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### 1 Electronic Supplementary Information

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# <sup>3</sup> Highly tunable anisotropic co-deformation of black

## 4 phosphorene superlattice

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Figure S1. Bimodal anisotropic co-deformation. (a–h) Change in CTAB thickness distribution in zigzag (a–d) and armchair (e–h) bending mode with surface density increasing from 0.34 to 2.31 no./nm<sup>2</sup>. All histograms can be described using a bimodal Gaussian distribution (dashed lines), with modes corresponding to the base layer (blue lines) and the CTAB aggregates (red lines). The right shifts of the blue and red peaks reflect the increasing average thickness in the base layer and CTAB aggregates, respectively. The changes in the areas under the red and blue curves indicate variations in the corresponding proportions of the two modes.

Supplementary Note 1. The distribution of the thickness of the CTAB layer is shown in Figure S1. 1 For both zigzag-bending (panels a-d) and armchair-bending (panels e-g) structures, the CTAB 2 thickness follows a bimodal distribution. Based on the corresponding morphologies, the two modes 3 are attributed to a base CTAB layer (blue lines) and to regions with locally clustered CTAB 4 molecules (red lines), which are schematically illustrated in the insets of the panels <sup>1</sup>. 5 6 In both zigzag- and armchair-bending scenarios, the mean thickness of each component of the bimodal distribution right-shifts to a higher value when the surface density of the CTAB increases. 7 This indicates a gradual growth in thickness of both regions (base layer and CTAB clusters) due to 8 9 the agglomeration of CTAB. In the zigzag-bending structures, the mean thickness of the CTABagglomerated region increases by approximately five times, from 0.5 nm at the surface density of 10 0.34 no./nm<sup>2</sup> (Figure S1a) to 2.5 nm at 2.3 no./nm<sup>2</sup> (Figure S1d). A similar trend is observed for the 11 12 armchair-bending structures, in which the mean thickness of the clustered CTAB layer shows a 13 seven-fold increase from 0.5 nm at the surface density of 0.34 no./nm<sup>2</sup> (Figure S1e) to 3.5 nm at 2.3 no./nm<sup>2</sup> (Figure S1h). 14

15 Unlike the symmetrical aggregate formation in the zigzag-bending structures, the armchairbending structures form uneven aggregates at the bottom and top of the structure. Basically, CTAB 16 molecules show a higher tendency to agglomerate at concave than convex bends. This is caused by 17 the compression of phosphorene induced at concave bends, which can better accommodate the 18 compressive forces exerted by the CTAB aggregates. This also leads to the uneven distribution of 19 CTAB aggregates in the structure. As shown in Figure S1e-h, CTAB clusters tend to form in high-20 21 curvature spots of the phosphorene structure, under the high compression levels at concave bends. When the thickness of the structure gradually increases, the CTAB clusters fit the shape of the bent 22 23 structure (Figure 2h). Compared with Figure S1d, in which the thickness distribution of the structure extends from 1.5 to 3 nm, the peaks in the corresponding distribution for the armchair-bending 24 structure in Figure S1h are broader, with a distribution ranging from 2 to 4 nm. This indicates a 25

- 1 relatively more uniform thickness distribution in the zigzag-bending than the armchair-bending
- 2 structure, due to the lower stiffness of phosphorene along the zigzag direction.



Figure S2. Pair distance distributions in phosphorene/CTAB superlattices. (a-c) Phosphorus 2 (top layer) – phosphorus (bottom layer) (Ptop-Pbottom, red solid lines), carbon-carbon (C-C, green 3 4 dashed lines), and bromide-bromide (Br-Br, blue dashed lines) radial distributions in armchairbending phosphorene/CTAB structures with surface densities of 0.83, 1.00 and 2.31 no./nm<sup>2</sup> from 5 left to right. (d-f) Ptop-Pbottom (red solid lines), C-C (green dashed lines), and Br-Br (blue dashed 6 7 lines) radial distributions in zigzag-bending phosphorene/CTAB structures with surface densities of 0.83, 1.35 and 2.31 no./nm<sup>2</sup> from left to right. The larger amounts of distinctive Br-Br peaks in 8 thinner (a, b and d, e) systems indicate higher levels of crystallisation of CTAB between more 9 confining phosphorene layers. A similar CTAB crystallisation trend is found in the zigzag- and 10 armchair-bending structures, indicating that the bending direction has negligible influence on the 11 12 CTAB crystallisation in phosphorene bilayers.

