Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Intriguing Strain-Governed Magnetic Phase Transitions in 2D Vanadium Porphyrin Sheet

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Supporting Information

Content

1. All Calculated Data

Table S1. The bond lengths and lattice constants (a/b) in different biaxial strains for the vanadium porphyrin sheet (V-PP4)

Biaxial strain	V-V (Å)	V-N (Å)	a/b (Å)
-0.08	7.732	1.789	15.460
-0.07	7.814	1.816	15.629
-0.06	7.898	1.843	15.797
-0.05	7.982	1.871	15.964
-0.04	8.066	1.899	16.133
-0.02	8.234	1.957	16.469
0	8.402	2.018	16.805
0.02	8.570	2.084	17.141
0.04	8.739	2.155	17.477
0.05	8.822	2.190	17.644
0.06	8.907	2.230	17.813
0.07	8.990	2.270	17.980
0.08	9.075	2.312	18.149

Table S2. The energies (FM/AFM1/AFM2/FIM) in different biaxial strains for the Vanadium porphyrin sheet (V-PP4)

Biaxial strain	**FM (eV)**	**AFM1 (eV)**	**AFM2 (eV)**	**FIM (eV)**
-0.08	-856.388	-856.617	-856.326	-856.543
-0.07	-869.236	-869.365	-869.146	-869.342
-0.06	-879.913	-879.961	-879.796	-879.964
-0.05	-888.572	-888.555	-888.433	-888.583
-0.04	-895.360	-895.292	-895.205	-895.329
-0.02	-903.881	-903.744	-903.720	-903.792
0	-906.457	-906.288	-906.318	-906.343
0.02	-904.102	-903.927	-904.010	-903.986
0.04	-897.593	-897.428	-897.557	-897.491
0.05	-892.981	-892.827	-892.975	-892.886
0.06	-887.643	-887.497	-887.667	-887.562
0.07	-881.637	-881.497	-881.687	-881.558
0.08	-875.018	-874.882	-875.093	-874.945

Table S3. The relative energies (FM/AFM1/AFM2/FIM) to its corresponding most stable structure (strain=0) in different biaxial strains for the vanadium porphyrin sheet (V-PP4)

Biaxial strain	FM(eV)	AFM1 (eV)	AFM2 (eV)	FIM (eV)
-0.08	50.069	49.991	49.990	49.799
-0.07	37.221	36.922	37.172	37.000
-0.06	26.544	26.327	26.521	26.378
-0.05	17.885	17.732	17.885	17.759
-0.04	11.097	10.996	11.113	11.014
-0.02	2.576	2.544	2.598	2.550
0.00	0.000	0.000	0.000	0.000
0.02	2.355	2.361	2.307	2.356
0.04	8.864	8.859	8.760	8.851
0.05	13.476	13.460	13.343	13.456
0.06	18.814	18.791	18.650	18.781
0.07	24.820	24.790	24.630	24.784
0.08	31.439	31.405	31.225	31.397

Table S4. The exchange energies (E_{ex}) in different biaxial strains for the vanadium porphyrin sheet (V-PP4)

Biaxial strain	E_{ex1}/eV (=E_{AFM1}-E_{FM})	E_{ex2}/eV (=E_{AFM2}-E_{FM})	E_{ex3}/eV (=E_{FIM}-E_{FM})
-0.08	-0.229	0.061	-0.155
-0.07	-0.129	0.090	-0.106
-0.06	-0.048	0.116	-0.051
-0.05	0.016	0.139	-0.011
-0.04	0.068	0.155	0.031
-0.02	0.137	0.161	0.089
0.00	0.169	0.139	0.114
0.02	0.174	0.091	0.115
0.04	0.164	0.035	0.101
0.05	0.153	0.006	0.095
0.06	0.146	-0.023	0.081
0.07	0.139	-0.050	0.078
0.08	0.135	-0.074	0.072

Table S5. The energies (FM/AFM1/AFM2/FIM) in different biaxial strains for the Vanadium porphyrin sheet (V-PP4), obtained by single point calculations using the optimized structure at the DFT-D3 level

