Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Atomically Thin Ferromagnetic Half-Metallic Pyrazine-Fused Mn-Porphyrin Sheet: A Slow Spin Relaxation System

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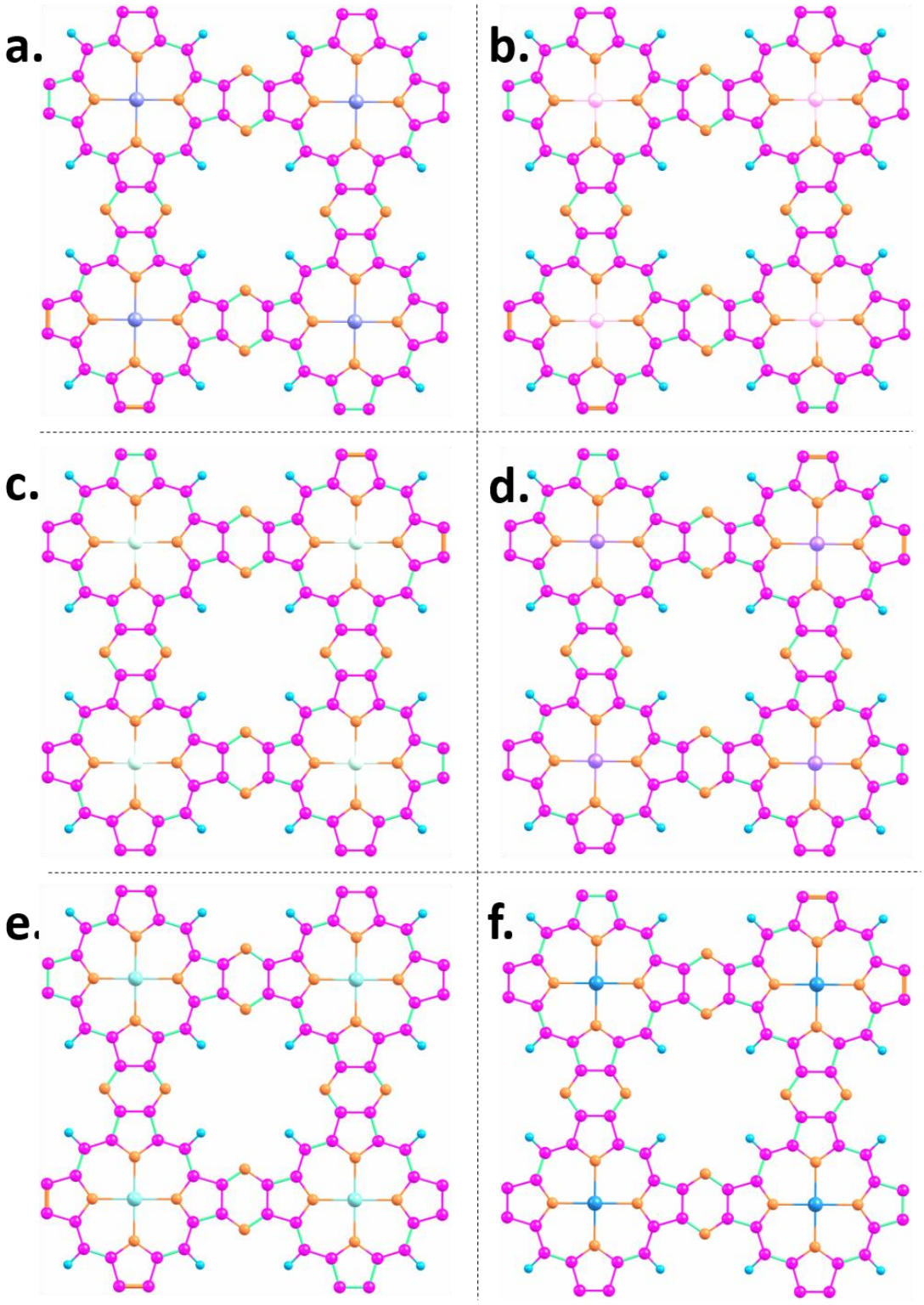


Figure S1. 2D TM-PP structures. a) Cr-PP, b) Fe-PP, c) Co-PP, d) Ni-PP, e) Cu-PP and f) Zn-PP.

