Two-dimensional Dirac nodal-line semimetal against strong spin-orbit coupling in real materials

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Abstract: Symmetry is one of the conceptual pillars underlying fundamental understanding of electronic band structures of materials¹. Unique symmetries have boosts continuous discoveries of Dirac materials with intriguing electronic phases in the past decade²-⁶. A long-standing challenge in the community lies in searching for robust Dirac nodal line semimetals (DNLSs) in two-dimensional (2D) systems⁷-¹⁰, where the low-energy fermionic excitations along the four-fold degenerate Dirac nodal line (DNL) would essentially dominate the electrical properties of the 2D materials.
However, such four-fold degenerate lines are usually vulnerable to spin-orbit coupling (SOC)\textsuperscript{7-11}. A real 2D DNLS material, that shows robustness to SOC, is yet to be experimentally discovered or proved. Here, by combing molecular beam epitaxy growth on black phosphorus substrates (BP), scanning tunneling microscopy (STM) characterization, density functional theory (DFT) calculations and space group theory analysis, we reveal a solely symmetry dictated SOC-robust DNL in real 2D crystalline structures. A tri-atomic layers bismuth (3-ALs Bi) exhibits a unique structure, defining a non-symmorphic space group 1) protecting the four-fold degeneracy of the nodal line no matter SOC is present or not; 2) introducing linear dispersion relations at the vicinity of the nodal line. This guarantees the robust DNL electronic phase without any orbital and element dependence. With this inherent relation, we expect and theoretically prove the generality of the robust DNL in a series of 2D layers that are isostructural to 3-ALs Bi. This opens the door towards growth, exploration and utilization of intrinsic 2D DNL materials. In the 3-ALs Bi case, the DNL state is near the Fermi level (E\textsubscript{F}) and is rather neat that other trivial bands open a gap around the E\textsubscript{F}, making the 3-ALs Bi one of the “cleanest” DNL semimetal (DNLSs) ever proposed.
Condensed matter physics is witnessing a rapid expansion of materials with Dirac fermion low-energy excitations. The seemingly diverse materials share the similarity of possessing four-fold degenerate Dirac nodes normally protected by certain crystalline symmetries except at 3D Weyl points, where it degrades into two-fold by breaking the $I\cdot T$. ($I$ and $T$ represent the central inversion and time reversal operations, respectively) symmetry. In particular cases of three-dimensional (3D) materials, a combination of $I\cdot T$ and mirror-glide symmetry could protect four-fold degenerate Dirac nodal points (DNPs) into a continuous line in the momentum space, accomplishing DNL phases. If a DNL spans across the $E_F$, a more specialized DNL phase, i.e. DNL semimetal (DNLS) state, emerges. The DNLS state hosts robust fermionic excitations around the band-crossing point for exploring unusual electronic, optical and magnetic behaviors. While inclusion of SOC usually gap out DNL states and the four-fold DNL often degrades to 2+2 ones under SOC. Although it was argued that the four-fold degeneracy could be approximately achieved in materials comprised of lighter elements where the effects of SOC are weak.

It is the same in the 2D systems where the nodal lines in experimentally observed or theoretically predicted 2D DNLSs gap out under strong SOC. Recently, it has been theory predicted and experiment proved that, in some 2D structures, non-symmorphic symmetry involving fractional lattice translations does protect the four-fold degeneracy of DNPs at certain isolated $k$ points against SOC. However, none of those DNPs extends to a DNL under SOC in any real 2D material. Here, we experimentally and theoretically show that a three mono-atomic layers (3-ALs) Bi grown on BP crystal substrates, a novel phase of Bi, is a robust four-fold DNLSs against SOC, protected by the non-symmorphic ${\mathcal{C}}_{2v} \times Z_2^T$ symmetry. The existence of the DNL state was experimentally identified using scanning tunneling spectroscopy (STS) quasi particle interference (QPI) techniques, We further demonstrated that 3-ALs Bi features a non-trivial edge state coexisting with DNL, which is usually not presented in symmetry protecting DNLSs. The SOC-robust DNL electronic phase is guaranteed by
the crystalline structure of the 3-ALs Bi as predicted by group theory analysis and revealed by density functional theory (DFT) calculations. These findings serve as a solid example to illustrate the essential symmetry physics of protecting DNLSs. Because the crystalline structure of 3-ALs Bi is strongly related with the substrate diatomic layers (2-ALs) BP-like structure, we suggest that the discovery of the novel Bi phase and its DNLS state in this work could be imposed to most VA group elements with possible extension to other 2D systems to create intrinsic DNLSs in real materials.
We grew bismuth nano-islands on a single crystal BP surface (Fig. 1a inset). The islands prefer a belt like shape with the longer side oriented along the zigzag (ZZ) azimuth of the underlying BP, exhibiting a clear Bi (110) structure (Extended Data Fig. 1). Each island appears a ladder shape (Fig. 1b) in STM images consisting of ~11.5 Å horizontally and ~50.0 Å vertically spaced bright stripes, adopting an 8 (zigzag, ZZ) × 10 (armchair, AC) superlattice structure on BP (Fig. 1c). The 8 times zigzag period

