Electronic Supplementary Material (ESI) for Nanoscale Advances.

Electronic Supplementary Information

Antiferromagnetic spin ordering in two-dimensional honeycomb lattice of SiP_3

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Details of VASP (Vienna Ab-initio Simulations Package) Calculations:

We use projector-augmented wave as implemented within VASP [1-4]. The exchange and correlation functional has been approximated with Perdew-Burke-Ernzerhof (PBE) scheme within generalized gradient approximation (GGA). An energy cutoff of 400 eV is considered with 12×12×1 Monkhorst-Pack k-point grid. The structural optimization is performed with a force tolerance of 0.01 eV/Å on each atom and the electronic energy convergence threshold is considered as 10^{-8} eV. A vacuum of 15Å is created in the non-periodic direction to avoid the interactions between adjacent unit cells.

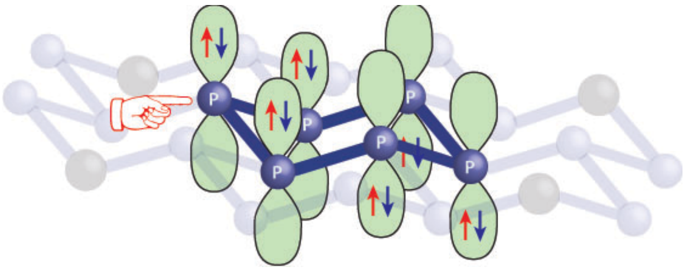
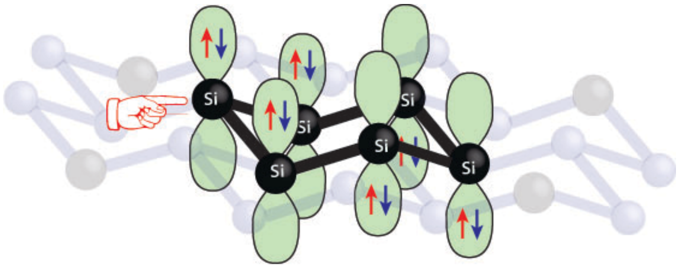
Table S1: The structural parameters of XP_3 systems: lattice constants of hexagonal unit cell (b_1), the bond-lengths of P-P (a) and P-X (b), $\angle P$-P-P (θ_1) and $\angle P$-P-X (θ_2) and out-of plane buckling parameters $\Delta_{z\,(P\text{-}P)}$ and $\Delta_{z\,(P\text{-}X)}$. The schematic representations of these parameters are shown in Fig.1(c) in the main manuscript. Note that, the lengths and the angles are in Å and degree, respectively. ***All these structural parameters are obtained from SIESTA calculations using the localized orbital basis.***

System	b_1	a	b	$\Delta_{z\,(P\text{-}P)}$	$\Delta_{z\,(P\text{-}X)}$	θ_1	θ_2
Pristine Blue P (2 X 2)	**6.65**	**2.31**	**2.31**	**1.28**	**1.28**	**92.22**	**92.22**
CP_3	6.299	2.33	1.81	1.41	0.34	87.41	106.09
SiP_3	**6.926**	**2.30**	**2.30**	**1.287**	**0.983**	**91.78**	**97.92**
GeP_3	6.996	2.22	2.51	0.769	1.567	108.65	98.57
SnP_3	7.157	2.22	2.71	0.723	1.798	109.9	97.97

Table S2: The structural parameters of XP_3 systems: lattice constants of hexagonal unit cell (b_1), the bond-lengths of P-P (a) and P-X (b), $\angle P$-P-P (θ_1) and $\angle P$-P-X (θ_2) and out-of plane buckling parameters $\Delta_{z\,(P\text{-}P)}$ and $\Delta_{z\,(P\text{-}X)}$. The schematic representations of these parameters are shown in Fig.1(c) in the main manuscript. Note that, the lengths and the angles are in Å and degree, respectively. ***All these structural parameters are obtained from VASP calculations using the plane wave basis.***

