Assembling phosphorene flexagons for 2D electron-density-guided nanopatterning and nanofabrication†

Kisung Kang,‡a,b Woosun Jang ‡d,a and Aloysius Soon ‡d,a∗

To build upon the rich structural diversity in the ever-increasing polymorphic phases of two-dimensional phosphorene, we propose different assembly methods (namely, the “bottom-up” and “top-down” approaches) that involve four commonly reported parent phases (i.e. the α-, β-, γ-, and δ-phosphorene) in combination with the lately reported remarkably low-energy one-dimensional defects in α-phosphorene. In doing so, we generate various periodically repeated phosphorene patterns in these so-called phosphorene flexagons and present their local electron density (via simulated scanning tunneling microscopy (STM) images). These interesting electron density patterns seen in the flexagons (mimicking symmetry patterns that one may typically see in a kaleidoscope) may assist as potential 2D templates where electron-density-guided nanopatterning and nanofabrication in complex organized nanoarchitectures are important.

I. Introduction

Nanoscale and nanotechnology will persist to play a key and dominant role in new functional materials research and development. Especially, two-dimensional (2D) nanomaterials are currently at the edge of this field. While graphene1–5 has garnered massive attention over the past few years, continuous identification of new and novel 2D nanomaterials has emerged – ranging from the low-dimensional transition metal dichalcogenides (TMDCs)6–9 to more recently identified monoelemental analogues of graphene – e.g. silicene,6 stanene,7 and phosphorene.8–10

Phosphorene – the 2D counterpart of black phosphorus – turns out to be a competitive challenger to the current members of the 2D family. Due to its outstanding physicochemical and mechanical properties, phosphorene promises a broad range of functionalities and applications.11–13 Of late, many researchers have further attempted to incorporate the use of phosphorene in various state-of-the-art nanodevices via dimensionality,14–17 strain-,18–22,61 and defect-engineering.23–29

Different from the sp2-bonded graphene, sp3-dominated phosphorene has much more to offer in terms of structural diversity. The mildly-buckled phosphorene is known to exhibit multiple energetically competitive polymorphic phases, with the thermodynamically most stable phase being that of the α-phase. Many other phases have been reported, namely the β-,18 γ-20 and δ-phases,21 and other non-honeycomb ε, ζ, η, and θ-phases,22 and the most recently reported ψ-phase.33

Each proposed and identified phase possess a slightly different structural motif, and this structural variation itself seems to promote unique intrinsic material properties attributed to that phase.34–38 Recently, Guan et al. have suggested an effective scheme to organize and categorize the different layered structures of phosphorene, by simply tiling the threefold coordinated P atoms in a 2D triangular patterns to expand this structural motif diversity.37

Very much inspired by this tiling approach, we have further taken diverse structural motifs due to the four commonly reported parent phases (i.e. the α, β, γ, and δ-P) in combination with the lately reported remarkably low-energy one-dimensional defects in α-phosphorene.24 Here, we report two different approaches – the “bottom-up” and “top-down” methods to assemble phosphorene nanoflakes (PNFs) from their parent phases to form so-called geometric models – flexagons – of phosphorene, further extending the already enlarging structural diversity in this simple sp3-bonded element.


†These authors contributed equally to this work.
II. Methodology and computational setup

We perform first-principles density-functional theory (DFT) calculations with the projector-augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP). In our DFT calculations, periodic boundary conditions are enforced with a vacuum region of 15 Å along the out-of-plane direction for all 2D models used in this work. A planewave kinetic energy cutoff of 500 eV is employed, and for geometry optimization, the semi-local approximation to the exchange-correlation functional due to Perdew, Burke, and Ernzerhof is used. To achieve a higher precision in our electronic band structure calculations, we have adopted the HSE06 hybrid DFT functional instead. A Γ-centered k-point grid of a reciprocal space sampling distance of 0.2 Å\(^{-1}\) and 0.15 Å\(^{-1}\) are used for all geometry optimization and electronic band structure calculations, respectively. All geometries are relaxed until the forces do not vary more than and 0.02 eV Å\(^{-1}\).