Fig. 1 | Atomic structure and electronic spectra of the Bi (110) thin films. a, STM image (V\text{bias} = +400 mV, I\text{t} = 100 pA) of a typical Bi island. The inset shows an area consisting two islands. b, The highlight of the STM contrast inside the rectangle area in (a). c, Atom-resolved STM image (V\text{bias} = +100 mV, I\text{t} = 100 pA) of the rectangle area in (b). Atomic ZZ chains are clearly resolved. The dotted white rectangle represents the unit of the superlattice ladder with 8L\text{ZZ}×10L\text{AC}. d, An amplified image highlights the STM contrast within one unit of the superlattice. The oranges balls are markers representing the appearing orientation of the ZZ contrast of the Bi atoms. The black rectangle shows the lattice constants of the Bi (110) unit cell. e, The line profiles along ZZ and AC direction cutting at the orange dashed lines in (c). f, Q-plus AFM image of the superlattice. g, The line profiles along ZZ and AC direction cutting at the blue dashed lines in (f). h, dI/dV spectra acquired on two typical locations (blue and red dots in (b)) in the center of an island. The inset shows the spectra with bigger bias range. i, dI/dV spectra acquired along the line perpendicular to the edge (black arrow on the inset STM image).
is further dividable into three sub-periods with 3, 2.5 and 2.5 times L_{ZZ} (Fig. 1d and Fig. 1e); this is a primarily electronic effect because of the missing sub-periods in nc-AFM images (Fig. 1f and Fig. 1g). It is, most likely, an electronic Moiré pattern in the ZZ direction. On the other hand, basing on the AFM data (Fig. 1g), the 10 times armchair period (10L_{AC}) is derived from an appreciable atomic corrugation along the AC direction. The Bi (110) thin films were generally thought grown with a 2-ALs BP-like model on different substrates. Nevertheless, the apparent heights of our islands, acquired at different bias voltages, center around 9.60 Å (Extended Data Fig. 2). This value is, however, inconsistent with the 2-ALs BP-like model (6.60 Å to 7.00 Å) but suggests a 3-ALs Bi structure, requiring to a closer examination on those islands.