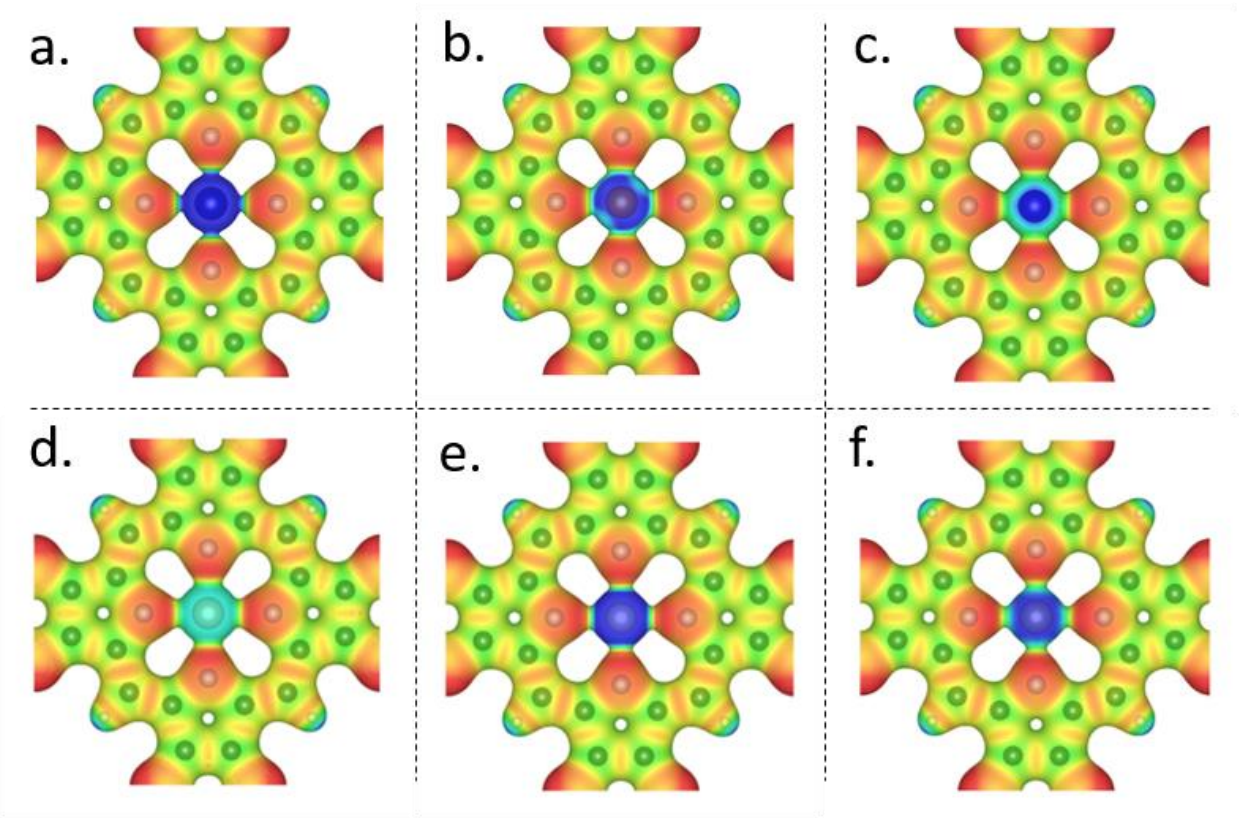


Figure S2. Electrostatic potential map for TM-PPs (Isosurface value $0.06\ \mathrm{eV/Å^3}$). a) Cr-PP, b) Fe-PP, c) Co-PP, d) Ni-PP, e) Cu-PP and f) Zn-PP. The blue and red colors denote less and more electron dense area in the electrostatic potential surface.

Table S1. Net effective charges on N and TM atoms form Bader charge analysis.

TM-PP	**Net effective charges**								
	Metal	**Pyrazine linker Nitrogen**				**Porphyrin moiety Nitrogen**			
		N1	**N2**	**N3**	**N4**	**N5**	**N6**	**N7**	**N8**
No Metal		−1.17	−1.11	−1.17	−1.11	−1.01	−1.01	−1.01	−1.00
Cr	1.26	−1.18	−1.15	−1.18	−1.15	−1.15	−1.15	−1.17	−1.17
Mn	1.25	−1.15	−1.15	−1.15	−1.14	−1.13	−1.13	−1.15	−1.15
Fe	1.15	−1.10	−1.14	−1.10	−1.14	−1.15	−1.15	−1.10	−1.10
Co	1.09	−1.10	−1.14	−1.10	−1.14	−1.15	−1.15	−1.12	−1.12
Ni	0.98	−1.10	−1.14	−1.10	−1.14	−1.14	−1.14	−1.12	−1.12
Cu	0.91	−1.18	−1.14	−1.18	−1.14	−1.10	−1.10	−1.13	−1.13
Zn	1.12	−1.18	−1.11	−1.18	−1.11	−1.13	−1.13	−1.20	−1.19

