

*Supplementary Information*

## 2D nonsymmorphic Dirac semimetal in chemically modified group-VA Monolayer with Black Phosphorene structure

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### I. Calculated lattice parameter and formation energy

The geometric parameters obtained from DFT calculations for pristine and functionalized group VA elements with 2D phosphorene structure are tabulated in Table SI. The thermodynamic stability of the functionalized group VA phosphorene structure was verified by calculating the per-atom formation energy,

$$E_F = E_D - (E_P + E_M),$$

where  $E_D$ ,  $E_P$ , and  $E_M$  are the total energies per atom of decorated group VA phosphorene structure, the pristine group VA phosphorene, and  $X_2$  ( $X=H, F, Cl$  and  $Br$ ) molecule, respectively. The formation energy data of decorated group VA phosphorene structure are presented in Table. SII. The functionalized structure with halide atoms ( $F, Cl$  and  $Br$ ) has negative  $E_F$ , indicating a higher thermodynamic stability relative to their elemental reservoirs.

TABLE SI: Lattice parameters of pristine group VA phosphorene structure and atomic decorated structure.

|    | pristine   | H                | F                | Cl               | Br |
|----|------------|------------------|------------------|------------------|----|
| P  | a = 4.62 Å | 4.79<br>(3.68%)  | 4.47<br>(-3.25%) | -                | -  |
|    | b = 3.3 Å  | 3.26<br>(-1.21%) | 3.31<br>(0.30%)  |                  |    |
|    |            |                  |                  |                  |    |
| As | 4.75       | 4.62<br>(-2.74%) | 4.72<br>(-0.63%) | 6.17<br>(29.89%) | -  |
|    | 3.69       | 3.63<br>(-1.63%) | 3.66<br>(-0.81%) | 3.6<br>(-2.44%)  |    |
|    |            |                  |                  |                  |    |

|    |      |                  |                  |                  |                  |
|----|------|------------------|------------------|------------------|------------------|
| Sb | 4.9  | 4.72<br>(-3.67%) | 4.81<br>(-1.84%) | 5.77<br>(17.76%) | 6.59<br>(34.49%) |
|    | 4.36 | 4.23<br>(-2.98%) | 4.25<br>(-2.52%) | 4.17<br>(-4.36%) | 4.15<br>(-4.82%) |
| Bi | 4.98 | 4.99<br>(0.20%)  | 5.00<br>(0.40%)  | 5.53<br>(11.04%) | 7.23<br>(45.18%) |
|    | 4.6  | 4.52<br>(-1.74%) | 4.55<br>(-1.09%) | 4.5<br>(-2.17%)  | 4.43<br>(-3.70%) |

TABLE SII: Calculated formation energy ( $E_F$ ) for functionalized group VA phosphorene structure.

|    | H       | F     | Cl    | Br    |
|----|---------|-------|-------|-------|
| P  | 0.14 eV | -0.76 |       |       |
| As | 0.18    | -0.67 | -0.14 |       |
| Sb | 0.23    | -0.75 | -0.20 | -0.14 |
| Bi | 0.28    | -0.66 | -0.20 | -0.16 |

## II. Phonon band structure

The phonon dispersion of P-F, As-F, Sb-F, and Bi-F are displayed in Fig. S1, which shows their dynamical stability. The P-F and As-F structure has no imaginary frequency along all momenta, which indicates that this structure is dynamically stable. We note experimentally Sb and Bi phosphorene structures have been synthesized on suitable substrates, although pristine Sb and Bi phosphorene structures show imaginary frequency. While Sb-F and Bi-F structures show imaginary frequency, it is possible to synthesize Sb-F and Bi-F structure. One interesting feature in phonon dispersion is phononic Weyl nodal line structure. At the Y and M point, there is a single band crossing unlike the electronic topological Dirac nodal lines. Along the high-symmetry Y-M line, there are double-degenerate phonon bands that forms phononic Weyl nodal line structure [Fig. S1(a)-(b)].