The islands show a semi-metallic character and a robust edge state, which is, together with the ladder-like STM contrast, substantially different from those of previously found in the 2-ALs BP-like Bi (110) thin-films or islands. Those structures show uniform STM contrast and the STS spectroscopy is either the topological insulator character with edge states or semi-metallic character without any edge state. Figure 1h depicts typical dI/dV STS spectra acquired on different locations at the center of an island. Despite on different STM contrast, the spectra show similar features (Inset in Fig. 1h). Zoomed into the energy range around E_F, the spectra consistently exhibit an asymmetric V-shaped dip centering at -10 mV and spanning from -96 mV to +125 mV. The V-shaped differential conductivity indicates that the measured local density of state (LDOS) could be attributed to a 2D Dirac system, as what has been revealed in the prototype example of graphene. When the acquiring position approaches an edge of the island, a new peak sitting around -25 mV fades in (Fig. 1i). The new state mainly locates at the edges of the island with a penetration depth of ~38.0 Å (Extended Data, Fig. 3). As both the dip and the edge state are reproducible and independent of the width of the islands (Extended Data, Fig. 3), their origin of quantum confinement effect is ruled out.
All these results compellingly indicate that our islands grown on BP are, most likely, a novel allotrope of Bi. This is reinforced by our DFT calculations. Given the apparent height of ~9.6 Å, our DFT considered four 3 ALs- Bi structures and reveals the most likely structure showing its perspective and side-views in Fig. 2a and 2b. This structure is, at least 40 meV/Bi more stable than other three considered 3-ALs Bi (110) stacking structures and becomes even more stable in thicker layers (Extended Data Fig. 4 and Extended Data Table 1), reinforcing the reliability of this structure. It is slightly prone to transform into a combined half 2-ALs plus half 4-ALs hetero-layer in the free-standing form, but could be stabilized using a single crystal BP substrate (Extended Data Table 1). In this 3-ALs Bi, the top and bottom Bi mono-atomic layers form two oppositely oriented BP-like layers shared by the middle mono-atomic layer, respectively. It thus adopts a Bi (110)-like surface structure with a rectangle lattice. The sideview of it appears a wall tessellated by vertically oriented bricks, we thus name this new allotrope as the "brick phase".
Figure 2d shows the electronic band structure under SOC of the 3-ALs Bi. The 3-ALs brick phase is a semimetal with a gap opening around time-reversal invariant point X (green angles). Within the bandgap, a four-fold degenerated Dirac point was identified at the M point (the red cross), which extends to all momenta along the entire Y-M line forming a DNL (the red curve). We plotted a 3D electronic band structure of the DNL in Fig. 2e to more clearly show this unique DNL, which illustrates the linear dispersion relations along other directions and four-fold Dirac bands degenerated in the Y-M line. In comparison with the band structure without SOC, the SOC only flattens the DNL dispersion, indicating the robustness of the DNL state in the 3-ALs Bi. Given the bandgap at X, there is no other trivial band existing in part of the energy window of the DNL, i.e. from 0 to +80 meV, giving rise to a rare ``neat” DNL state around $E_F$. In addition, theoretical analysis shows a band inversion occurring around the X point, resulting the 3-ALs Bi to have nontrivial edge states at its boundary. Figure 2f plots the edge states in the $\Gamma$–X direction, which yields few clear and flat edge states just
below $E_F$. This result is highly consistent with the experimentally observed edge state of our Bi islands (Fig. 1i). The results confirm the assessment of the 3-ALs brick phase and attribute the experimentally observed edge state as the topologically nontrivial edge state origin. Thus a nontrivial edge state coexists with the DNL in this 3-ALs brick phase Bi allotrope.

This unique DNL state is expected to be observed in the grown 3-ALs Bi islands. Our DFT calculations fully reproduced the experimental $8L_{ZZ} \times 10L_{AC}$ 3-ALs Bi superlattice in the model shown in Fig 3a. A smooth vertical corrugation of 8-16 pm is found along the AC direction, consistent with the AFM results (Fig. 1f). Figure 3b shows a simulated STM contrast, which well reproduces the high-low contrasts along the ZZ direction and resolve the three sub-periods within the $8L_{ZZ}$ (Fig. 3c). These results, again, support the reliability of our DFT structure. The corrugations are not solely the bottom Bi atoms’ business that they are well followed by the middle and top layer Bi atoms (Extended Data Fig. 5) in 3-ALs Bi. Thus, the grown Bi thin film shares the same symmetry with the free-standing 3-ALs Bi, except some substrate perturbations as elucidated later.

Because of the $8L_{ZZ} \times 10L_{AC}$ 3-ALs Bi superlattice formed on BP substrate, the original unit-cell BZ of the free-standing 3-ALs Bi folds to an eight- and ten-times smaller superlattice BZ (SLBZ, Fig. 2c). We use $X', Y', M'$ to represent the boundary of the SLBZ. In this BZ, the original Y-M line, where the DNL develops, folds to the $\Gamma-X'$ line, along which the DNL scatters several times appearing rhombus-like shapes in the band structure plotted in Fig. 3d and 3e. In Fig. 3d the green triangles highlight the rhombus formed by the pure DNL after folding. In Fig. 3e, the red dots highlight the DNL which hybridizes with the $p_z$ orbitals of P atoms underneath in certain energy window. As a result, the DNL slightly lifts the fourfold degeneracy and leads to a tiny but appreciable splitting. The folding DNL state complicates its appearance in the $k$-space; this hinders probing the DNL using angle-resolved photoemission spectroscopy (ARPES), which has not been successful yet. However, such band folding provides a
feasible chance of utilizing the STS-QPI approach\textsuperscript{50,51} to characterize the DNL state from real-space.

Our QPI spectra well confirm the theoretically predicted DNL in the 3-ALs Bi superlattice. Figure 3f depicts the QPI revealed E-q relations along the X−Γ−X' line by acquiring continuous STS spectra (Extended Data Fig. 6) across a typical surface defect along the x (AC) direction. It, guiding by green triangles, clearly shows several bands exhibiting nearly linear relations which construct the rhombus folded by the pure DNL.