Biaxial strain	FM (eV)	AFM1 (eV)	AFM2 (eV)	FIM (eV)
-0.08	-858.015	-858.248	-857.954	-858.172
-0.06	-881.679	-881.732	-881.565	-881.345
-0.04	-897.330	-897.267	-897.177	-896.774
-0.02	-906.048	-905.913	-905.887	-905.961
0.00	-908.800	-906.578	-906.605	-907.949
0.02	-906.561	-906.390	-906.472	-905.857
0.04	-900.075	-899.915	-900.044	-899.310
0.06	-890.081	-889.939	-890.110	-890.003
0.08	-877.371	-877.238	-877.450	-877.300

Table S6. The exchange energies (E_{ex}) in different biaxial strains for the vanadium porphyrin sheet (V-PP4), obtained by single point calculations using the optimized structure at the DFT-D3 level

Biaxial strain	E_{ex1}/eV (=E_{AFM1}-E_{FM})	E_{ex2}/eV (=E_{AFM2}-E_{FM})	E_{ex3}/eV (=E_{FIM}-E_{FM})
-0.08	-0.232	0.060	-0.157
-0.06	-0.053	0.114	0.333
-0.04	0.063	0.153	0.556
-0.02	0.134	0.161	0.086
0.00	2.221	2.195	0.850
0.02	0.170	0.088	0.704
0.04	0.160	0.031	0.765
0.06	0.141	-0.029	0.077
0.08	0.132	-0.079	0.070

Table S7. The energies (FM/AFM1/AFM2/FIM) in different uniaxial strains (at the direction ***a***) for the vanadium porphyrin sheet (V-PP4)

Uniaxial strain(a)	**FM (eV)**	**AFM1 (eV)**	**AFM2 (eV)**	**FIM (eV)**
-0.08	-888.912	-888.945	-888.863	-888.940
-0.06	-896.868	-896.793	-896.771	-896.838
-0.04	-902.322	-902.186	-902.191	-902.249
-0.02	-905.454	-905.294	-905.309	-905.352
0	-906.458	-906.289	-906.318	-906.343
0.02	-905.522	-905.342	-905.342	-905.405
0.04	-902.853	-902.669	-902.759	-902.744
0.06	-898.624	-898.466	-898.584	-898.537
0.08	-893.067	-892.945	-893.084	-892.347

Table S8. The exchange energies (E_{ex}) in different uniaxial strains (at the direction ***a***) for the vanadium porphyrin sheet (V-PP4)

Uniaxial strain(a)	**E_{ex1}/eV (=E_{AFM1}-E_{FM})**	**E_{ex2}/eV (=E_{AFM2}-E_{FM})**	**E_{ex3}/eV (=E_{FIM}-E_{FM})**
-0.08	-0.033	0.049	-0.027
-0.06	0.074	0.096	0.029
-0.04	0.136	0.131	0.073
-0.02	0.159	0.144	0.101
0	0.169	0.139	0.114
0.02	0.180	0.180	0.116
0.04	0.183	0.093	0.108
0.06	0.157	0.039	0.086
0.08	0.121	-0.016	0.719

Table S9. The Magnetic Moments of V atom, N atom and Total Magnetic Moments of FM in Vanadium Porphyrin Sheet (V-PP4) in Different Biaxial Strains

Biaxial strain	Magnetic Moment (V)	Magnetic Moment (N)	Magnetic Moment (FM/V-PP4)
-0.08	1.458	-0.037	5.391
-0.07	1.600	-0.040	6.048
-0.06	1.707	-0.043	6.533
-0.05	1.804	-0.045	6,972
-0.04	1.894	-0.047	7.373
-0.02	2.043	-0.051	7.991
0	2.183	-0.055	8.533
0.02	2.316	-0.058	9.047
0.04	2.441	-0.060	9.501
0.05	2.499	-0.061	9.685
0.06	2.561	-0.060	9.879
0.07	2.620	-0.057	10.043
0.08	2.672	-0.054	10.180

Table S10. The bond lengths in different biaxial strains for the Vanadium porphyrin sheet (V-PP2)