Phosphorene flexagons presented in this work are assembled using separate phosphorene nanoflakes (PNFs) as a basic “building blocks”. The PNFs are derived from previously reported phosphorene polymorphs (i.e. the α-, β-, γ-, and δ-phases of phosphorene), or by joining α- or β-PNFs together with 1D line defects (i.e. 6:6, and 5:7 as reported in ref. 23) via different PNF contact angles. Here, we note that the PNFs obtained by the former method preserve the symmetry of the specific parent phosphorene polymorph, while the latter method results in a more versatile and diverse spectrum of structures and symmetries – e.g. two-, three-, four-, and six-fold symmetries that may seem unusual for phosphorene systems, at the first glance. The detailed atomic structures of these PNFs are shown in the ESI Fig. S1.

The α-P derived PNFs exhibit a plate-shaped flat structure, while the PNF structures from β-P resemble that of a “rumpled bowl”, and here we provide the nomenclature of Teller and Schüssel structures, respectively. Due to the structural similarity and the P-P bonding nature in the many polymorphs of phosphorene, the Teller-PNFs comprise mainly of α- and δ-P characteristics, while the Schüssel-PNFs are β- and γ-P dominant. The cohesive energy (\(E_{\text{coh}}\)) difference between the reported most stable α-P and the PNFs considered in this work is less than 300 meV per atom, implying that it may be thermodynamically feasible to stabilize these PNFs under experimental conditions. Moreover, many researchers reported that PNFs can be formed in different experimental conditions, with various flake sizes depending on the solution used in the liquid exfoliation process.

From these PNFs, using a “bottom-up” approach, we then proceed to design and construct various two-dimensional phosphorene flexagons which are formed by assembling the various types of Teller and Schüssel PNFs as described above, as shown in Fig. 1. In our scheme, there are two unique ways to bring these PNFs together, and they can be distinguished by the different arrangement of adjacent PNFs, resulting in the so-called hetero- and homo-type flexagons.

The hetero-flexagons are formed by performing a 180° out-of-plane flip for adjacent PNFs, while the homo-flexagons are the case where each PNF is connected in the same in-plane arrangement. As a result of this “bottom-up” assembly, the hetero-flexagons can possess two-, three-, and four-fold symmetries in their structures, while the homo-flexagons have either two-, four-, or six-fold symmetry structures. Specifically, for the hetero-flexagons, an extension of this construction to a six-fold symmetry structure can be achieved by considering the “top-down” approach from β-phosphorene (which has an intrinsic 6-fold symmetry). This alternative “top-down” method will be discussed and demonstrated later in section E.

Upon a closer look at the connecting edges of the PNFs in our flexagons (or in another words, “flake boundary”), for the hetero-flexagons, the P-P bonding sequence at the edge follows that of the corresponding parent phosphorene polymorph, preserving its bonding nature. On the other hand, the connecting edges of the homo-flexagons do not directly comply with the P-P bonding nature of known phosphorene polymorphs. Instead, very low-energy one-dimensional line defects (as firstly identified in ref. 24) – namely, the 5:5:8s defect structure lines the connecting edges of the homo-flexagons. Owing to its very low defect formation energy of 0.01 eV Å\(^{-1}\), we deem these structures to be thermodynamically and energetically competitive.

By virtue of the complexity of this tiling/assembly method, besides the known polymorphic phases of phosphorene, two new and different types of “void motifs” are created in the process and identified. One occurs in the flake center of the PNFs, which is shown as white regions of Fig. 1, and the other is the joint center of the PNFs, which is denoted as the yellow region in Fig. 1. Those centers retain their polygonal shape, but still follows the conventional sp\(^3\) bonding nature of P atoms in phosphorene, with three coordinating P atoms nearby.

To effectively discuss these phosphorene flexagons, we name the phosphorene flexagon structures by “method-symmetry-shape”, and will be used for the following discussion. For instance, the six-fold symmetry phosphorene homo-flexagon that is assembled from Teller-PNFs will be given the annotation of “ho-6F-s”, and likewise, e.g., the four-fold hetero-flexagon that is assembled from Schüssel-PNFs will be “he-4F-a”.