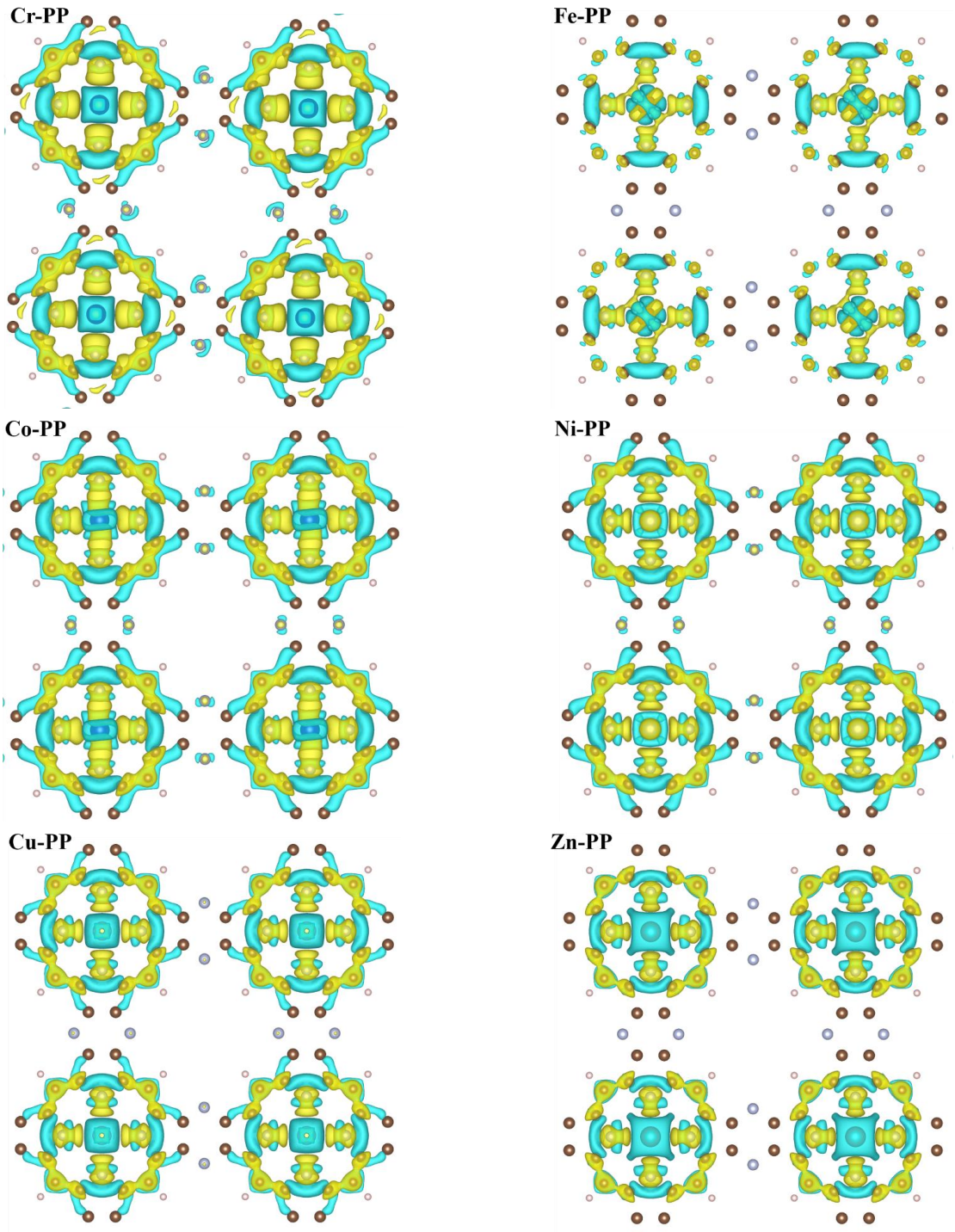


Figure S3. Charge density difference plot for all the TM-PPs. (Isosurface value 0.004 eV/Å^3). The yellow color shows accumulation of charge and cyan color shows depletion of charge.

Section S1. Charge density difference

We have plotted the charge density difference for the better understanding of charge transfer between the transition metal and Nitrogen of porphyrin cavity.

The definition of charge density difference is defined by:

$$\Delta\rho = \rho_{\mathrm{PP-TM}} - \rho_{\mathrm{PP}} - \rho_{\mathrm{TM}}$$

Where $\rho_{\mathrm{Por-M}}$, ρ_{Por} and ρ_{M} are the charge densities of TM-PPs, porphyrin moiety without transition metal incorporation and the transition metal. From the analysis of charge density difference. It clearly shows the accumulation of charge on N-atom (in porphyrin moiety) and depletion of charge on the transition metal. [1]