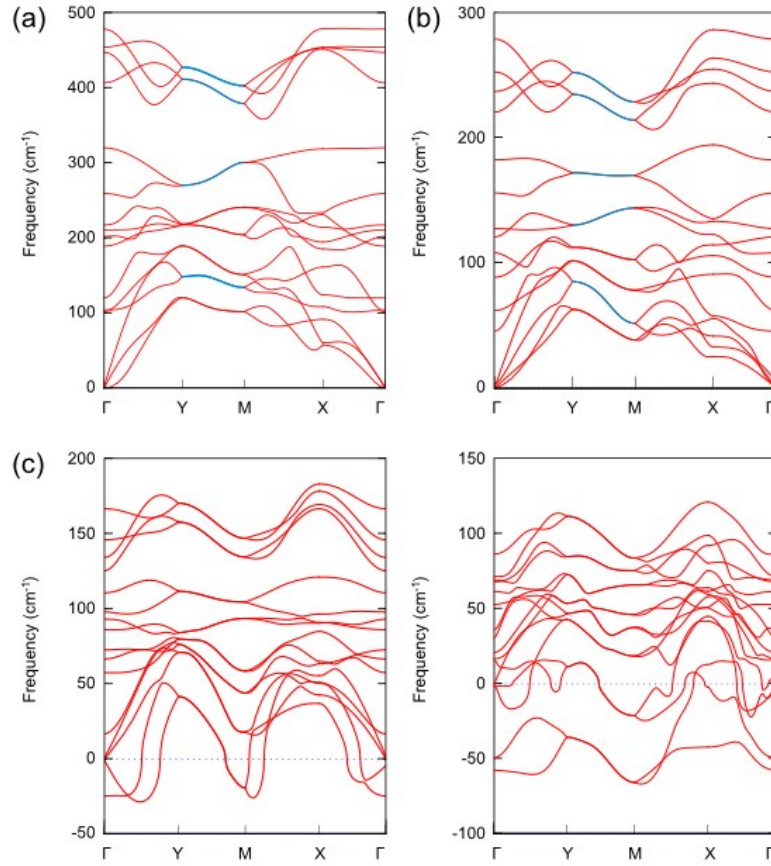


Figure S1. Calculated phonon band structures for (a) P-F, (b) As-F, (c) Sb-F and (d) Bi-F, respectively. Blue thick bands correspond to double-degenerate phononic Weyl nodal line.

### III. Tight binding model

The tight-binding Hamiltonian is represented as a 16x16 matrix with atomic basis of  $3s$ ,  $3p_x$ ,  $3p_y$  and  $3p_z$  at A, B, A' and B' sites in Fig 1(a) and Fig S2.

$$H(k) = \begin{pmatrix} M_0 & M_1 & M_2 & 0 \\ M_1^\dagger & M_0 & 0 & M_3 \\ M_2^\dagger & 0 & M_0 & M_1^\dagger \\ 0 & M_3^\dagger & M_1 & M_0 \end{pmatrix}$$

The diagonal 4x4 matrix expresses the onsite energies of four atomic sites with

$$M_0 = \begin{pmatrix} \varepsilon_s & 0 & 0 & 0 \\ 0 & \varepsilon_p & 0 & 0 \\ 0 & 0 & \varepsilon_p & 0 \\ 0 & 0 & 0 & \varepsilon_p \end{pmatrix}.$$

Here,  $\varepsilon_s = -9.10$  eV and  $\varepsilon_p = -1.33$  eV are the energy levels of  $3s$  and  $3p$  orbitals, respectively. The nearest-neighbor interaction between A (B') and B (A') and the next-nearest-neighbor interaction

between A (B) and A' (B') are denoted by the matrices  $M_{i=1,2,3}$ , respectively.

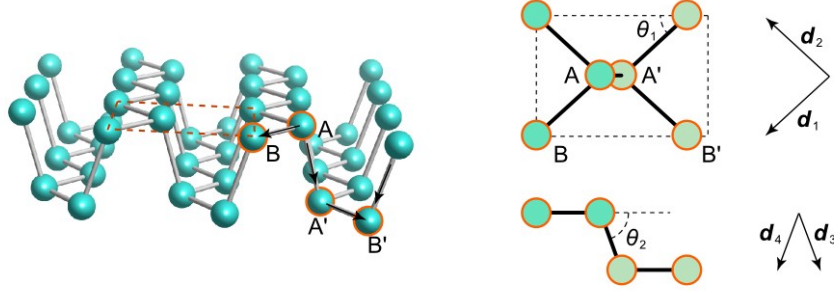


Figure S2. The crystal structure and unit cell of phosphorene.