**Fig. 3** | **Atomic model and E-q dispersions of the folded Dirac nodal lines in 3-ALs Bi (110) on BP surface.** a, Atomic model structure of the $8L_{ZZ} \times 10L_{AC}$ Bi (110) superlattice. The red dotted-rectangle corresponds the superlattice. b, Simulated STM image of the superlattice ($V_{bias} = +100$ mV). c, The amplified image highlights the simulated STM contrast of the Bi atoms. The oranges balls are markers representing the STM contrast orientation of the Bi ZZ chain. d, Band structures along the X−Γ−X' direction of the superlattice highlighting the folded pure DNL state by green triangles. e, Band structures along the X−Γ−X' direction of the superlattice highlighting the folded hybridized DNL state by red dots. The red hollow stars represent the electronic bands not related to the DNL state but observable in the experiments. The same scheme of markers was applied to (f) and (g). Compared with the experimental $dI/dV$ spectra, DFT calculations lift all states by a 0.028 eV, which is comparable with other experiments. f, g, E-q dispersions along X−Γ−X' obtained from QPI scattering by the surface defect (f) or by the edge (g) by performing FFT on the corresponding series $dI/dV$ spectra. In the QPI patterns, the obtained wave vector $q$ represents allowed scatterings of the electron Bloch waves from the initial state of $k_i$ to the final state $k_f$.  

Our QPI spectra well confirm the theoretically predicted DNL in the 3-ALs Bi superlattice. Figure 3f depicts the QPI revealed E-q relations along the X−Γ−X' line by acquiring continuous STS spectra (Extended Data Fig. 6) across a typical surface defect along the x (AC) direction. It, guiding by green triangles, clearly shows several bands exhibiting nearly linear relations which construct the rhombus folded by the pure DNL.
state (from -140 mV to -10 mV). The QPI acquired at edges (Fig. 3g) of the islands have a stronger scattering strength and thus yield sharper contrast, especially for those DNL states hybridizing with the substrate (red dots in Fig. 3e). In this case, the rhombuses-shaped band dispersions are observed from 90 mV to 145 mV. These features are within the energy windows of the folded hybridized DNL from 10 meV to 152 meV as predicted with DFT (red dots in Fig. 3e).

Similar measurements, revealing the E-q relations along Y’–Γ–Y’ (the ZZ direction, Extended Data Fig. 7), further validate our STS-QPI measurements along X’–Γ–X’. The appearance of E-q relations in STS-QPI highly depends on the type of surface defects, which is, most likely, resulted from the existence of periodically atomic corrugations in the Bi islands and the complicated hybridization of DNL with the substrate. Nevertheless, our QPI results performed across the surface defect and from the edge are complementary to reveal their DNL origin, which unambiguously demonstrated direct observations of DNL in 3-ALs Bi.

Space group theory analysis elucidates the detailed symmetries protecting the DNL state in 3-ALs Bi. The symmetry of 3-ALs Bi is described by the non-symmorphic space group Pnma, whose point group G = D_{2h} × Z_{2}^{T} is generated by C_{2x}, C_{2y}, M_{z} and T with $\tilde{T} = IT$. As the combined operation $\tilde{T} = IT$ with $\tilde{T}^{2} = -1$ guarantees a two-fold Kramers degeneracy in the spin degrees of freedom at any $k$ point, in order to obtain a DNL, the extra 2-fold degeneracy needs to come from orbital degrees of freedom. We found that the non-symmorphic $C_{2v} × Z_{2}^{T}$ group ($\{C_{2x}| (0, 1/2, 0)\}$ and $\{M_{y}| (0, 1/2, 0)\}$) in 3-ALs Bi is the exact symmetry to protect the two-fold orbital degeneracy along the Y-M ($k_{x}, \pi, 0$) line no matter SOC is present or not. Figure 4a, 4b and 4c, 4d illustrates the symmetry operation of $\{C_{2x}| (0, 1/2, 0)\}$ and $\{M_{y}| (0, 1/2, 0)\}$ respectively. Without SOC these two operations are commute with each other but are anti-commute with the I.T symmetry along Y-M, offering two double orbital degenerations (Fig. 4e). By including SOC, $\{C_{2x}| (0, 1/2, 0)\}$ is still anti-commute with I.T., resulting a two-fold orbital degeneracy. However, $\{C_{2x}| (0, 1/2, 0)\}$ and $\{M_{y}| (0, 1/2, 0)\}$ becomes anti-
commute along Y-M; this additional anti-commute relation protects spin degeneracy.