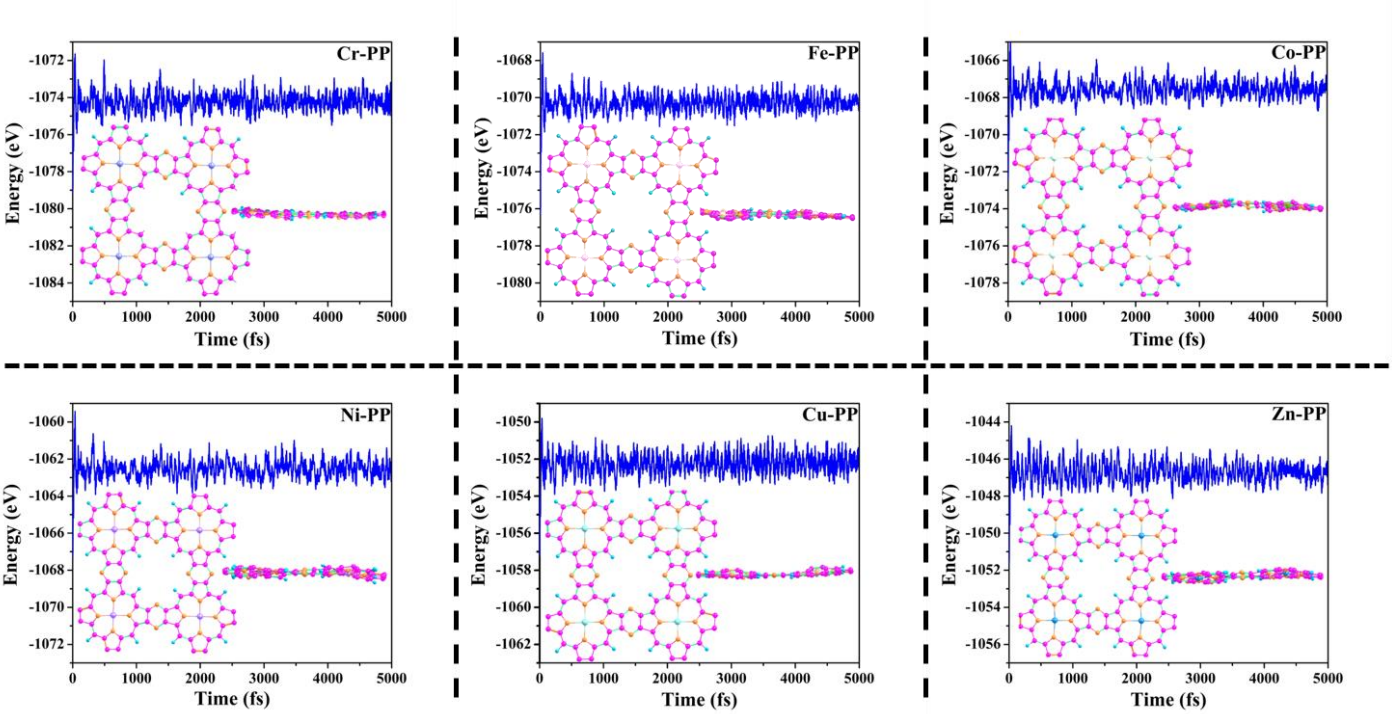
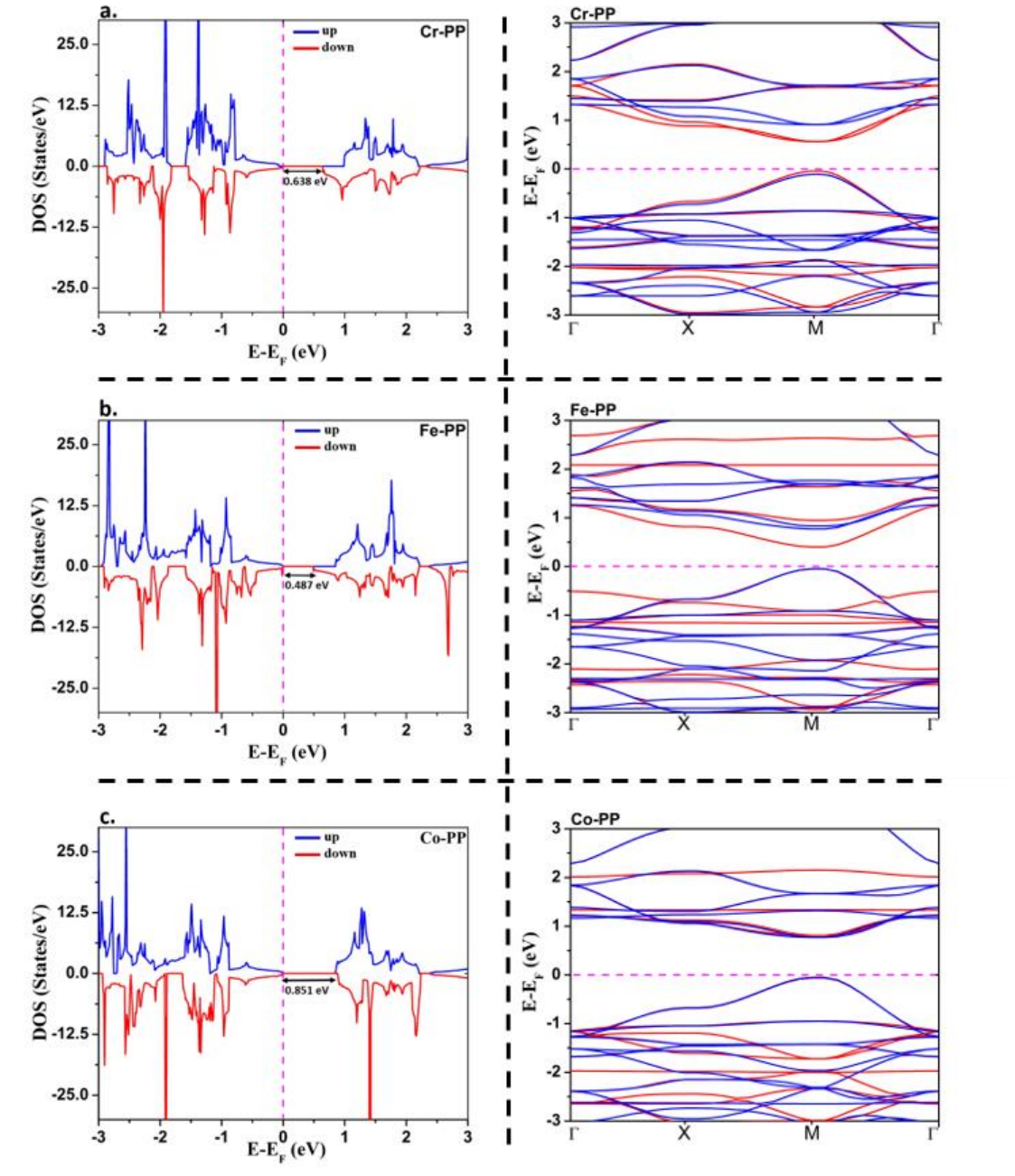


Figure S4. AIMD simulations of 2 × 2 TM-PP sheets for 5 ps with a time step of 1 fs at 300 K

Table S2. Summary of elastic constants (C_{ij} in N/m) and Poisson's ratio for all the TM-PPs.