The coupling matrices  $M_{i=1,2,3}$  are expressed in detail below.

$$M_1 = \begin{pmatrix} m_{111} & m_{112} & m_{113} & 0 \\ -m_{112} & m_{122} & m_{123} & 0 \\ -m_{113} & m_{123} & m_{133} & 0 \\ 0 & 0 & 0 & m_{144} \end{pmatrix}$$

where,  $m_{111} = t_{1ss\sigma} (e^{i\mathbf{k} \cdot \mathbf{r}_d^1} + e^{i\mathbf{k} \cdot \mathbf{r}_d^2})$ ,  $m_{112} = t_{1sp\sigma} \cos \theta_1 (e^{i\mathbf{k} \cdot \mathbf{r}_d^1} + e^{i\mathbf{k} \cdot \mathbf{r}_d^2})$ ,  $m_{113} = t_{1sp\sigma} \sin \theta_1 (e^{i\mathbf{k} \cdot \mathbf{r}_d^1} - e^{i\mathbf{k} \cdot \mathbf{r}_d^2})$ ,

$m_{122} = t_{1pp\sigma} \cos^2 \theta_1 (e^{i\mathbf{k} \cdot \mathbf{r}_d^1} + e^{i\mathbf{k} \cdot \mathbf{r}_d^2}) + t_{1pp\pi} \sin^2 \theta_1 (e^{i\mathbf{k} \cdot \mathbf{r}_d^1} + e^{i\mathbf{k} \cdot \mathbf{r}_d^2})$ ,

$m_{123} = t_{1pp\sigma} \cos \theta_1 \sin \theta_1 (e^{i\mathbf{k} \cdot \mathbf{r}_d^1} - e^{i\mathbf{k} \cdot \mathbf{r}_d^2}) - t_{1pp\pi} \cos \theta_1 \sin \theta_1 (e^{i\mathbf{k} \cdot \mathbf{r}_d^1} + e^{i\mathbf{k} \cdot \mathbf{r}_d^2})$ ,

$m_{133} = t_{1pp\sigma} \sin^2 \theta_1 (e^{i\mathbf{k} \cdot \mathbf{r}_d^1} + e^{i\mathbf{k} \cdot \mathbf{r}_d^2}) + t_{1pp\pi} \cos^2 \theta_1 (e^{i\mathbf{k} \cdot \mathbf{r}_d^1} + e^{i\mathbf{k} \cdot \mathbf{r}_d^2})$ ,  $m_{144} = t_{1pp\pi} (e^{i\mathbf{k} \cdot \mathbf{r}_d^1} + e^{i\mathbf{k} \cdot \mathbf{r}_d^2})$ .

$$M_2 = \begin{pmatrix} m_{211} & m_{212} & 0 & m_{214} \\ -m_{212} & m_{222} & 0 & m_{224} \\ 0 & 0 & m_{233} & 0 \\ -m_{214} & m_{224} & 0 & m_{244} \end{pmatrix}$$

where,  $m_{211} = t_{2ss\sigma} e^{i\mathbf{k} \cdot \mathbf{r}_d^3}$ ,  $m_{212} = -t_{2sp\sigma} \cos \theta_2 e^{i\mathbf{k} \cdot \mathbf{r}_d^3}$ ,  $m_{214} = -t_{2sp\sigma} \sin \theta_2 e^{i\mathbf{k} \cdot \mathbf{r}_d^3}$ ,

$m_{222} = t_{2pp\sigma} \cos^2 \theta_2 e^{i\mathbf{k} \cdot \mathbf{r}_d^3} + t_{2pp\pi} \sin^2 \theta_2 e^{i\mathbf{k} \cdot \mathbf{r}_d^3}$ ,  $m_{224} = t_{2pp\sigma} \cos \theta_2 \sin \theta_2 e^{i\mathbf{k} \cdot \mathbf{r}_d^3} - t_{2pp\pi} \cos \theta_2 \sin \theta_2 e^{i\mathbf{k} \cdot \mathbf{r}_d^3}$ ,

