018718	-0.007826		C	4.257218	-0.706805	-0.352841
N	2.038146	-0.039090	-0.429355		C	2.878673	-1.134982	-0.317916
N	0.018471	-2.084489	-0.294025		C	2.456509	-2.461961	-0.202286
N	-2.028194	-0.076178	-0.539960		C	1.131260	-2.904443	-0.198766
N	-0.008871	1.967210	-0.673518		C	0.720997	-4.285812	-0.107203
H	3.235136	-3.225119	-0.120551		C	-0.651769	-4.298816	-0.147407
H	-3.180521	-3.285247	-0.304296		C	-1.082051	-2.925356	-0.262768
H	-3.222962	3.102994	-0.915146		C	-2.412960	-2.507474	-0.340975
H	3.191959	3.161897	-0.745521		C	-2.852643	-1.188181	-0.477382
H	-1.325078	-5.156490	-0.106919		C	-4.235110	-0.785976	-0.587107
H	1.407038	-5.130532	-0.027158		C	-4.244523	0.581107	-0.717769
H	5.115075	-1.377890	-0.287227		C	-2.867781	1.015678	-0.687330
H	5.096650	1.342438	-0.555429		C	-2.445652	2.342500	-0.802343
H	1.339258	5.024517	-1.015375		C	-1.120112	2.784029	-0.804729
H	-1.393256	4.999250	-1.087535		C	-0.708365	4.159332	-0.960824
H	-5.101101	1.247547	-0.830421		C	0.664333	4.171983	-0.924518
H	-5.082199	-1.473586	-0.570505		C	1.092490	2.804399	-0.746446
C	2.863811	1.068460	-0.533741		C	2.423922	2.387111	-0.673466
C	4.248017	0.659896	-0.487807		Cl	-0.071830	0.185690	2.229841

TABLE II. Cartesian coordinates (Å) of the relaxed [Fe^{III}(P)(Cl)] complex in the high spin state at the TPSS/def2-TZVP:def2-SVP level of theory.