Moduli	Cr-PP	Mn-PP	Fe-PP	Co-PP	Ni-PP	Cu-PP	Zn-PP
C_{11}	148	114	106	111	106	97	96
C_{12}	37	24	39	31	36	44	52
C_{44}	57	45	33	40	35	26	22
ν	0.18	0.17	0.27	0.22	0.25	0.31	0.35



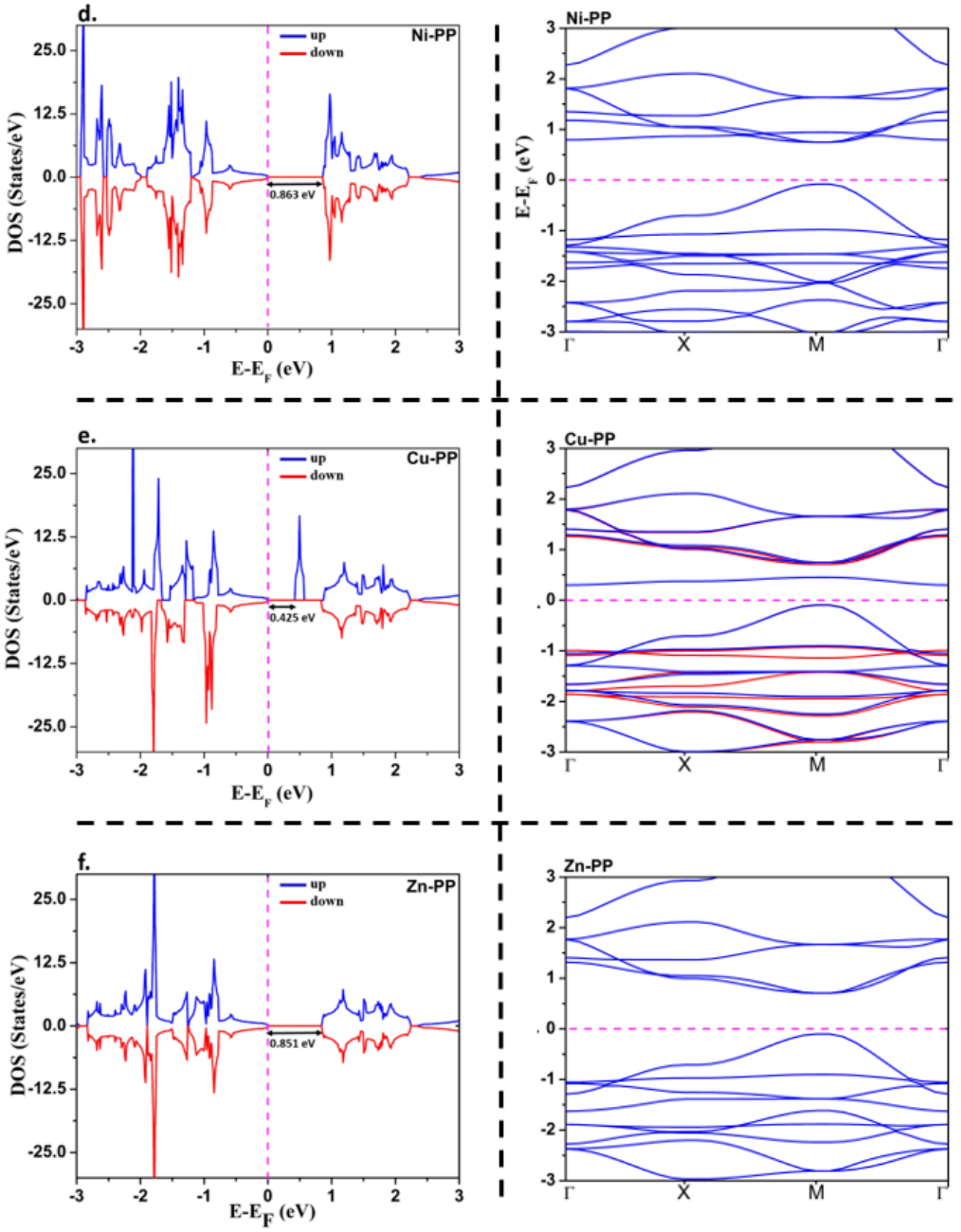


Figure S5. Spin polarized density of states, electronic structures and electrostatic potentials plots for TM-PPs a.) Cr; b.) Fe; c.) Co; d.) Ni; e.) Cu and f.) Zn. (Blue represents the up-spin component and Red represents the down-spin component).

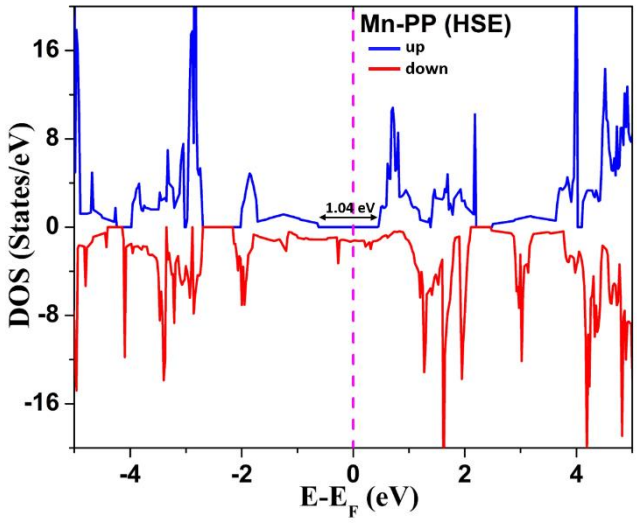


Figure S6. Density of states of Mn-PP using HSE06 level of theory.