III. Results and discussion

A. Thermodynamic stability of phosphorene flexagons

As a first step, we examine the thermodynamic/energetic stability of these proposed phosphorene flexagons with respect to the known polymorphic phases of phosphorene. Here, we choose to calculate both the cohesive energy (\(E_{\text{coh}}\), with respect to the spin-polarized P atom energy) and the formation
energy/enthalpy ($E_{\text{form}}$ with the corresponding PNFs and line defect energy):

$$E_{\text{coh}} = \frac{E_{\text{sys}} - E_{\text{atom}}}{N_{\text{sys}}}.$$  \hspace{1cm} (1)

**homo-flexagons**:

$$E_{\text{form}} = \frac{E_{\text{sys}} - N_{\text{NF}} \times E_{\text{NF}}}{N_{\text{sys}}}.$$  \hspace{1cm} (2)

**hetero-flexagons**:

$$E_{\text{form}} = \frac{E_{\text{sys}} - N_{\text{NF}} \times E_{\text{NF}} - N_{\text{LD}} \times E_{\text{LD}}}{N_{\text{sys}}}.$$  \hspace{1cm} (3)

where $E_{\text{sys}}$, $E_{\text{atom}}$, $E_{\text{NF}}$, and $E_{\text{LD}}$ are total energy of the flexagon, spin-polarized P atom, PNFs (per P atom), and the 5:5:8s line defect (per P atom), respectively, and $N_{\text{sys}}$, $N_{\text{NF}}$, and $N_{\text{LD}}$ denotes the number of atoms in the flexagon, PNFs, and the 5:5:8s line defect, accordingly. Due to the absence of defects lining the edges of the PNFs in the *hetero*-flexagons, we have simply adjusted its $E_{\text{form}}$ to not include the effects of line defects.

As shown in the Table 1, our calculated $E_{\text{coh}}$ for the known and reported phosphorene phases are in a good agreement with literature (see ref. 31 and references therein). The difference in our calculated $E_{\text{coh}}$ for all phosphorene flexagons and the most stable $\alpha$-P is found to be only less than 150 meV per atom. Interestingly, three of the *hetero*-flexagons (he-2F-t, he-2F-s, and he-3F-t) possess lower $E_{\text{coh}}$ (i.e. more stable) than the two reported metastable phosphorene phases, *i.e.* $\gamma$ and $\delta$-P, while all other flexagons are just slightly less stable than $\gamma$-P.

Amongst the flexagons considered here, he-2F-t shows the lowest $E_{\text{coh}}$ of $\sim 3.432$ eV per atom, while ho-4F-t shows the highest $E_{\text{coh}}$ of $\sim 3.338$ eV per atom. In general, the *homo*-flexagons are found to have a slightly higher $E_{\text{coh}}$ than the *hetero*-flexagons, in part due to the inclusion of low-energy 5:5:8s line defects. In most cases, the flexagons become more stable (i.e. having a more negative $E_{\text{coh}}$) as the symmetry of the flexagon is lowered. Also, the Teller-PNF containing flexagon is calculated to be more stable than the Schüssel-PNF containing counterparts, and we attribute this to the relative (meta)stabi-
livity of the parent polymorphic phosphorene phases. As pointed out above, the Teller-PNFs comprise mainly of the relatively more stable α- and δ-phases of phosphorene, while the SchüSSL-PNF is generally derived from the less stable β- and γ-phases.

From an energetic point of view, all phosphorene flexagon structures considered in this work yield a negative $E_{\text{form}}$ (cf. eqn (2) and (3)), with respect to the corresponding PNFs and line defect structures, implying there will be a thermodynamic drive for the PNFs to agglomerate and form these unique low-dimensional flexagons under suitable experimental conditions.

