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Supporting Information

Dramatic Magnetic Phase Designing in Phosphorene

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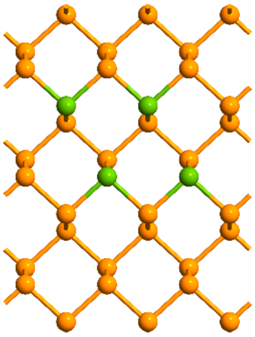
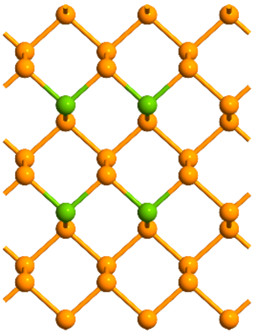
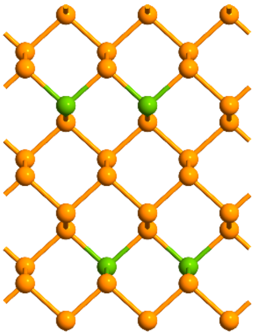
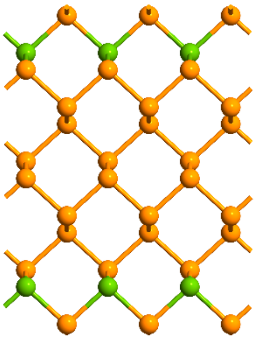
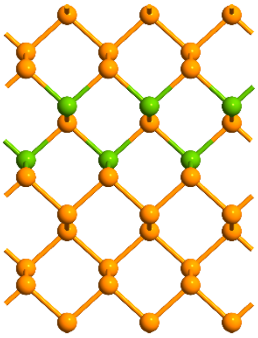
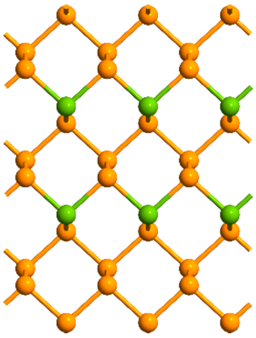
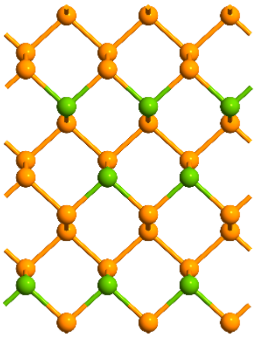
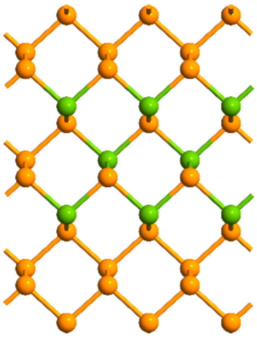
Result and Discussion

S1. Additional Doping Configurations

In addition to the configuration mentioned in Fig. 1, several additional doping configurations were constructed at each doping level as indicated in the Table S1. For each of the configurations, various FM and AFM arrangements were designed in a manner as mentioned in the main article.

Table S1. Doping configurations in phosphorene layer at different doping concentrations

Doping level (%)	**Old Configuration**	**New Configurations**	
	Configuration 0	**Configuration 1**	**Configuration 2**
11.1			
16.7			
22.2			

The energies of these new configurations (configuration 1 and configuration 2) were estimated in various FM and AFM configurations and the differences between them has been listed in Table S2 for Mn-doping.

Table S2. Energy difference $\Delta E = (E_{FM} - E_{AFM})$ for Mn-doping in various doping concentrations.

Doping level (%)	**$\Delta E = (E_{FM} - E_{AFM})$ in meV**	
	Configuration 1	**Configuration 2**
11.1	7.892 (AFM)	-16.918 (FM)
16.7	284.076 (AFM)	-25.894 (FM)
22.2	133.475 (AFM)	

The results indicate that the nature of ground state in configuration 0 and configuration 1 is AFM, while for configuration 2; it shows a FM state for 11.1% and 16.7% doping concentrations. At 22.2% doping level, the ground state is AFM as also observed earlier in Configuration 0.

S2. Energy difference calculation using GGA+U

To include the effect of strong electron correlation in 3d block elements, the Hubbard U term is a useful quantity to consider. Here, we have considered U = 2.5 eV for our calculations as also used earlier (**New Journal of Physics**, 12, 053012, 2010) and the results obtained from it are listed in Table S3.

Table S3. Energy difference $\Delta E = (E_{FM} - E_{AFM})$ calculated with U=2.5 eV for different doping concentrations for doped phosphorene.