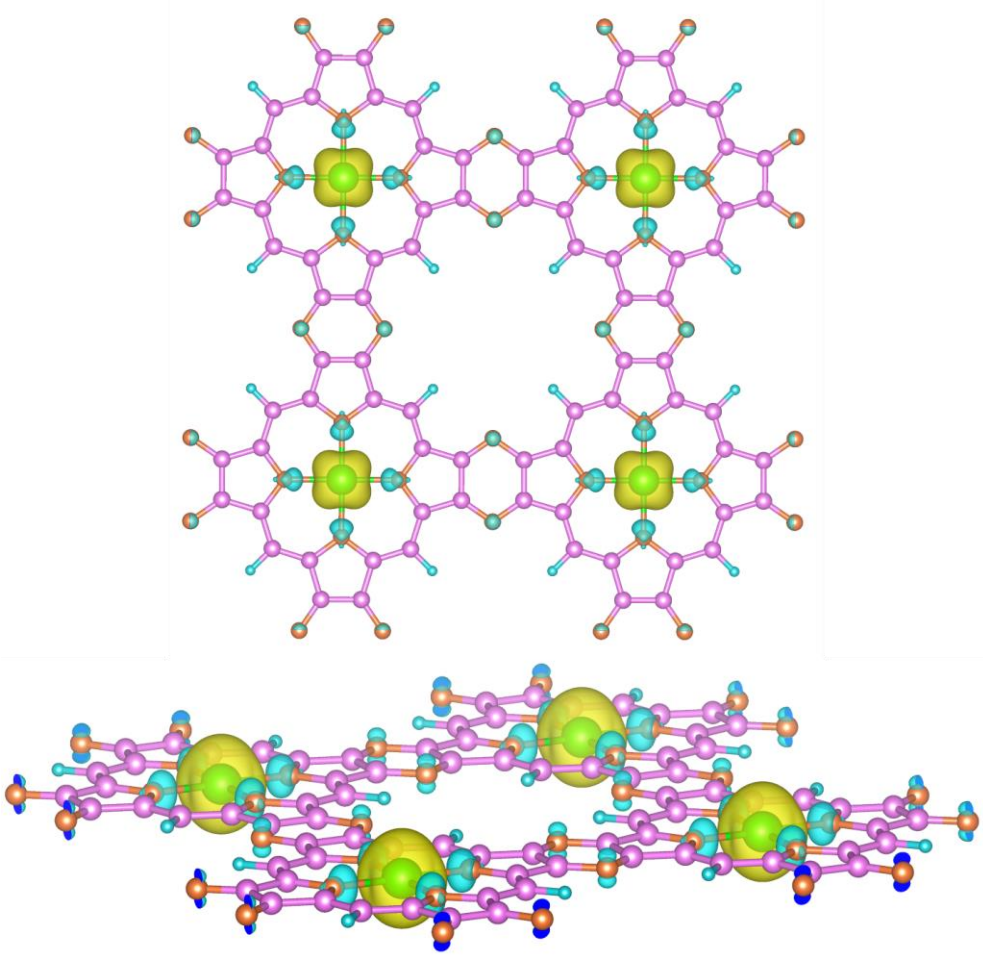


Figure S7. Spin density difference for ferromagnetic Mn-PP structure (Isosurface value 0.007 eV/Å^3). The yellow color shows up-spin density whereas cyan color shows down-spin density.