Biaxial strain	**V-V (Å)**	**V-N (Å)**
-0.08	7.730	1.789
-0.06	7.898	1.843
-0.04	8.066	1.899
-0.02	8.234	1.957
0	8.402	2.018
0.02	8.570	2.084
0.04	8.738	2.153
0.06	8.906	2.227
0.08	9.074	2.309

Table S11. The energies (FM/AFM1') and the exchange energies ($E_{ex}=(E_{AFM}-E_{FM})$/eV) in different biaxial strains for the Vanadium porphyrin sheet (V-PP2)

Biaxial strain	FM (eV)	AFM1' (eV)	E_{ex1}/eV ($=E_{AFM1'}-E_{FM}$)
-0.08	-428.220	-428.306	-0.085
-0.06	-439.976	-439.987	-0.010
-0.04	-447.676	-447.634	0.041
-0.02	-451.930	-451.848	0.081
0.00	-453.240	-453.139	0.100
0.02	-452.059	-451.959	0.099
0.04	-448.801	-448.711	0.090
0.06	-443.833	-443.755	0.078
0.08	-437.503	-437.441	0.062

Table S12. The energies (FM/AFM2') and the exchange energies ($E_{ex}=(E_{AFM}-E_{FM})$/eV) in different biaxial strains for the Vanadium porphyrin sheet (V-PP2)

Biaxial strain(a)	FM (eV)	AFM2' (eV)	E_{ex2}/eV ($=E_{AFM2'}-E_{FM}$)
-0.08	-428.182	-428.109	0.072
-0.06	-439.949	-439.847	0.101
-0.04	-447.662	-447.550	0.111
-0.02	-451.920	-451.806	0.114
0.00	-453.239	-453.139	0.100
0.02	-452.065	-451.994	0.070
0.04	-448.814	-448.777	0.036
0.06	-443.849	-443.846	0.003
0.08	-437.524	-437.554	-0.029

Table S13. The Magnetic Moments of V atom and Total Magnetic Moments of V-PP2 in different biaxial strains

Biaxial strain	Magnetic Moment (V)	Magnetic Moment (V-PP2)
-0.08	1.449	2.682
-0.06	1.701	3.268
-0.04	1.908	3.754
-0.02	2.068	4.096
0.00	2.189	4.299
0.02	2.316	4.494
0.04	2.441	4.718
0.06	2.560	4.906
0.08	2.669	5.064