System	b_1	a	b	$\Delta_{z\,(P\text{-}P)}$	$\Delta_{z\,(P\text{-}X)}$	θ_1	θ_2
Pristine Blue P (2 X 2)	**6.55**	**2.26**	**2.26**	**1.24**	**1.24**	**92.9**	**92.9**
CP_3	6.25	2.29	1.78	1.34	0.33	89.19	106.78
SiP_3	**6.84**	**2.25**	**2.28**	**1.26**	**0.94**	**91.82**	**98.50**
GeP_3	6.96	2.17	2.50	0.71	1.55	109.70	99.60
SnP_3	7.15	2.17	2.71	0.66	1.75	111.01	99.49

Table S3: Orbital occupancy and hybridization analysis of the marked atoms in pristine blue phosphorene, silicene and SiP$_3$ systems. The schematic structures along with the spin distribution are given in the first column. The relative sizes of the arrows indicate the magnitude of the spin moments. The numbers of electrons participating in sp^2 hybridization are given in second column. The π-electrons with up and down-spin polarizations for the marked atoms are shown in highlighted columns. ***All these numerical values are obtained from SIESTA calculations using the localized orbital basis.*** Note that, the hybridization of Si and P atoms in SiP$_3$ remains unaltered as compared to that in pristine silicene and blue phosphorene. There is a transfer of down spins from marked P atom to marked Si atom in SiP$_3$, resulting in higher local up-spin density on P atom.

System	*sp^2 $(s + p_x + p_y)$*	*π (p_z)*	
		Up spin (↑)	**Down spin (↓)**
Blue Phosphorene 	3.466	0.614	0.614
Silicene 	2.966	0.387	0.387
SiP$_3$	**P** **3.475**	**0.614**	**0.573**

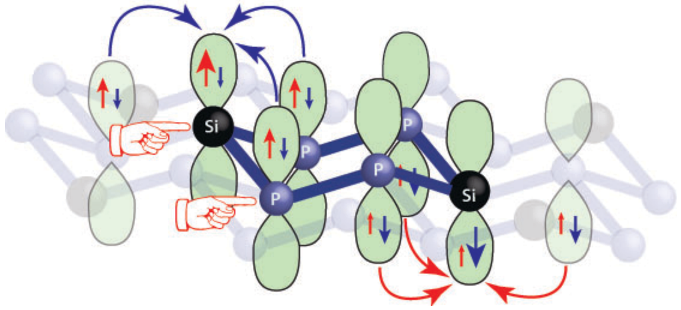
	**Si** **2.887**	**0.631**	**0.242**

Table S4: The total energy per atom (in *eV*) of all XP_3 systems in different ground states. NM, FM and AFM denote the non-magnetic, ferromagnetic and antiferromagnetic ground states, respectively. The FM and AFM energies are same as the NM energies in all the systems except SiP_3 with no local spin-polarization. It can be concluded that, these systems do not gain any stability with explicit consideration of spins and therefore the entries in the tables are kept blank. ***Note that, these energies are obtained from SIESTA calculations using the localized orbital basis.***

System	**NM**	**FM**	**AFM**
Pristine Blue P	-4.038	~	~
CP_3	-4.732	~	~
SiP_3	-4.137	-4.138	**-4.146**
GeP_3	-3.992	~	~
SnP_3	-4.386	~	~

Table S5: The total energy per atom (in *eV*) of all XP_3 systems in different ground states. NM, FM and AFM denote the non-magnetic, ferromagnetic and antiferromagnetic ground states, respectively. The FM and AFM energies are same as the NM energies in all the systems except SiP_3 with no local spin-polarization and that is why the entries are left blank. ***Note that, these energies are obtained from VASP calculations using the plane wave basis.***

System	NM	FM	AFM
Pristine Blue P	-3.476	~	~
CP_3	-4.151	~	~
SiP_3	-3.5070	-3.5087	-3.5089
GeP_3	-3.341	~	~
SnP_3	-3.258	~	~