As a result, the quadruple degeneracy along Y-M is thus kept under SOC (Fig. 4f). The results indicate that the nonsymmorphic symmetry play a pivotal role in protecting the quadruple degeneracy against SOC in 2D systems. We further proved that all these states are of linear dispersion relation guaranteeing their character of Dirac states\(^{41}\).

This structural symmetry is, to the best of our knowledge, the exact one in 2D that intrinsically offers quadruple-degenerated DNL\(^{41}\). The DNL is symmetry protected, i.e., it is independent of specific orbital and does not need band inversion. Therefore, the DNL is an inevitable occurrence in each system that satisfies the above symmetry, which could be imposed by most VA group elements with possible extension to other 2D systems. Our DFT calculations verified that 1- and 5-ALs Bi, 3-ALs P, As and Sb are all DNLSs against SOC\(^{41}\). Experimentally, we have observed similar STM ladder contrasts and robust edge states in 5-ALs Bi, proving the DNLS are symmetrically
guaranteed (Extended Data Fig. 8). We also expect less substrate influence to DNL in 5-ALs or thicker Bi thin films than those in the 3-ALs crystal.

On the basis of STM experiments, first principle calculations and symmetry analysis, we discovered a symmetry guaranteed simple 2D DNLS in the rationally designed and artificially built 3-ALs Bi brick phase thin-films. It is a novel allotrope of Bi few-layers and the DNL is immune to very strong SOC. In fact, strong SOC becomes an advantage enriching the electronic characters in the 3-ALs Bi brick phase rather than degrading the four-fold degeneracy of the DNL. First, the strong SOC of the Bi element results in a small dispersion of the DNL around \( E_F \). Second, the SOC opens a gap around \( E_F \), which making part of the DNL neat without any interference with other states. These two results would facilitate the probe and manipulation of the physical behaviors essentially governed by the fermionic excitations around protected Dirac nodes. Third, the strong SOC introduces a band-inversion induced non-trivial edge state in 3-ALs Bi. Its first time’s coexistence with the symmetry guaranteed DNL within one system provides additional degrees of freedom where the two could be individually manipulated and/or interacted by external perturbations to produce emergent Dirac states.

We emphasize that the DNL in 3-ALs Bi is solely symmetry dictated. This implies 1) its generality in a series of 2D layers with iso-structure as that of the 3-ALs Bi brick phase. Because BP substrates favors of the formation of this unique 3-ALs Bi brick structure, we speculate realization of similar brick phase for most VA group elements to boost experimental achievement of intrinsic 2D DNLSs; 2) its robustness against lattice distortions that keeps the nonsymmorphic symmetry. Experimentally, narrow-width 3-ALs Bi islands are created in which the surface stress fully releasing along the AC-direction (Extended Data Fig. 9). Such narrow islands exhibit similar LDOS as those of 3-ALs Bi superlattice. Moreover the narrow islands reveal a well-defined V-shaped differential conductivity compared with that of Bi superlattice and offer mysterious S or O-like 1D electronic states that are subject to future investigations. All
these intriguing properties compellingly provide that the discovered 3-ALs Bi brick phase holds promise as a new platform for future exploring the fundamental Dirac states physics.
Methods

Sample preparation and STM/STS measurements. The BP crystals are home-grown using a chemical vapor transport (CVT) method (red phosphorus, tin iodide (SnI\textsubscript{4}), and tin powders as the starting materials) in a two-zone tube furnace in a temperature gradient of 600°C to 540°C. The STM and spectroscopy experiments are carried out in an ultrahigh vacuum low temperature STM system (CreaTec). Prior to STM experiments, the BP crystals are cleaved \textit{in-situ} in a preparation chamber under ultrahigh vacuum at room temperature (RT). Bismuth atoms (99.999% purity, Aldrich) are evaporated from a resistively heated evaporator onto a freshly prepared BP surface. The BP substrates are kept at ambient temperature during the evaporation. The prepared sample is then immediately transferred into the STM chamber, and cooled down to 77 K and/or 4.5 K. STM topographic images are acquired in the constant-current mode. The \(dI/dV\) spectra are measured using the standard lock-in technique with a bias modulation of 8 mV at 321.333 Hz. The STM tips are chemically etched tungsten or mechanically cut Pt-Ir wires, which are further calibrated spectroscopically against the Shockley surface states of cleaned Cu (111) or Au (111) surfaces before being utilized on Bi islands/BP.