### B. Elastic stability of phosphorene flexagons

To assess the thermo-mechanical stability of low-dimensional nanomaterials, it is of usual practice to perform either molecular dynamics simulation at elevated temperatures and/or supercell phonon calculations. Although it is largely prohibitive to conduct these expensive lattice dynamics calculations to test the dynamical stability of these two-dimensional phosphorene flexagons, in this work we opt to examine their elastic stability (i.e. the positive-definiteness of the elastic-strain energy upon lattice distortion) at the first instance.  

Namely, we consider the elastic constants of these phosphorene flexagon structures via total energy calculations under applied in-plane strain (in Fig. S5 of the ESI†), and determine if they fulfill the Born–Huang criteria for the elastic stability of 2D crystals.  

$$E(\theta) = C_{11} s^4 + C_{22} c^4 + \left( C_{11} C_{22} - C_{12}^2 \right) s^2 c^2,$$  

where $C_{ij}$ values are calculated via the following equations:

$$U_{\text{ortho}} = \frac{1}{2} C_{11} \delta_{xx}^2 + \frac{1}{2} C_{22} \delta_{yy}^2 + C_{12} \delta_{xx} \delta_{yy} + 2 C_{44} \delta_{xy}^2,$$

where $U_{\text{ortho}}$ and $U_{\text{ortho}}$ are the elastic energy changes for the orthorhombic and trigonal structures upon applied strain, $\delta_{ij}$ are the infinitesimal strain tensors, and $C_{ij}$ are the elastic stiffness constants, respectively.

Here, we have manually applied a series of lateral strain values between $-5\%$ to $5\%$ along the corresponding $x$ and $y$ directions, and from the calculated total energies, we determine the corresponding $C_{ij}$. As a benchmark, our calculated $C_{ij}$ values for α-P is found to be $C_{11} = 24.31$ GPa, $C_{12} = 103.95$ GPa, $C_{12} = 17.48$ GPa, and $C_{44} = 22.65$ GPa, agreeing well with previous reports.  

From our calculations, we have specifically picked representative flexagon structures for all considered symmetries (he-2F-t, he-3F-t, he-4F-t, and ho-6F-t), and calculate their $C_{ij}$ values from strain–energy relationship (as shown in Fig. S5 and Table S1 of the ESI† for selected phosphorene flexagons). We find that the Born–Huang criteria for elastic stability is fulfilled for all considered phosphorene flexagons. Specifically for the he-2F-t and he-4F-t flexagons, we observe that their $C_{12}$ values are slightly negative, implying that if the 2D crystal is compressed in the $y$ direction, the stress component in the $xx$ direction is tensile rather than compressive. This, however, does not violate the Born–Huang criteria for elastic stability.

After calculating the $C_{ij}$ constants and determining the elastic stability of the phosphorene flexagons, we then proceed to derive and plot the two-dimensional Young’s modulus ($E(\theta)$) and Poisson’s ratio ($\nu(\theta)$) of these selected structures as a function of the planar strain directions ($\theta$), as shown in Fig. 2. Here, we have also included the corresponding results for the parent phosphorene phases – namely, the α, β, γ, and δ phases of phosphorene.

The Young’s modulus and Poisson’s ratio of these two-dimensional materials are derived from substituting our calculated $C_{ij}$ constants into the following equations:

$$E(\theta) = \frac{C_{11} C_{22} - C_{12}^2}{C_{44}},$$  

$$\nu(\theta) = \frac{C_{44} - C_{12}}{C_{44} + C_{12}},$$

where $s$ and $c$ simply denotes $\sin(\theta)$ and $\cos(\theta)$, respectively.

It is clearly shown in Fig. 2 that $E(\theta)$ and $\nu(\theta)$ of the parent phosphorene phases and their flexagons are closely related to the 2D crystal symmetry, and most of structures exhibit anisotropic $E(\theta)$ and $\nu(\theta)$ upon strain. Comparing to the parent phosphorene phases, the phosphorene flexagons generally show smaller magnitudes of $E(\theta)$, while their $\nu(\theta)$ values are typically larger than that of the parent phases. This points to the case where the considered flexagons here can be thought to be mechanically more flexible than their parent phases.
Referring to Fig. 2e, it is worth noticing that the sign of the calculated \( \nu(\theta) \) in \( \delta\)-P oscillates as a function of the strain direction, while the \( \nu(\theta) \) value of the other parent phases are consistently negative for all strain directions. This is very much in line with previous reports, emphasizing their potential as auxetic low-dimensional materials.\(^{34,54} \)