2. Four Magnetic Configurations

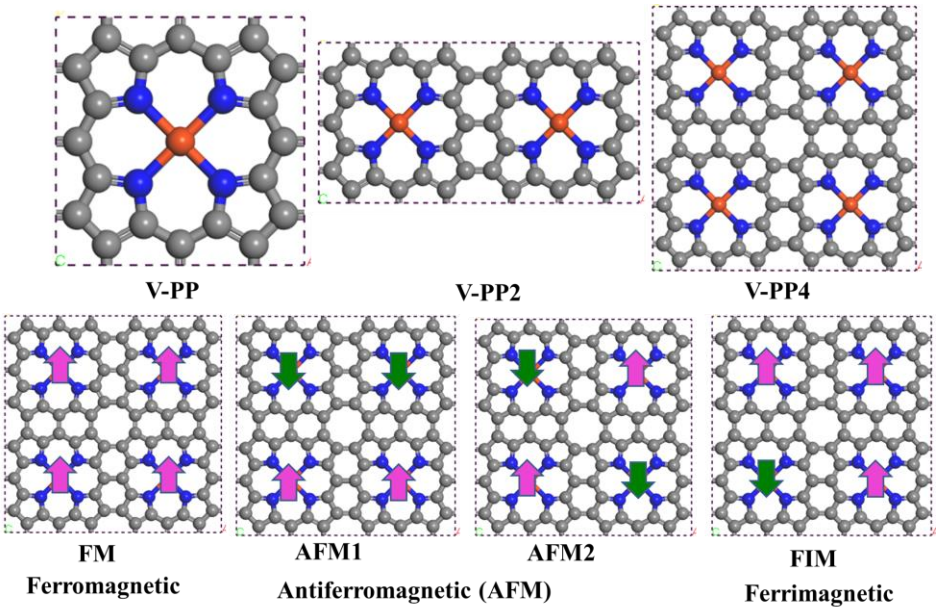

Figure S1. Two-dimensional vanadium porphyrin structure and magnetic configurations, where V-PP means a primitive unit cell and V-PP2 contains two primitive unit cell, and the 2×2 supercell composed of four primitive unit cells are represented by V-PP4. Four magnetic configurations (ferromagnetic (FM), antiferromagnetic (AFM1 and AFM2) and ferromagnetic (FIM)) of vanadium porphyrin sheet, where the pink arrow denote spin up and the green arrow denote spin down. Red, gray and blue balls represent vanadium (V), carbon (C) and nitrogen (N) atoms, respectively.

3. AIMD Simulation of the V-PP4 Sheet

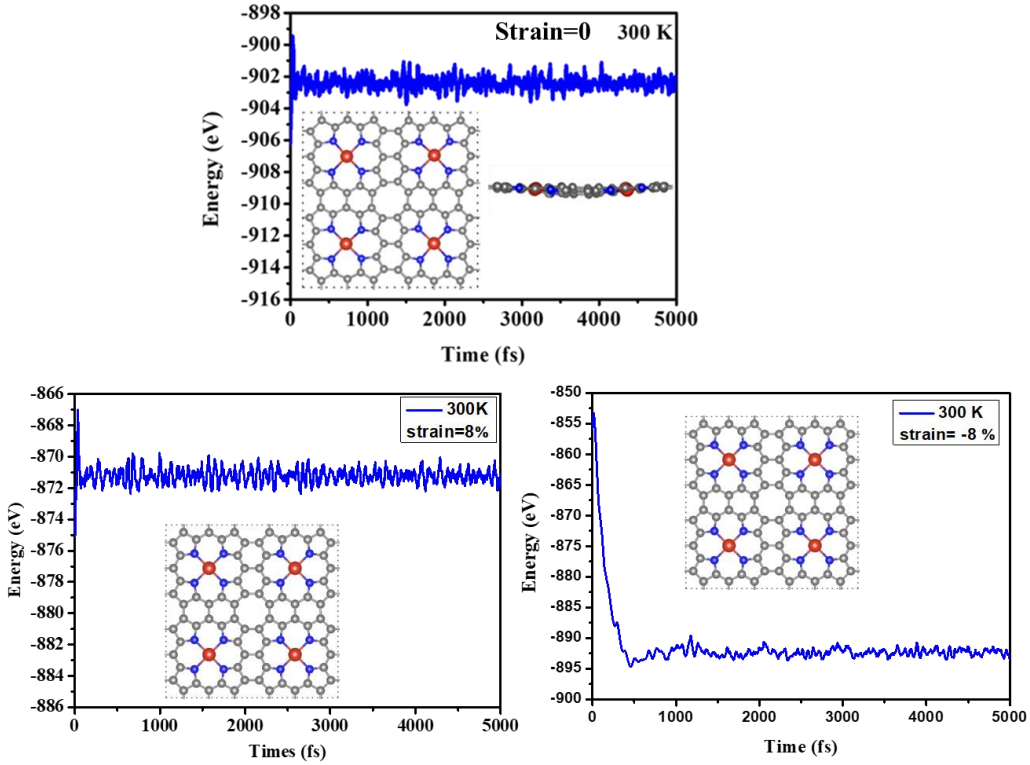

Figure S2. AIMD simulation of the 2×2 VPP4 sheet.