DFT calculations. DFT calculations were performed using the generalized gradient approximation for the exchange-correlation potential, a plane-wave basis, and the projector augmented wave method set as implemented in the Vienna \textit{ab-initio} simulation package (VASP)\textsuperscript{52-54}. The energy cutoff for plane wave was set to 650 and 350 eV for variable volume structural relaxation of pure Bi 2D materials and invariant volume structural relaxation of Bi island on BP surface. For freestanding Bi layers, the k-points sampling of the first Brillouin zone is \(14 \times 14 \times 1\), generated automatically by Monkhorst-Pack method\textsuperscript{55}. The k-points sampling is with only the \(\Gamma\)-point for Bi island on BP surface. The vacuum layers of all supercells are larger than 15 Å. The bottom BP layer were kept fixed and all other atoms were fully relaxed until the residual force per atom was less than 0.05 eV/Å during the relaxations of Bi island on BP surface and less than 0.001 eV/Å during all the other structural relaxations. In structural relaxation
and electronic property calculations, DFT-D3 correction method is considered with the Perdew-Burke-Ernzerhof (PBE) exchange functional (PBE-D3)\textsuperscript{56,57}. The Bi-BP superstructure was modeled using a superlattice consisting of a $8L_{zz} \times 10L_{ac}$ Bi 3-AL and $11L_{zz} \times 11L_{ac}$ BP 2-AL with a 15 Å vacuum layer perpendicular to the Bi and BP layers. All electronic properties of the superlattice were calculated with the consideration of SOC. The STM simulation was performed using the Tersoff-Hamann method\textsuperscript{58}. The edge states are calculated using Wannier90\textsuperscript{59} and WannierTools\textsuperscript{60}.

**Data availability:** The data that support the findings of this study are available from the corresponding authors upon request.

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**Author Contributions**

X.X.C, Y.F.L and C.C.L grew the Bi samples and performed STM measurements; D.P.G. and W.J. performed first principle calculations; P.J.G., Z.X.L and W.J. conducted the symmetry analysis; G.Q.Mei and L.M.C. grew the BP crystals; M.F. and L.M.C initiated the project and experiments; W.J. conceived the theoretical calculations and analysis; C.L. and S.J.Tan. participated in experiments of electronic structure.
studies; K.L. and Z.Y.L. participated in data analysis and discussions; M.F., W.J., H.P. and L.M.C. analyzed the data, and wrote the manuscript with input from all authors.

Additional information

Additional data related to this paper are available from the corresponding authors upon request.

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Extended Data

Two-dimensional Dirac nodal-line semimetal against strong spin-orbit coupling in real materials

Extended Data Figure 1

Extended Fig. 1 STM topographic images of Bi islands grown on BP surface. a, Large scale STM image showing that the islands grow with a preferred azimuth along the zigzag direction of the substrate. b, High resolution STM topographic height image showing the atomic contrast in Bi island and in BP substrate. c, Current image of (b) showing the zigzag chains inside Bi island and in BP substrate. Because of the big height difference, the atomic feature of both the Bi island the BP substrate is more clearly resolved by the topographic current image. It is clear that the BP zigzag chains and Bi zigzag chains are oriented almost in parallel. All the images are obtained at LN$_2$ temperature.
Extended Fig. 2 STM measured height of Bi islands on BP surface under different biases. 

a, The height of the Bi islands varies upon different bias and centers at ~960 pm in the bias range from -0.7 eV to -0.2 eV and 0.35 eV to 0.5 eV. We suggest this is because at the bias away from these energy ranges, the BP substrate is characterized with a higher density of state (DOS), as shown in b. This makes the STM measured height of Bi islands on BP smaller than the real value. This phenomenon is more obvious at positive voltages, where the BP substrate hosts a very high DOS in the conduction band (Guo et al., Linear Scanning Tunneling Spectroscopy Over A Large Energy Range in Black Phosphorus, J. Appl. Phys. 124, 045301 (2018)). To exclude the influence of the DOS from BP substrate, we conclude that the measured height under the bias around the band gap edges is close to the real value. The measured average 960 pm height in this energy range is consistent with three atomic layer height of Bi (110) structure.
Extended Data Fig. 3 Topological edge states of 3-ALs Bi (110) 8x10 superlattice.