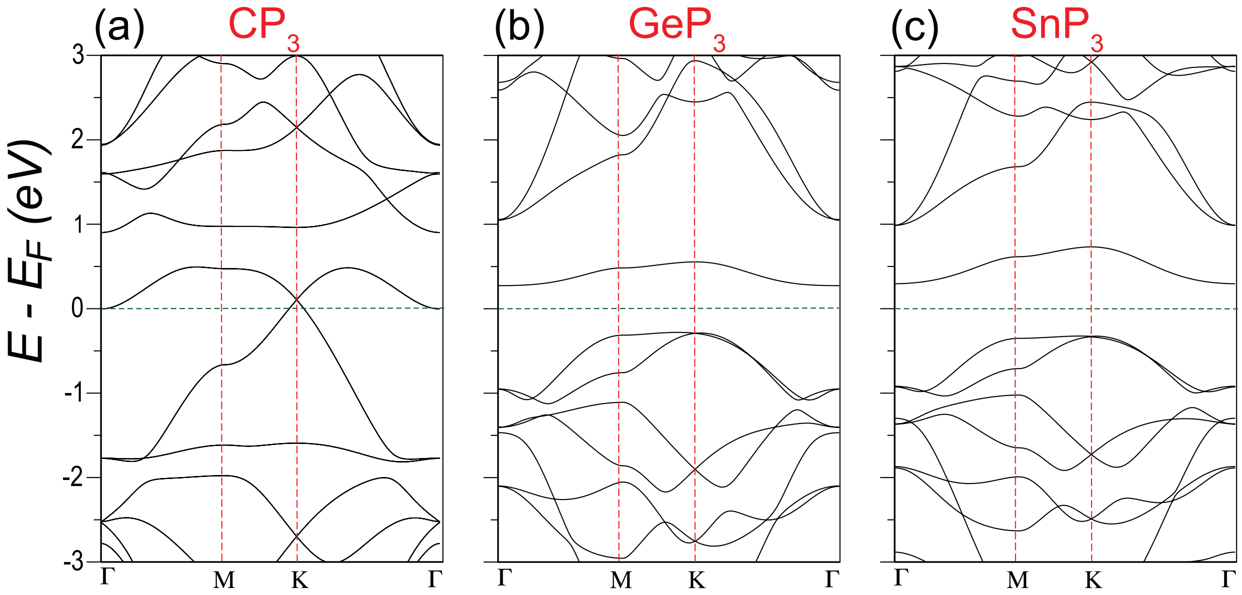


Figure S1: The band structures of (a) CP_3, (b) GeP_3 and (c) SnP_3 systems in nonmagnetic ground state, as obtained from calculations considering localized orbital basis using SIESTA. The vertical (horizontal) lines show the high-symmetric points (Fermi energy). The band structures remain unchanged for initial guesses of FM and AFM spin alignments.