4. Strain Energies of Four Magnetic Configurations

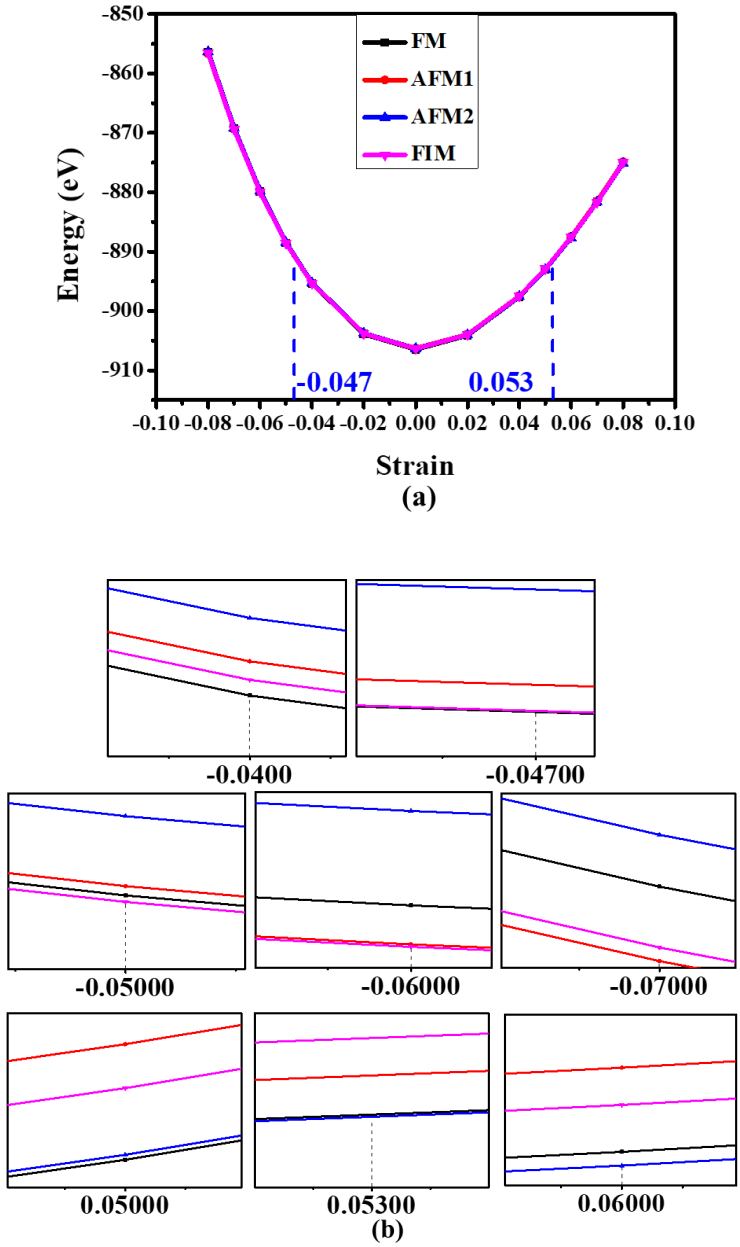

Figure S3. The strain-induced energy changes of four magnetic configurations (ferromagnetic (FM), ferromagnetic (FIM) antiferromagnetic (AFM1 and AFM2)) of vanadium porphyrin sheet under biaxial strains (**a**), and the refined variations of them under the correspnding strains (**b**). In (**b**) the red line coincides with the black line under compress strain (-0.047) and the blue line coincides with the black line under tensile strain (0.053).