**a**, Series STS $dI/dV$ spectra measured along a line normal to the edge. The island has a width of 56 nm. The islands show an edge state at -0.025 eV, which is at the same energy value from 33 nm wide island in Fig. 1e. The edge state penetrates into the island for ~3.8 nm, similar as that observed in Fig. 1e. **b**, $dI/dV$ mapping acquired at -0.025 eV. The bright contract at edge denotes the real space location of the edge state. We notice that there is an uneven contract brightness from the edge state. This unevenness might result from the fact of partly irregular atomic organization at edges and the hybridization of edge state with substrate (Drozdov et al., One-dimensional topological edge states of bismuth bilayers, Nat. Phys. 10, 664-669 (2014)). The robustness and reproducibility of the measured edge state in islands with different sizes eliminate the possibility of quantum confinement effect induced additional electronic peaks in the spectra.
Extend Data Fig. 4 Different stacking configurations and energies for 3-ALs Bi. 

Four different stacking configurations (1-4) considered in 3-ML Bi (atoms in different layers are presented in different colors). b, Energy per Bi atom of the four different stacking configurations in 3-ALs Bi. It can be seen that the energy of configuration (4) is about 40 meV per Bi atom lower than that of configuration (3), showing that configuration (4) is the most stable configuration.
**Extended Data Table 1**

| Freestanding Layers | E<sub>total</sub> (meV/Bi atom) | On substrate (BP) Layers | E<sub>Adorption</sub> (meV/Bi atom) | E<sub>1</sub> (meV/Bi atom) |
|---------------------|-------------------------------|--------------------------|-----------------------------------|--------------------------|
| 2 AL                | -3939.2                       | 2 AL                     | -78.9                            | -4018.1                  |
| 3 AL                | -3984.1                       | 3 AL                     | -102.0                           | -4086.1                  |
| 4 AL                | -4043.3                       | 4 AL                     | -46.6                            | -4089.9                  |
| (2AL+4AL)/2         | -3991.2                       | (2AL+4AL)/2              | -62.75                           | -4054.0                  |

\[ \Delta E_{\text{total}} = -7.2 \]
\[ \Delta E_{\text{adsorption}} = 46.6 \]
\[ \Delta E_1 = 32.1 \]

**Extended Data Table 1**

**Total energy of different Bi atom layers and the adsorption energy on BP substrate.**

E<sub>total</sub> represents total energy of freestanding Bi atom layers. 

E<sub>Adorption</sub> = (E<sub>total1</sub> − N<sub>Bi</sub>·E<sub>Bi</sub> − N<sub>P</sub>·E<sub>P</sub>) / N<sub>Bi</sub>, where E<sub>Adorption</sub> is the adsorption energy of Bi atom layers on BP substrate, E<sub>total1</sub> is the total energy of the system, N<sub>Bi</sub>, N<sub>P</sub>, E<sub>Bi</sub>, E<sub>P</sub> represent the number of Bi atoms and P atoms, the energy of single freestanding Bi atom and P atom, respectively. E<sub>1</sub> = E<sub>total</sub> + E<sub>Adorption</sub>, ΔE = (E<sub>2AL+4AL</sub> / 2) − E<sub>3AL</sub>. Without BP substrate, the total energy of bilayer, tri-layer and four monolayer Bi is −3939.2, −3984.1 and −3991.2 meV/Bi atom, respectively. Comparing the total energy of the (2 AL+4 AL)/2 and 3 AL Bi, it is found that the former energy is 7.2 meV/Bi lower. This indicates that 3 ML Bi is less stable than (2 AL+4 AL)/2 Bi without substrate. On BP substrate, the adsorption energy of bilayer, tri-layer and four monolayer Bi is −78.9, −102 and −62.75 meV/Bi, respectively. The adsorption energy of 3 AL Bi is higher than those of 2 AL and 4 AL Bi, and the difference between (2 AL+4 AL)/2 and 3 ML Bi is 46.6 meV/Bi. The E<sub>1</sub> of 3 ML Bi is −4086.1 meV/Bi as the result of adsorption energy of 3 AL Bi on the BP substrate is the largest, and it is 68 and 32.1 meV/Bi lower than 2 AL Bi and (2 AL+4 AL)/2 Bi, respectively. This suggests that the 3-AL Bi structure is more stable than 2-AL Bi when adsorbed on BP substrate.
Extended Data Figure 5