From this point of view, the phosphorene flexagons discussed here do possess a much larger value of \( \nu(\theta) \) than their parent phosphorene phases, and more strikingly, the \( he\)-3F-\( t \) and \( ho\)-6F-\( t \) flexagons present a large constant negative value of \( \nu(\theta) \), which may be advantageous for potential auxetic applications. On the other hand, the \( he\)-2F-\( t \) flexagon uniquely displays continuous positive values of \( \nu(\theta) \) for all considered \( \theta \), which is rarely reported for phosphorene-derived structures.\(^{32} \) It is encouraging that the mechanical properties of these phosphorene flexagons can be highly tunable via its unique tiling system.

C. Electronic structure of phosphorene flexagons

After investigating the thermodynamic and elastic stability of these phosphorene flexagons, we turn our attention to their electronic structure. HSE06-calculated \( E_g \) of these phosphorene flexagons and their parent phases are listed in Table 1, and their calculated electronic band structures and density-of-states (at the semi-local GGA-PBE level) are shown in the Fig. S2 and S3 of the ESI.† We note that we have carefully cross-checked with the more accurate hybrid HSE06 \( xc \) functional and found that the bands are only laterally shifted, and will not change the discussion or conclusions drawn here.

As listed in Table 1, HSE06-determined \( E_g \) of the phosphorene flexagons are found to be within the range of their parent phases (0.73–2.79 eV) and are generally larger in \( s\)-flexagons.
than in $t$-flexagons (with the exception for the $ho$-6F flexagons). This trend also can be rationalized by considering the parent phases, where $s$-flexagons are primarily composed of $\beta$- and $\gamma$-P which exhibit a larger $E_g$ value than $\alpha$- and $\delta$-P (found mainly in $t$-flexagons). Given that the presence of a larger portion of line defects in the $ho$-6F flexagons, this could account for $ho$-6F-$t$ to have an almost similar (but slightly larger) $E_g$ than $ho$-6F-$s$.

It is also interesting to note that the $E_g$ of $he$-4F-$s$ and $he$-4F-$t$ are also found to be fairly similar but much smaller when compared to the other $he$-flexagons. As reported in ref. 21, tensile strain on phosphorene is found to reduce $E_g$, and we have deliberated that this observation in the $he$-4F flexagons is a result of the large lattice strain induced to maintain its structural four-fold symmetry.

To capture the interplay of the s and p states of P in these unique phosphorene flexagons, we calculate and plot the partial electron densities at both the valence and conduction band edges (in Fig. S2 and S3 of the ESI†). At a glance, we observe that the electron densities at the conduction band edges are more delocalized as compared to that at the valence band edges for most flexagons. It is also found that the sp states are generally more localized at the constituent PNF flake centers and joint centers, regardless of the shape of the constituent PNFs (i.e. $t$- and $s$-PNFs).

Evidently, the electron densities in $he$-3F and $ho$-6F flexagons are found to be rather structural-site specific at both band edges – i.e. localizing on opposite atomic sites, highly depending on the shape of the constituent PNFs. We associate this observation to the presence of the large PNF flake centers and joint centers which may lower the symmetry and thus induce this site specific localization. We find that this may not apply for the flexagons with four-fold symmetry as their overall atomic structure very much resembles their parent phases and show bulk-like electron density distributions.