$m_{233} = t_{2pp\pi} e^{i\mathbf{k} \cdot \mathbf{r}_d^3}$ ,  $m_{244} = t_{2pp\sigma} \sin^2 \theta_2 e^{i\mathbf{k} \cdot \mathbf{r}_d^3} + t_{2pp\pi} \cos^2 \theta_2 e^{i\mathbf{k} \cdot \mathbf{r}_d^3}$ .

$$M_3 = \begin{pmatrix} m_{311} & m_{312} & 0 & m_{314} \\ -m_{312} & m_{322} & 0 & m_{324} \\ 0 & 0 & m_{333} & 0 \\ -m_{314} & m_{324} & 0 & m_{344} \end{pmatrix}$$

$$\begin{aligned} m_{311} &= t_{2ss\sigma} e^{i\mathbf{k} \cdot \mathbf{d}_4}, \quad m_{312} = t_{2sp\sigma} \cos \theta_2 e^{i\mathbf{k} \cdot \mathbf{d}_4}, \quad m_{314} = -t_{2sp\sigma} \sin \theta_2 e^{i\mathbf{k} \cdot \mathbf{d}_4}, \\ m_{322} &= t_{2pp\sigma} \cos^2 \theta_2 e^{i\mathbf{k} \cdot \mathbf{d}_4} + t_{2pp\pi} \sin^2 \theta_2 e^{i\mathbf{k} \cdot \mathbf{d}_4}, \\ m_{324} &= -t_{2pp\sigma} \cos \theta_2 \sin \theta_2 e^{i\mathbf{k} \cdot \mathbf{d}_4} + t_{1pp\pi} \cos \theta_2 \sin \theta_2 e^{i\mathbf{k} \cdot \mathbf{d}_4}, \quad m_{333} = t_{2pp\pi} e^{i\mathbf{k} \cdot \mathbf{d}_4}, \\ m_{344} &= t_{2pp\sigma} \sin^2 \theta_2 e^{i\mathbf{k} \cdot \mathbf{d}_4} + t_{2pp\pi} \cos^2 \theta_2 e^{i\mathbf{k} \cdot \mathbf{d}_4}. \end{aligned}$$

Here,  $t_{iss\sigma}$ ,  $t_{isp\sigma}$ ,  $t_{ipp\sigma}$ , and  $t_{ipp\pi}$  ( $i=1,2$ ) are hopping parameters. The band dispersion of monolayer phosphorene are shown in Fig. S3. The tight-binding (TB) model shows good agreement with the DFT calculation. For the functionalized phosphorene structure, we have tuned the  $p_z$ -orbital-involved hopping parameters for interlayer interaction. One can define the hopping strength  $\kappa$  ( $= t'_i/t_i$ ,  $i=sp\sigma, pp\sigma, pp\pi$ ) between  $p_z$  orbital of A (B) site and  $s, p_x, p_y, p_z$  orbitals of A'(B') site, and vice versa.