Extended Data Fig. 5 Height variation of Bi atoms in different layers of the 3-ALs. Bi in a row of 10×L_ac atoms along the AC direction. It shows that the heights of some Bi atoms decrease, while others increase, but the height variation of Bi atoms in different layers features the similar tendency. This indicates that the Bi atoms in three layers follow exactly the same real space trajectory.
Extended Data Figure 6

Extended Data Fig. 6 2D $dI/dV$ spectrum map of series $dI/dV$ spectra along AC direction. a, b 2D $dI/dV$ spectrum map of series $dI/dV$ spectra acquired on a line along ZZ direction, by crossing a typical defect on surface (a) and from the edge (b) of the island. The insets in both images show the locations where the spectra are acquired. One can see the QPI features when closing to the defect and edge.
Extended Data Figure 7

**Extended Data Fig. 7 Band E-q dispersions of 3-ALs Bi (110) on BP surface along Y’–Γ–Y’ direction.**

**a,** Calculated band structures along Y’–Γ–Y’ direction for Bi (110) 8×10 superlattice on BP. The 1st BZ of the superlattice is shown as the inner red rectangle in Fig. 1c. The green color highlights the bowtie-shaped rhombuses in the band structure along Y’–Γ–Y’, which is caused the folded linear bands from X-M to Γ–Y’. The red dots highlight the folded Dirac cones at Y point. **b, c,** 2D dI/dV spectrum map of series dI/dV spectra acquired on a line along ZZ direction, by crossing a typical defect on surface (b) and from the edge (c) of the island. The insets in both images show the locations where the spectra are acquired. One can see the spectrum changes caused by QPI when closing to the defect and edge. **d, e,** E-q dispersions along Y’–Γ–Y’ obtained from QPI scattering by surface defect (d) or by the edge (e) by performing FFT on the corresponding series dI/dV spectra. Several bow-tie shapes (marked by the blue-white arrows), originating from the crossing of the linear bands, are seen in (d). Because of the strong scattering at the edge, the QPI pattern is relatively sharp in (e).
and a clear Dirac point appears in the QPI as marked by the red-white arrow. The colored arrows help to point out the resolved $q$ as those marked in (a).
Extended Data Fig. 8 Topographic STM images of 5-ALs Bi nanoribbons grown on BP substrates and the topological edge states measured by STS $dl/dV$ spectra. 

**a,** STM image shows the coexistence of 3-ALs Bi and 5-ALs Bi on BP substrate. When continually increasing the Bi atom deposition, 3-ALs Bi will form large area continuous thin films. Then 5-ALs Bi structures are obtained with two additional atomic Bi layer grown on top of the 3-ALs Bi. 

**b,** The zoom in STM image shows the edge
at the 3-ALs and 5-ALs Bi interface. The 5-ML Bi shows similar STM contrast as those in 3-ALs Bi. c to e, The series STS $dI/dV$ spectra measured along the red, blue and pink arrows in (b). In (c), the data shows an obvious edge state at -0.055 eV. When moving slightly away from the edge to the center as shown in (d), the edge state peak becomes gradually weaken. When far away from the edge as shown in (e), the edge state totally disappears. The inset in (f) shows STS spectrum at small energy range, indicating very similar electronic characters of 5-ALs Bi with that of the 3-ALs Bi. f, The $dI/dV$ mapping acquired at -0.055 eV clearly shows the space distribution of edge state of a 5-ALs Bi island. The edge of 5-ALs Bi is much more ordered than that of 3-ALs Bi, and there is no hybridization with BP substrate. These make the edge state mapping possesses a uniform contrast. The edge state penetrates into the island for ~4.0 nm.
Extended Fg. 9 STM topographic and mapping images of narrow Bi islands grown on BP surface. **a**, STM topography image showing that the island does not have the corrugation along AC direction, as a result of the narrow width of the island. At the edge of the island, STM image shows continuous “s”- shaped contrast. **b**, STM $dI/dV$ mapping image highlights the DOS at the edges. The orange and green balls are markers to show two kinds of edge defects locations. It could be seem that the DOS escape perfectly from the defects to form “s”- shaped distributions at the edges, indicating that electronic state could pass the defects smoothly. This S -like 1D electronic state is typical at the energy within the DNL energy window and is subject to future investigations.