#### 1 Supplementary Note 2

- 2 Derivation of phosphorene bending energy
- 3 According to Euler buckling theory, the bending energy of phosphorene, U, can be expressed as:

$$U = \int_{0}^{l} \frac{1}{2} M \kappa dx = \int_{0}^{l} \frac{K}{2} \kappa^{2} dx$$
(S1)

5 where κ is the curvature of the beam, K is the bending stiffness, and *l* is the length of the beam. If w(x)
6 and κ represent the global bending deformation of the trilayer and its second derivative, U can be
7 expressed as:

$$U = \int_{0}^{l} \frac{K}{2} (w'')^2 dx$$
(S2)

9 Eq. (S2) can be solved for w(x) using Fourier series expansion:

$$w(x) = \sum_{n=1}^{N} a_n \phi_n(x - \theta)$$
(S3)

11 where  $\phi_n(x)$  is a sinusoidal function that can be written as:

$$\frac{\phi_n(x) = \sin \frac{2k\pi(x-\theta)}{l}}{l}$$
(S4)

13 Taking into account the boundary conditions and symmetry of the problem, the solution can be

14 represented via the first three terms in the expansion:

15 
$$w(x) = a_1 \sin \frac{2\pi (x - \theta_1)}{l} + a_2 \sin \frac{4\pi (x - \theta_2)}{l} + a_3 \sin \frac{8\pi (x - \theta_3)}{l}$$
(S5)

16 where  $a_n$  is the amplitude. Taking the second derivative of w(x) and integrating along x, we obtain:

$$U = \frac{K}{2} \left( \left(\frac{2\pi}{l}\right)^4 a_1^2 \frac{l}{2} + \dots + \left(\frac{8\pi}{l}\right)^4 a_3^2 \frac{l}{2} + \left(\frac{\pi}{l}\right)^2 \left(\frac{2\pi}{l}\right)^2 a_1 a_2 C_1 + \dots + \left(\frac{\pi}{l}\right)^2 \left(\frac{8\pi}{l}\right)^2 a_1 a_3 C_3 \right)$$
(S6)

18 where the  $C_n$  are the coefficients of the polynomial that describes the superimposition and 19 cancellation of the sinusoids.

### 1 Supplementary Note 3

- 2 Gaussian decomposition
- 3 The local deformation of the phosphorene/CTAB structure can be decomposed using a multimodal
- 4 Gaussian distribution:

5 
$$P(x) = \sum_{1}^{m} \frac{1}{\sigma_i \sqrt{2\pi}} e^{-\frac{(x-\mu_i)^2}{2\sigma_i^2}}$$
 (S7)

- 6 where μ<sub>i</sub> and σ<sub>i</sub> (i = 1 to m) are the medians and standard deviations, respectively, of the Gaussian
  7 components, and m is the number of modals used.
- 8
- 9
- 10



Figure S3. Curvature of local deformation as superimposed Gaussian functions for (a, b) zigzagbending and (c, d) armchair-bending phosphorene/CTAB structures at different surface densities of
intercalated CTAB. The dashed and solid lines correspond to the actual cluster shapes and the
decomposed Gaussian distributions, respectively.



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2 Figure S4. Maps of normalised bond stretching energy  $E_b$  between top and bottom phosphorene

3 layers for (a-e) zigzag- and (f-g) armchair-bending structures. The maximum bond stretch energy in

4 each case is normalised to 1.

Supplementary Note 4. Further information on the local deformation of both zigzag- and armchairbending structures is provided by the curvatures shown in Figure S3, which were obtained as second
derivatives of the Gaussian models. Although a similar local deformation is observed in both
bending scenarios at the low CTAB surface density of ~0.50 no./nm<sup>2</sup> (Figure S3a and c), a large
difference emerges at 2.00 no./nm<sup>2</sup>, where the armchair-bending structure (Figure S3d) displays
larger curvatures (indicating a less uniform local deformation) than the zigzag-bending case (Figure 7 S3c).