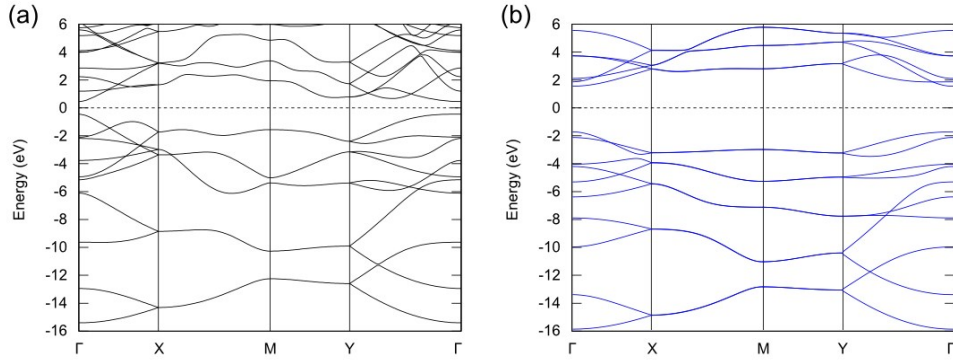


Figure S3. The calculated band structures using (a) DFT calculation and (b) TB model with hopping parameters  $t_{1ss\sigma}=-1.95$  eV,  $t_{1sp\sigma}=2.56$  eV,  $t_{1pp\sigma}=4.50$  eV,  $t_{1pp\pi}=-1.13$  eV,  $t_{2ss\sigma}=-1.88$  eV,  $t_{2sp\sigma}=2.47$  eV,  $t_{2pp\sigma}=4.35$  eV, and  $t_{2pp\pi}=-1.09$  eV.

#### IV. Plasmon excitation

As an potential application of DNL, its collective plasmon excitation is calculated. Using the Lindhad function, the non-interacting polarization function

$$\Pi(\mathbf{q}, \omega) = -\frac{2}{(2\pi)^2} \int_{BZ} d^2k \sum_{l,l'} \left| \langle \mathbf{k}+\mathbf{q}, l' | e^{i\mathbf{q}\cdot\mathbf{r}} | \mathbf{k}, l \rangle \right|^2 \frac{f(E_{\mathbf{k},l}) - f(E_{\mathbf{k}+\mathbf{q},l'})}{E_{\mathbf{k},l} - E_{\mathbf{k}+\mathbf{q},l'} + \omega + i\delta},$$

where the integral is over the first Brillouin zone (BZ). A temperature  $T=300$  K in the Fermi-Dirac distribution function and an infinitesimal broadening  $\delta=1$  meV are used in our numerical calculation. Under the random phase approximation, the dielectric function is defined as

$$\varepsilon(\mathbf{q}, \omega) = 1 - V(\mathbf{q})\Pi(\mathbf{q}, \omega),$$

where  $V(\mathbf{q})=2\pi e^2/4\pi\epsilon_0\epsilon_r q$  is the Fourier component of the 2D Coulomb interaction.  $\epsilon_0$  and  $\epsilon_r$  are the vacuum and background relative dielectric constants, respectively. In order to compare with the experiments, it is more convenient to calculate the electron energy loss spectrum (EELS), whose broadened peaks indicate the plasmons,

$$\text{EELS} = -\text{Im} [1 / \varepsilon(\mathbf{q}, \omega)].$$

The EELS of the P-F is shown in Fig. S4. The plasmon excitation follows  $\omega \propto \sqrt{q}$  behavior in the small momentum region. Due to the anisotropic DNL band shape, the plasmon dispersion is an ellipse at each energy [Fig. S4(d)-(f)]. Interestingly, the anisotropy is still preserved for very small energy.