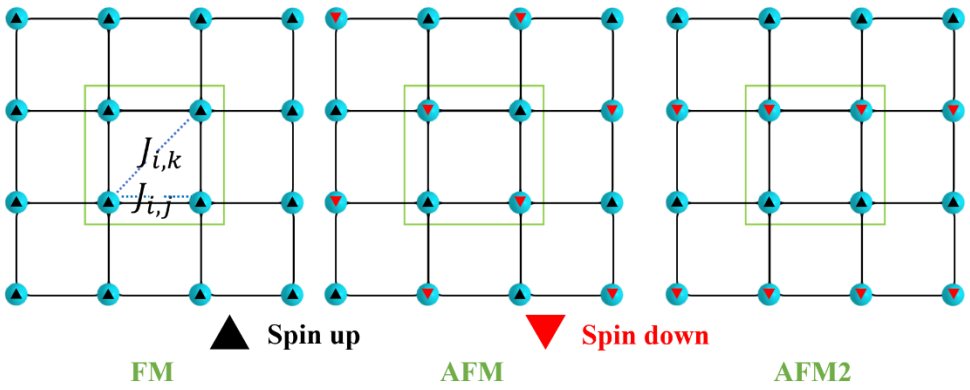
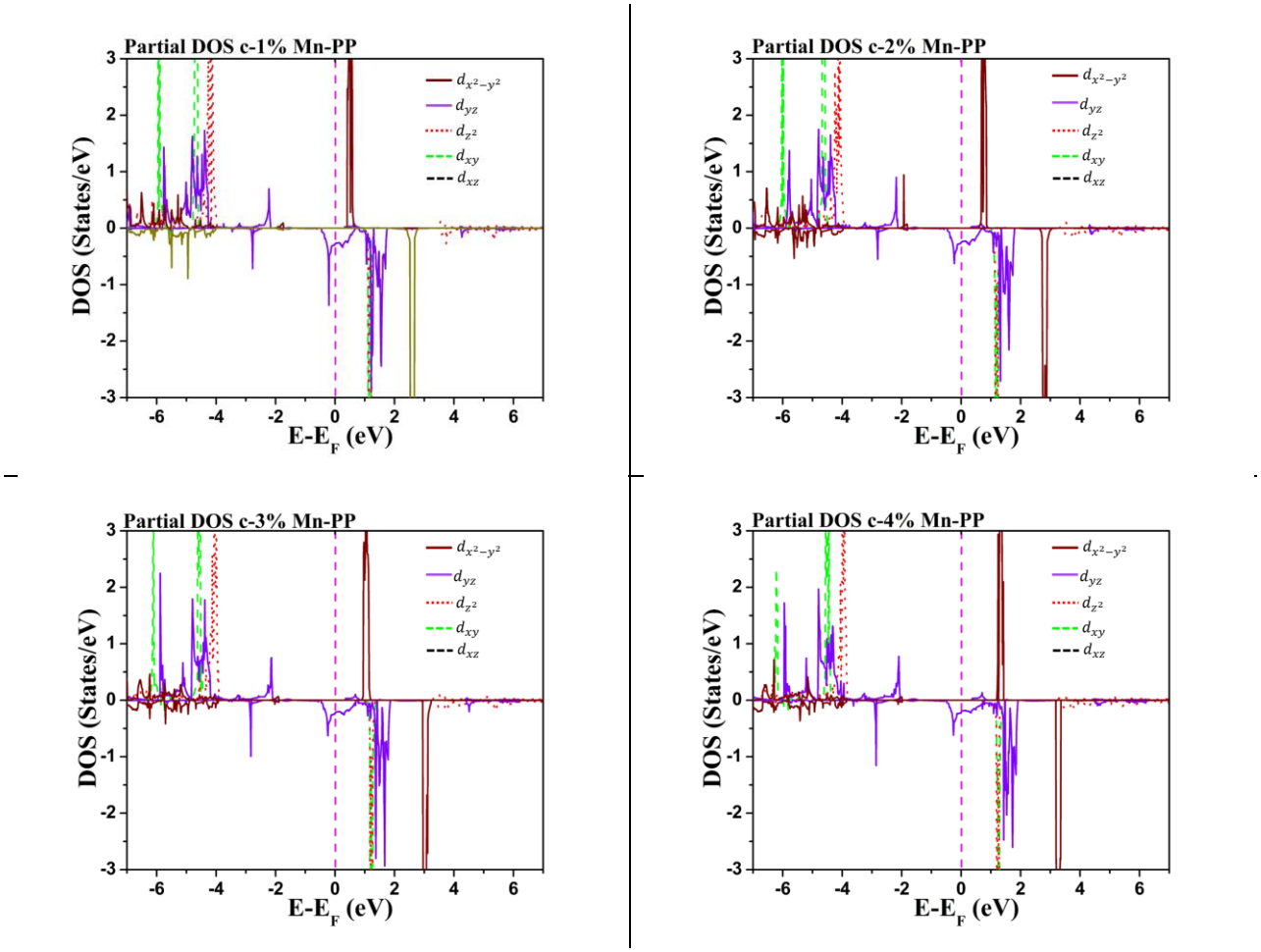


Figure S8. Ising model considering both nearest and next-nearest exchange interactions. Each lattice point represents a magnetic Mn atom.