The normalised bond stretch energy mappings in the top and bottom layers of phosphorene are a further indicator of the local deformation along the zigzag- and armchair-bending structures. The  $E_b$ maps shown in Figure S4a-e exhibit a regular sequence of stripes for all the zigzag-bending structures. Since the bond stretch energy between the top and bottom layers of phosphorene is dependent on their separation distance, the periodic pattern of the stripes suggests uniform deformation at the local level. In contrast, the armchair-bending structures feature relatively larger and more irregular variations of  $E_b$ , indicating fewer uniform local deformations.



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Figure S5. Schematic illustration of free energy of CTAB assembly (*W*) for two representative cases
with different CTAB packing geometries. The purple spheres represent CTAB molecules and the
orange strips represent phosphorene. *W* includes contributions from all pair interactions between
adjacent CTAB molecules and the interaction between each CTAB molecule and phosphorene.



**2** Figure S6. Modelling of phosphorene bent to Gaussian curves. (a) The deformation of the centreline 3 and the shear deformation constraint, rotation of atoms based on its projection on the centreline ( $\theta$ ), 4 control by factor *k*. When k =1, the shear deformation is fully constrained, as the line connecting the 5 atom and its projection is perpendicular to the centreline. (b-c) The model of phosphorene with 6 various k for (b) zigzag-bending and (c) armchair-bending, respectively. (d) Energy of each atom, 7  $E_{pa}$ , vs *k* in zigzag-bending and (c) armchair-bending. For comparison purposes,  $E_{pa}$  is offset by – 8 min( $E_{pa}$ ) for each curve.

Supplementary Note 5. Further information on the modelling of bent phosphorene in first-principle 1 calculations. It can be seen from Figure S6a that, when bending is applied to a phosphorene, the level 2 of shear deformation of the top and bottom layers of P atoms needs to be considered. When the 3 model is constructed, the centreline of an undeformed phosphorene is first aligned with a designated 4 curve, in this case, a Gaussian curve (see parameters in the Method section). It should be noted that 5 the length of the phosphorene is maintained during this alignment process. The P atoms in the top 6 and bottom layers are shifted during the alignment, together with their projections on the centreline 7 (red dots in Figure S6a). These result in a deformation pattern as shown in Figure S6a. This pattern 8 9 might not be preferred, however, as there is a significant amount of shear. In the natural bending of materials, there is a tendency to have a partly shear constraint while compressive and tensile forces 10 are generated at the top and bottom of a beam<sup>2</sup>. The effect of this constraint is evaluated here in 11 12 order to create a further optimised model for DFT calculations. We used a factor, k, to control the effect of the shear constraint, as shown in Figure S6, and the results suggest that the optimum k for 13 zigzag- and armchair-bending is ~1.0 and ~0.7 respectively. The optimum k is therefore adopted for 14 model bending in the DFT calculations. 15



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Figure S7. The effect of adsorbed CTAB on the electron density and band structure of BP. 2 Comparison between total electron density of BP only and BP with attached CTAB (isosurface 3 represents 0.08 eV) for bending in (a) armchair direction and (b) zigzag direction, respectively. Band 4 structure of (c) armchair bending BP without CTAB, (d) armchair bending BP with CTAB, (e) 5 zigzag bending BP without CTAB and (f) zigzag bending BP with CTAB. The band gap in (c-f) are 6 0.989, 0.955, 0.947 eV and 0.932eV, respectively. The adsorption of CTAB on BP is found to 7 introduce insignificant impact on the band structure and band gap of BP. The results shown in the 8 calculation here is consistent with the reported results in Reference 3<sup>3</sup>. Therefore, for the simplicity 9 and efficiency of DFT calculation, the CTAB molecules are excluded from the models presented in 10 Figure 5 of main text. 11

#### 12 REFERENCES

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