Atom	x	y	z		Atom	x	y	z		Atom	x	y	z
Fe	0.416965	0.396253	0.274903		C	0.250000	0.250000	0.130769		C	0.208333	0.166667	0.130769
N	0.531945	0.426209	0.256818		C	0.250000	0.375000	0.130769		C	0.208333	0.291667	0.130769
N	0.448830	0.511718	0.257262		C	0.250000	0.500000	0.130769		C	0.208333	0.416667	0.130769
N	0.301986	0.366302	0.256820		C	0.250000	0.625000	0.130769		C	0.208333	0.541667	0.130769
N	0.385105	0.280794	0.257259		C	0.250000	0.750000	0.130769		C	0.208333	0.666667	0.130769
H	0.107898	0.244178	0.253478		C	0.250000	0.875000	0.130769		C	0.208333	0.791667	0.130769
H	0.150567	0.398669	0.252731		C	0.375000	0.000000	0.130769		C	0.208333	0.916667	0.130769
H	0.419822	0.665306	0.254978		C	0.375000	0.125000	0.130769		C	0.333333	0.041667	0.130769
H	0.573608	0.705341	0.255507		C	0.375000	0.250000	0.130769		C	0.333333	0.166667	0.130769
H	0.726036	0.548330	0.253480		C	0.375000	0.375000	0.130769		C	0.333333	0.291667	0.130769
H	0.683362	0.393836	0.252750		C	0.375000	0.500000	0.130769		C	0.333333	0.416667	0.130769
H	0.260330	0.087172	0.255475		C	0.375000	0.625000	0.130769		C	0.333333	0.541667	0.130769
H	0.414116	0.127208	0.254958		C	0.375000	0.750000	0.130769		C	0.333333	0.666667	0.130769
H	0.286281	0.530836	0.255147		C	0.375000	0.875000	0.130769		C	0.333333	0.791667	0.130769
H	0.647916	0.624946	0.256345		C	0.500000	0.000000	0.130769		C	0.333333	0.916667	0.130769
H	0.547653	0.261675	0.255158		C	0.500000	0.125000	0.130769		C	0.458333	0.041667	0.130769
H	0.186018	0.167565	0.256340		C	0.500000	0.250000	0.130769		C	0.458333	0.166667	0.130769
Cl	0.416964	0.396250	0.359825		C	0.500000	0.375000	0.130769		C	0.458333	0.291667	0.130769
C	0.317779	0.498368	0.256070		C	0.500000	0.500000	0.130769		C	0.458333	0.416667	0.130769
C	0.592239	0.569812	0.256915		C	0.500000	0.625000	0.130769		C	0.458333	0.541667	0.130769
C	0.516156	0.294143	0.256076		C	0.500000	0.750000	0.130769		C	0.458333	0.666667	0.130769
C	0.241696	0.222698	0.256912		C	0.500000	0.875000	0.130769		C	0.458333	0.791667	0.130769
C	0.238015	0.291593	0.256418		C	0.625000	0.000000	0.130769		C	0.458333	0.916667	0.130769
C	0.272581	0.416786	0.255880		C	0.625000	0.125000	0.130769		C	0.583333	0.041667	0.130769
C	0.399475	0.542419	0.256739		C	0.625000	0.250000	0.130769		C	0.583333	0.166667	0.130769
C	0.524109	0.574877	0.257143		C	0.625000	0.375000	0.130769		C	0.583333	0.291667	0.130769
C	0.309825	0.217634	0.257134		C	0.625000	0.500000	0.130769		C	0.583333	0.416667	0.130769
C	0.434459	0.250094	0.256736		C	0.625000	0.625000	0.130769		C	0.583333	0.541667	0.130769
C	0.561350	0.375724	0.255886		C	0.625000	0.750000	0.130769		C	0.583333	0.666667	0.130769
C	0.595918	0.500918	0.256416		C	0.625000	0.875000	0.130769		C	0.583333	0.791667	0.130769
C	0.166577	0.295085	0.254748		C	0.750000	0.000000	0.130769		C	0.583333	0.916667	0.130769
C	0.188033	0.372759	0.254381		C	0.750000	0.125000	0.130769		C	0.708333	0.041667	0.130769
C	0.444720	0.626925	0.256131		C	0.750000	0.250000	0.130769		C	0.708333	0.166667	0.130769
C	0.522060	0.647056	0.256446		C	0.750000	0.375000	0.130769		C	0.708333	0.291667	0.130769
C	0.667355	0.497424	0.254750		C	0.750000	0.500000	0.130769		C	0.708333	0.416667	0.130769
C	0.645899	0.419750	0.254391		C	0.750000	0.625000	0.130769		C	0.708333	0.541667	0.130769
C	0.311877	0.145457	0.256425		C	0.750000	0.750000	0.130769		C	0.708333	0.666667	0.130769
C	0.389217	0.165588	0.256117		C	0.750000	0.875000	0.130769		C	0.708333	0.791667	0.130769
C	0.000000	0.000000	0.130769		C	0.875000	0.000000	0.130769		C	0.708333	0.916667	0.130769
C	0.000000	0.125000	0.130769		C	0.875000	0.125000	0.130769		C	0.833333	0.041667	0.130769
C	0.000000	0.250000	0.130769		C	0.875000	0.250000	0.130769		C	0.833333	0.166667	0.130769
C	0.000000	0.375000	0.130769		C	0.875000	0.375000	0.130769		C	0.833333	0.291667	0.130769
C	0.000000	0.500000	0.130769		C	0.875000	0.500000	0.130769		C	0.833333	0.416667	0.130769
C	0.000000	0.625000	0.130769		C	0.875000	0.625000	0.130769		C	0.833333	0.541667	0.130769
C	0.000000	0.750000	0.130769		C	0.875000	0.750000	0.130769		C	0.833333	0.666667	0.130769
C	0.000000	0.875000	0.130769		C	0.875000	0.875000	0.130769		C	0.833333	0.791667	0.130769
C	0.125000	0.000000	0.130769		C	0.083333	0.041667	0.130769		C	0.833333	0.916667	0.130769
C	0.125000	0.125000	0.130769		C	0.083333	0.166667	0.130769		C	0.958333	0.041667	0.130769
C	0.125000	0.250000	0.130769		C	0.083333	0.291667	0.130769		C	0.958333	0.166667	0.130769
C	0.125000	0.375000	0.130769		C	0.083333	0.416667	0.130769		C	0.958333	0.291667	0.130769
C	0.125000	0.500000	0.130769		C	0.083333	0.541667	0.130769		C	0.958333	0.416667	0.130769
C	0.125000	0.625000	0.130769		C	0.083333	0.666667	0.130769		C	0.958333	0.541667	0.130769
C	0.125000	0.750000	0.130769		C	0.083333	0.791667	0.130769		C	0.958333	0.666667	0.130769
C	0.125000	0.875000	0.130769		C	0.083333	0.916667	0.130769		C	0.958333	0.791667	0.130769
C	0.250000	0.000000	0.130769		C	0.208333	0.041667	0.130769		C	0.958333	0.916667	0.130769
C	0.250000	0.125000	0.130769										

TABLE III. Fractional coordinates of the relaxed [Fe^{III}(P)(Cl)] complex absorbed graphene (named bridge 2 in the main text) within GGA + U (U = 4 eV) with the lattice parameters of a_H = 19.68 Å and c_H = 26 Å in VASP. Here H denotes the hexagonal unit cell with $\overrightarrow{a_1}$=a_H(1,0,0), $\overrightarrow{a_2}$=a_H($-\frac{1}{2}$,$\frac{\sqrt{3}}{2}$,0), and $\overrightarrow{a_3}$=c_H(0,0,1).

INCAR tags						
ISTART= 0		EDIFF= 1.0E-6		BMIX_MAG= 0.00001		SIGMA= 0.05
ICHARG= 2		ISPIN= 2		LDAU= .TRUE.		IVDW = 1
INIWAV= 1		MAGMOM= 5.0 165*0.0		LDAUTYPE= 1		BMIX= 0.00001
ENCUT= 500.00 eV		LORBIT= 11		LDAUL= 2 10*-1		AMIX_MAG= 0.8
PREC= Accurate		ISYM= 2		LDAUU= 4.0 10*0.0		LDAUPRINT = 2
ISMEAR= 0		AMIX= 0.2		LDAUJ= 1.0 10*0.0		LMAXMIX= 4

TABLE IV. Details of INCAR tags used in the VASP calculations. INCAR is one of the vital input files in VASP.