5. The magnetic moment of V, N and C atom in the different biaxial strain

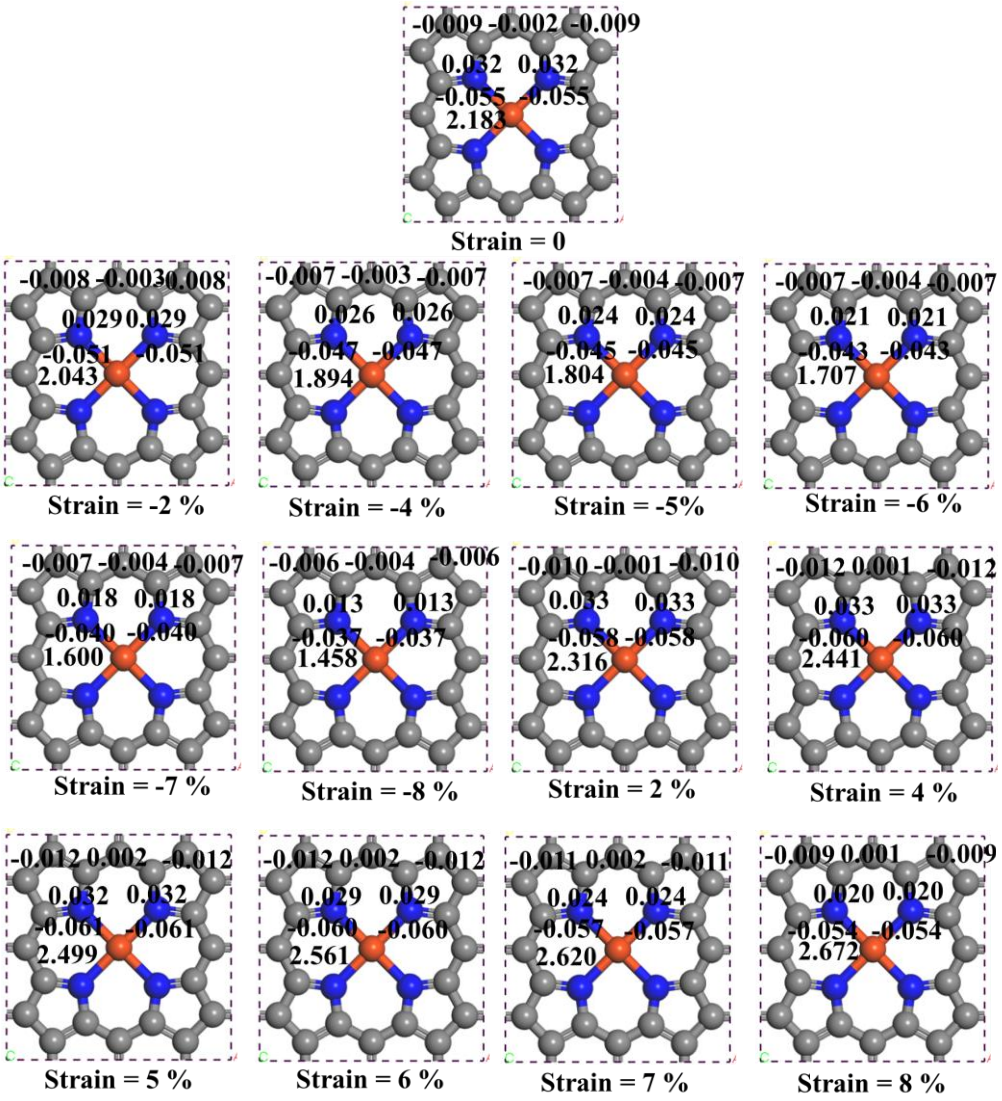

Figure S4. The magnetic moment of V, N and C atoms in the different biaxial strain, where a vanadium porphyrin sheet was intercepted from 2×2 supercell (V-PP4) to observe spin magnetic moment.

6. Net effective charges on N and V atoms form Bader charge analysis

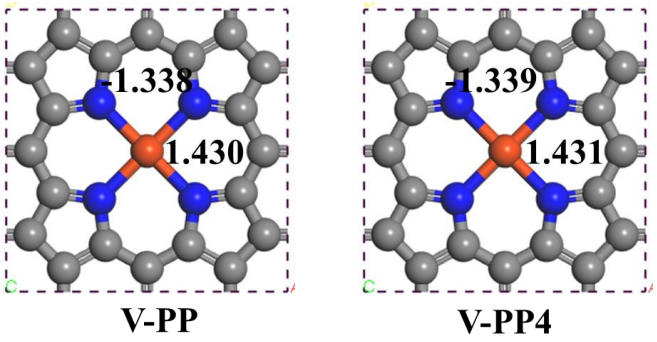

Figure S5. Net effective charges on N and V atoms form Bader charge analysis, where the V-PP is the primitive unit cell and the V-PP4 denotes that a vanadium porphyrin sheet was intercepted from 2×2 supercell (V-PP4) to observe electron transfer.