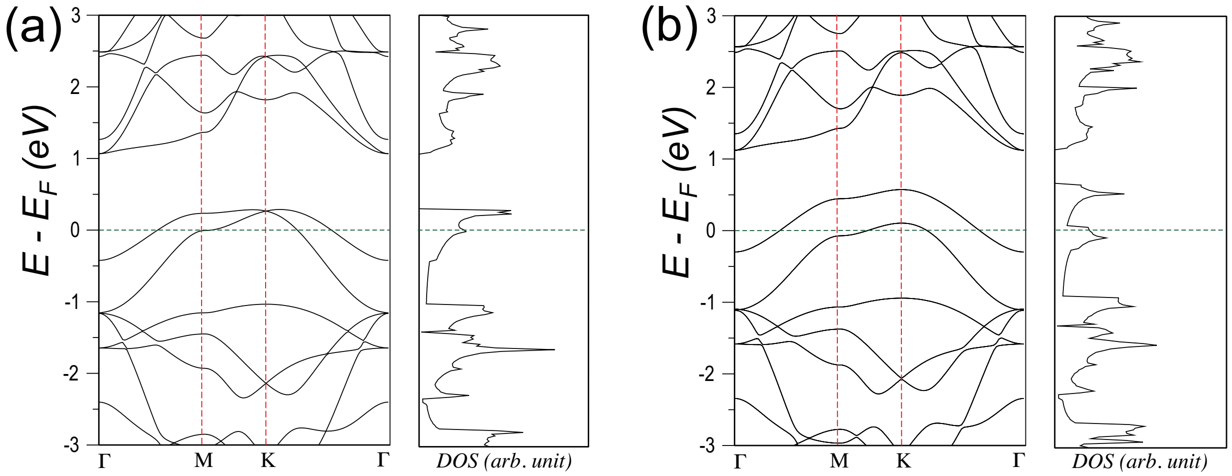


Figure S2: The band structures and density of states (DOS) of SiP_3 system in (a) nonmagnetic (NM) and (b) antiferromagnetic (AFM) ground states, as obtained from calculations considering plane wave basis using VASP. The vertical (horizontal) lines show the high-symmetric points (Fermi energy). The AFM ground state shows dispersive bands at Fermi energy and consequent metallic behavior, unlike the small semiconducting gap obtained from the SIESTA calculations using localized basis (see Fig.3(b) in main manuscript).

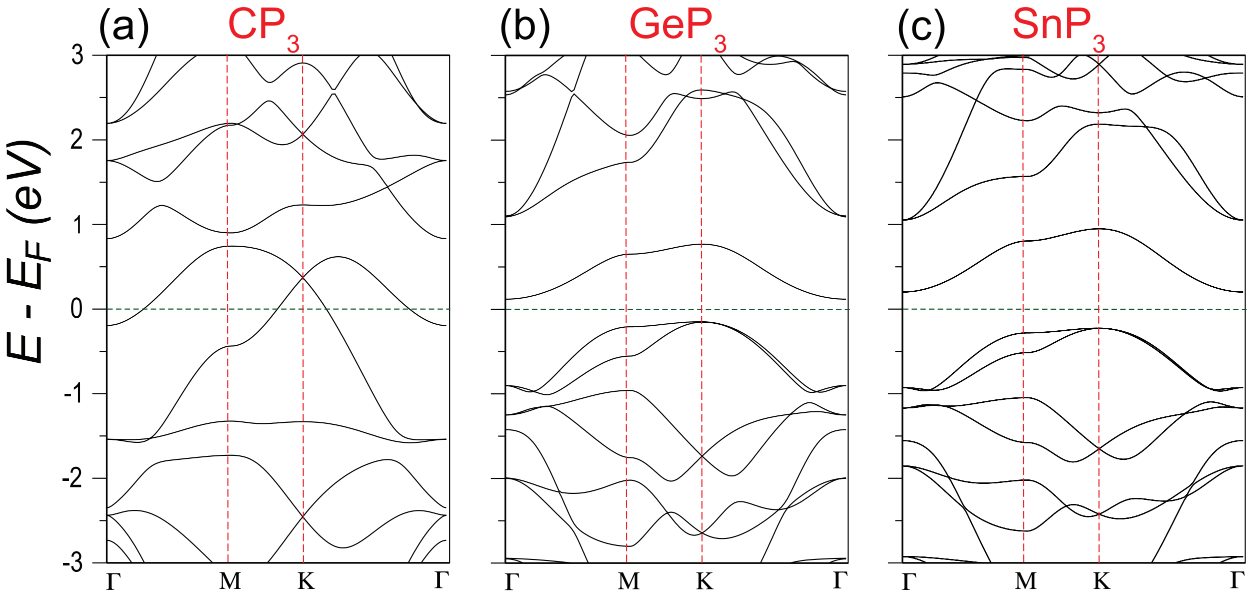


Figure S3: The band structures of (a) CP_3, (b) GeP_3 and (c) SnP_3 systems in nonmagnetic ground state, as obtained from calculations considering plane wave basis using VASP. The vertical (horizontal) lines show the high-symmetric points (Fermi energy). The band structures remain unchanged for initial guesses of FM and AFM spin alignments.

References:

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2. G. Kresse and J. Furthmüller, Efficient iterative schmes for ab initio total-energy calculations using plane-wave basis set. *Phys. Rev. B*, 1996, **54**, 11169
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