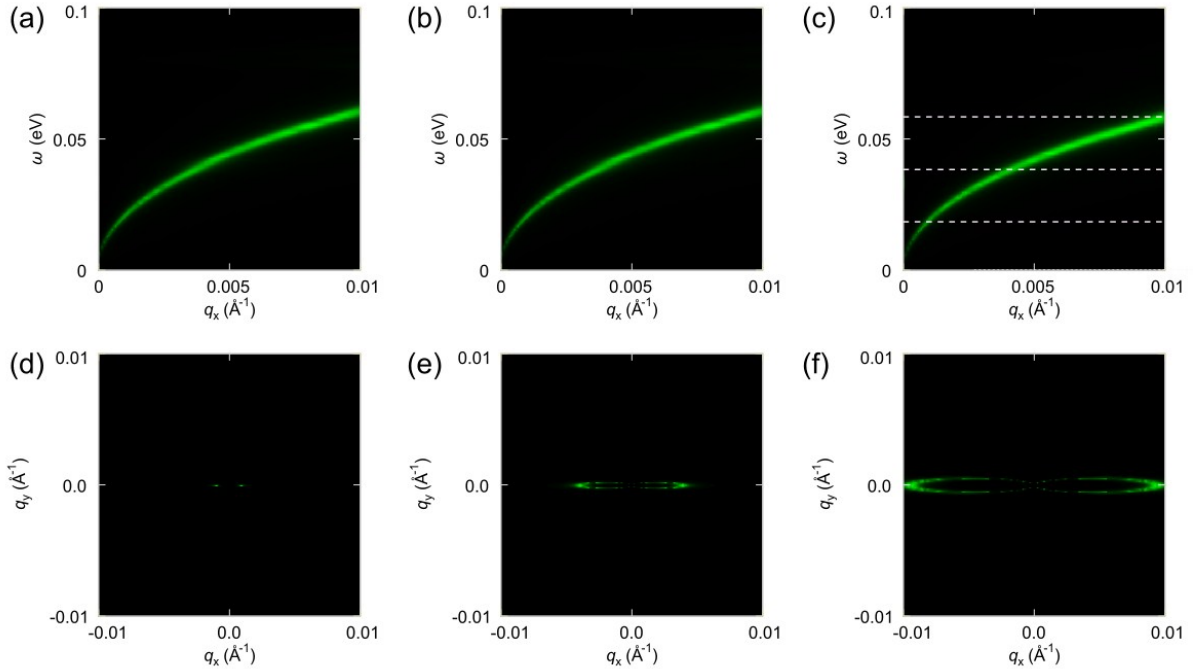


Figure S4. (a)-(c) EELS for doped Dirac band with  $E_F=0$  eV,  $E_F=0.05$  eV, and  $E_F=0.15$  eV, respectively. (d)-(f) are 2D momentum space plots of the EELS for (c) at different excitation energies 0.02 eV, 0.04 eV, and 0.06 eV, respectively.

## V. Band structure without SOC

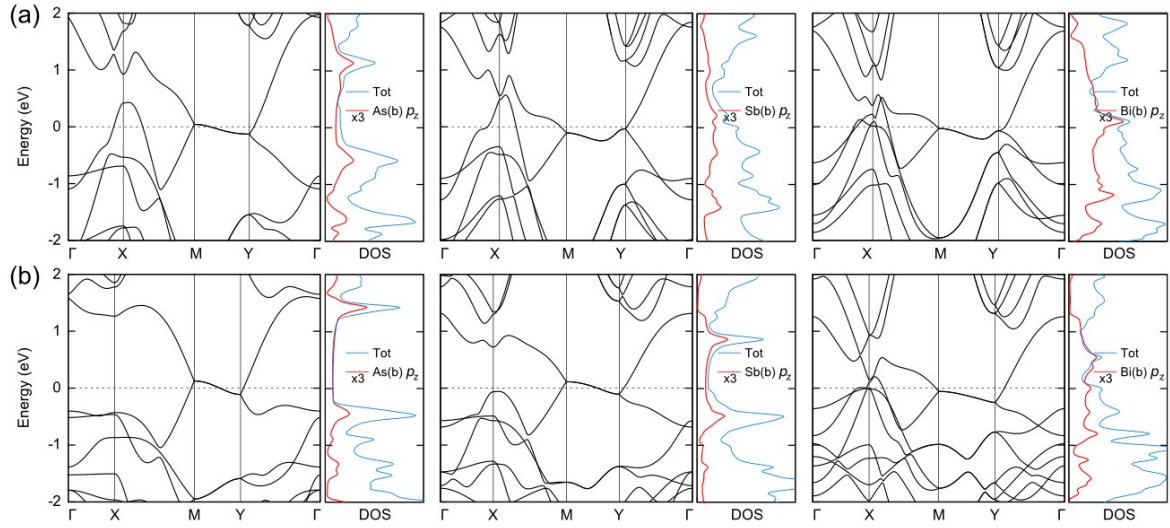


Figure S5. (a) The calculated band structure and density of states for As-F, Sb-F and Bi-F without SOC, respectively. (b) The calculated band structure and density of states for As-Cl, Sb-Cl and Bi-Cl without SOC, respectively.

## VI. The variation of DOS in Bi-F

The variation of DOS in Bi-F comes from additional contribution of  $p_z$  orbital states at the X point. Fig. S6. shows the  $p_z$  orbital resolved band structure for P-F and Bi-F structure. For P-F, the DNL states near Fermi level are contributed by  $p_z$  orbitals of bottom P layer. The Bi-F band structure also shows that the hourglass fermion states are dominated by Bi  $p_z$  orbitals in pristine side. On the other hand, there are additional contributions from the  $p_z$  orbital at X point. The Bi  $p_z$  orbital hybridize with  $p_{x,y}$  orbitals in other layer. Due to this contribution, the constant DOS feature is modulated for Bi-F case.