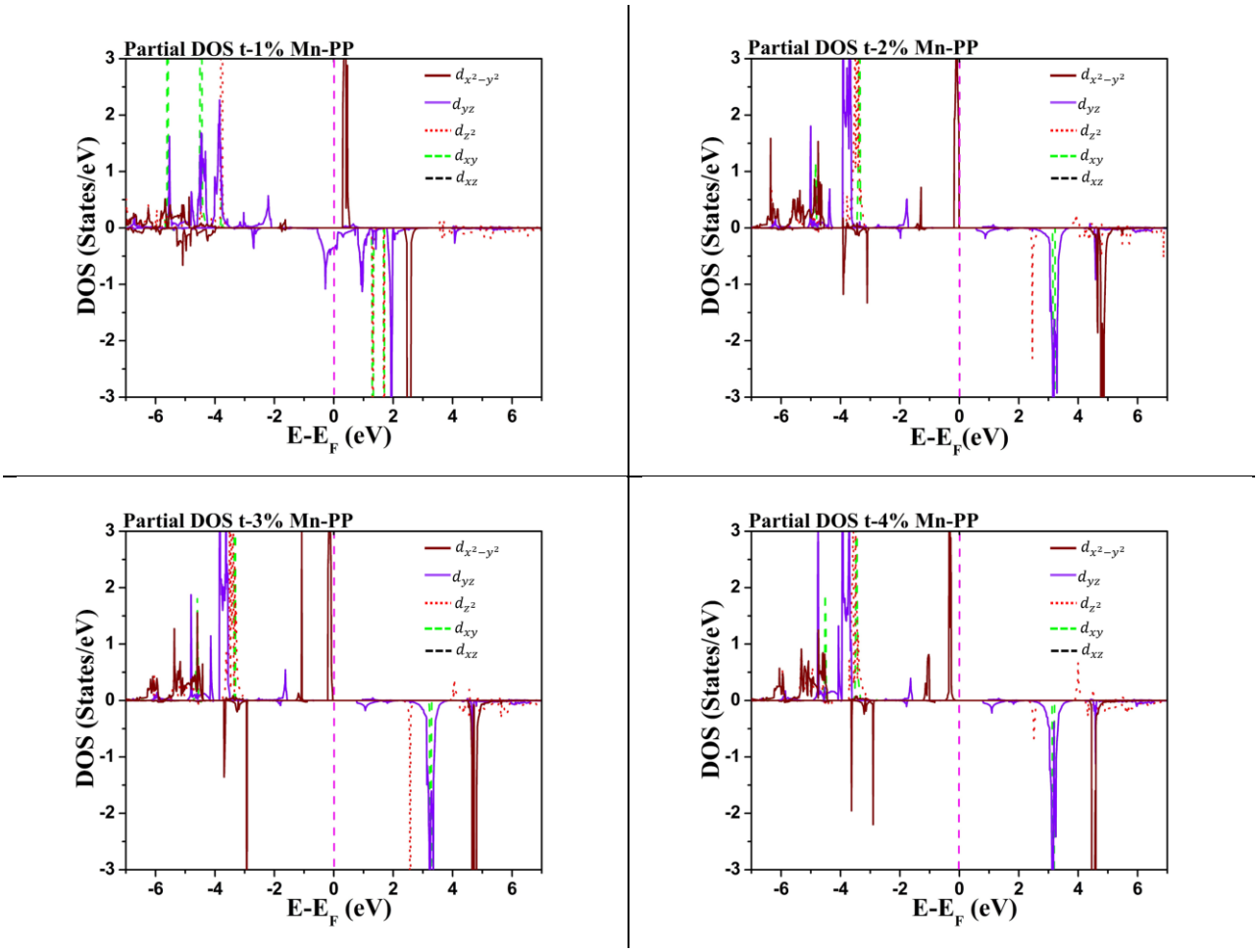


Figure S9. Partial DOS Mn-PP under compressive and tensile strain.

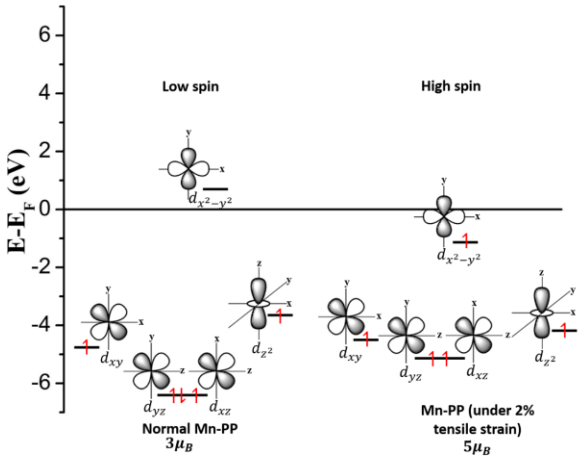


Figure S10. Qualitative description of d-orbitals and magnetic moments under normal and tensile (2%) strain conditions (GGA + U approach).

Table S3: Onsite Spin-orbit coupling energy for Mn-PP (atom resolved) under normal condition as well as biaxial strain (where T represents tensile strain and C as Compressive).

		Unstrained	C-4%	C-3%	C-2%	C-1%	T-1%	T-2%	T-3%	T-4%
E_{soc}	001	−0.0127509	−0.0031846	−0.0204375	−0.0162915	−0.0140363	−0.0130289	−0.0304598	−0.0071021	−0.0069149
	100	−0.0096328	−0.0018703	−0.0180670	−0.0138112	−0.0112889	−0.0093012	−0.0157078	−0.0056189	−0.0054952
	$diff_{001-100}$	−0.0031181	−0.0013143	−0.0023705	−0.0024803	−0.0027474	−0.0037277	−0.014752	−0.0014832	−0.0014197

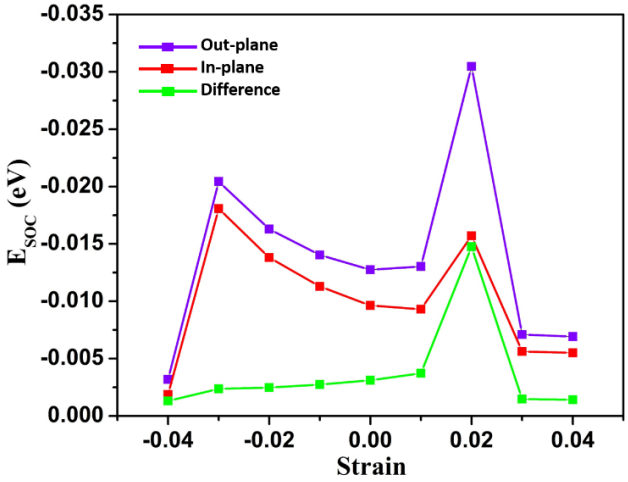


Figure S11. Variation of E_{SOC} under the strain for perpendicular (out-plane) and parallel (in-plane) direction of Mn-PP.

References

1. S. Deng, L. Wang, T. Hou, and Y. Li, *J. Phys. Chem. C*, 2015, **119**, 28783−28788.