Dopants	**$\Delta E = (E_{FM} - E_{AFM})$ in meV for various doping levels (x%)**			
	x=5.5%	**x=11.1%**	**x=16.7%**	**x=22.2%**
Cr	140.26	-68.923	32.652	-196.992
Fe	299.266	533.944	393.888	522.375
Mn	-3.977	360.027	116.49	-20.592
V	27.107	31.928	189.345	-19.592

Table S4. Critical temperature estimated with U=2.5 eV for different doping concentrations in doped phosphorene

Dopants	**Critical temperature (K) for various doping levels (x%)**			
	x=5.5%	**x=11.1%**	**x=16.7%**	**x=22.2%**
Cr	542	133	42	190
Fe	1156	1031	507	504
Mn	15	695	150	20
V	104	61	243	19

S3. Energy difference calculation through addition of charge on the layer

It is not possible to introduce charge on a specific dopant atom using Quantum ATK explicitly. However, it is possible to change the charge state of the entire layer by a value q = ±ne, where e is the electronic charge and n is an integer ; which we have done for n = 0, 1, 2. We have estimated the energies of various FM and AFM configurations in each of these cases and the difference of the energy is given in Table S5. The Mn-doped phosphorene layer with impurity concentration of 11.1% is taken as a sample case for this job.

Table S5. Energy difference $\Delta E = (E_{FM} - E_{AFM})$ through charge addition on 11.1% Mn doped phosphorene

Charge (q)	$\boldsymbol{\Delta E = (E_{FM} - E_{AFM})}$ **in meV**
q=0e	360.027 (AFM)
q=+1e	303.368 (AFM)
q=+2e	319.71 (AFM)

It is observed that with the change in the charge state of the system, the nature of the magnetic ground state does not change. However, the ΔE values are not same and minor variation is observed with a change in q.

S4. Estimation of T_C from HOMO-LUMO gap

The critical temperature can be estimated from the electronic splitting of the spin-splitted molecular energy levels. The spin-splitted HOMO and LUMO levels estimated from the molecular energy spectrum of Mn-doped system at various doping levels is given below:

Table S6. The HOMO and LUMO levels at various Mn-doping concentration in Phosphorene

Doping level	**LUMO/eV**	**HOMO/eV**
5.5%	0.01	0
11.1%	0.13	-0.19
16.7%	0.08	-0.05
22.2%	0.12	-0.08

The energy difference and T_c estimated from this is given in Table S7.

Table S7. Energy difference (ΔE) and T_C obtained through spin splitted HOMO-LUMO gap.

Doping conc.(%)	$\boldsymbol{\Delta E\ (LUMO - HOMO)}$ **in meV**	$\mathbf{T_C}$ **(K)**
5.5%	10	39
11.1%	320	618
16.7%	130	167

22.2%	200	193

Table S8. Energy difference (ΔE) and T$_C$ obtained from the energies of FM and AFM configurations

Doping concentration (%)	$\Delta E\ (E_{FM} - E_{AFM})$ **in meV**	**T$_C$ (K)**
5.5%	6.33	24
11.1%	385.912	745
16.7%	237.141	305
22.2%	257.311	248

Comparing between Table S7 and Table S8, one can see a similarity in the HOMO-LUMO gap and the value of T$_c$ estimated between the two approaches with some differences in specific cases.

S5. Projected Density of States (PDOS) analysis

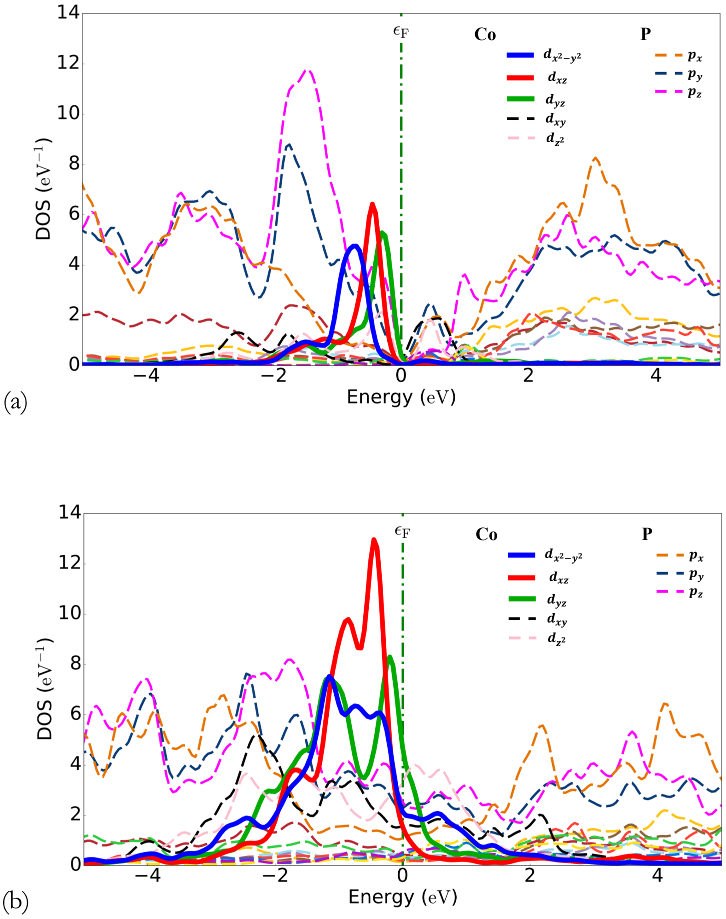


Figure S5: The projected density of states for Phosphorene doped with Mn at (a) 5.5% and (b) 22.2%.