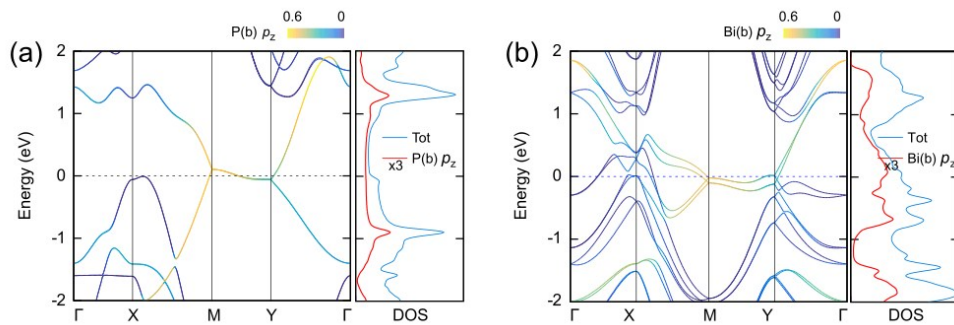


Figure S6. The band structure for (a) P-F and (b) Bi-F with the contribution of  $p_z$  orbital of atoms in pristine side.

## VII. The vdW heterostructure of As-F and BN sheet

For the further development of chemically modified 2D group VA puckered materials, one needs to find a benign substrate that provides stable mechanical support yet retains the Dirac semimetal properties. We calculate the electronic properties of vdW heterostructure of As-F and BN. For the vdW heterostructure, we choose the As-F structure for the small lattice mismatch ( $<3\%$ ) and supercell size. Fig. S7(a) shows the As-F/BN heterostructure. The calculated interlayer distance is  $3.58\text{\AA}$  which indicates that the interlayer interaction is vdW type. Fig. S7 (c),(d) show the band structure of As-F/BN heterostructure without and with SOC. The DNL structure is still preserved along the  $\Gamma$  to X directions. Due to the band folding effect, the original DNL structure along the Y to M directions appears along the  $\Gamma$  to X directions. With SOC, the DNL structure becomes Weyl nodal line similar to pristine case. Moreover, the DNL states are mainly contributed from the  $p_z$  orbitals of As atoms in the unsaturated layer [Fig. S7(b)].

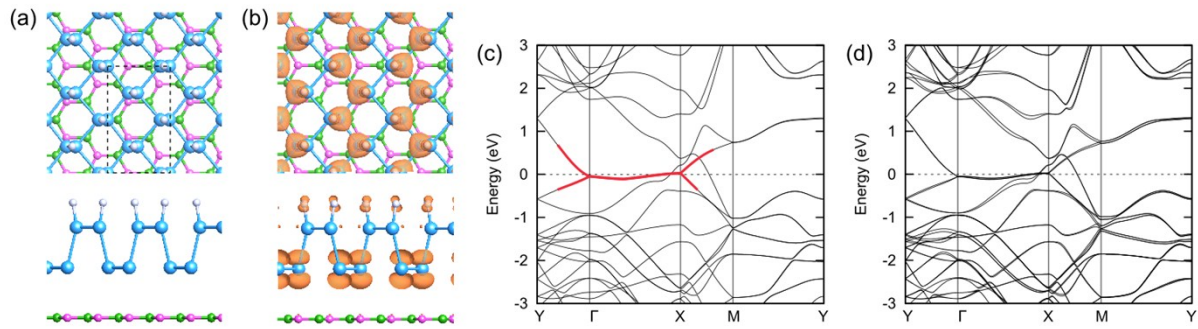


Figure S7. (a) Top and side view of the As-F/BN heterostructure. The As-F/BN structure is constructed by a  $1\times 2$  supercell of As-F and a  $\sqrt{3}\times 3$  supercell of BN. (b) The squared wave functions of the DNL states. (c),(d) Calculated band structure of the As-F/BN heterostructure without and with SOC, respectively.