D. Simulated STM images for electron-density-guided nanopatterning and nanofabrication

To provide a better snapshot of this unusual electron density distribution mentioned above at the band edges, we further compute the simulated scanning tunneling microscopy (STM) images of the selected phosphorene flexagons within the Tersoff–Hamann scheme as implemented in Hive program, as shown in Fig. 3. Here, we integrate DFT-calculated local
density-of-states (LDOS) within an energy window of 1.0 eV below the Fermi level to capture the occupied states in each system. To aid discussion and comparison to the STM images for the considered flexagons, we have also shown the corresponding images of their parent phases in Fig. S6 of the ESI.†

There is a clear relation between the atomic arrangements, symmetry, and electron density patterns (as expressed in the simulated STM images) for these unique flexagons of phosphorene. In particular, for the he-flexagons (in the upper panel of Fig. 3), we find that the electron density patterns in the occupied states are a little more “vague”, i.e. showing a more gradual change between the connecting PNFs, especially for the s-type he-flexagons. This is in contrast to the ho-flexagons (in the lower panel of Fig. 3) where the electron density patterns show more details and characteristics of both the PNFs as well as the line defects connecting them in the ho-flexagons.

Refering to Fig. S6 of the ESI,† we can clearly see that the parent phases possess either “stripes” or “hexagonal” patterns in their electron density, lacking the diversity in electron density patterns seen in the assembled flexagons. We also note that the periodicity of the patterns in the parent phases are also much shorter (i.e. below the sub-nanometer range) than the considered flexagons. While it may not be apparent at the first instance, but the unique electron density patterns seen in the flexagons may assist as potential 2D templates where electron-density-guided nanopatterning and nanofabrication in complex organized nanoarchitectures are important.37–39

E. Extension to the phosphorene flexagon family: the top-down approach

In order to form symmetry-matching interfaces with known 2D nanomaterials with a six-fold symmetry (e.g. graphene, hexagonal-BN, and MoS2), it will be desirable design energetically stable he-flexagons with a corresponding 6-fold symmetry. As outlined above, via the “bottom-up” approach, it will not be possible to introduce a family of he-6F flexagons by construct.

So here, borrowing the intrinsic six-fold symmetry in β-phosphorene and the six-fold PNF motif in the ho-flexagons, we proceed to build a family of six-fold he-flexagons via the “top-down” approach. From pristine β-phosphorene, we begin to “cut-off” hexagonal-shaped parts and replace them with the six-fold PNF motif as expressed in the ho-6F flexagons. By varying the lateral distances between the six-fold PNF motifs and the introduction of γ-phosphorene to connect these motifs, we can generate this new extension to the he-flexagon family – namely, he-6F-β1, he-6F-β2, and he-6F-β3 (as shown in Fig. 4). Here, the superscript on the β label denotes the amount of the parent β-phosphorene in the flexagon structure.

This so-called “top-down” approach differs from the “bottom-up” approach introduced above by starting from the parent β-phosphorene rather than assembling PNFs in the latter case. This is also conceptually less similar to other reported “tiling” methods found in literature.31,37

Using eqn (1) and (3), we calculate both the $E_{coh}$ and $E_{form}$ for he-6F-β1, he-6F-β2, and he-6F-β3, and list these quantities and their $E_g$ in Table 2. Likewise, we find both $E_{coh}$ and $E_{form}$ to be energetically competitive to other pristine phosphorene and flexagons considered in this work (but not more than the parent β-phase and α-phosphorene). It is also clear that the stability of these he-6F flexagons improve and the $E_g$ increases as the amount of β-phase is increased. The simulated STM images corroborate with these trends, and can come in handy when designing electron-density-guided nanopatterning with symmetry-matching 2D heterointerfaces.

![Fig. 4](image-url)  Top-view of the atomic structures and STM images of phosphorene he-flexagons with a six-fold (6F) symmetry: he-6F-β1, he-6F-β2, and he-6F-β3. These 6F he-flexagons are an extension of the hetero-family in Fig. 1 by the so-called top-down approach.
molecular gas-phase synthesis methods, cyclically see in a kaleidoscope. Given the advent of new large-scale systems, very much mimicking symmetry patterns that one may typi-
cally see in a kaleidoscope. The calculated STM images of these new
flexagon structures show interesting electron density patterns,
where electron-density-guided nanopatterning and nanofabri-
cation in complex organized nanoarchitectures are important.

IV. Conclusion

In summary, building upon the assembly concepts of tiling phosphorene nanoflakes derived from four commonly reported parent phases (i.e. the $\alpha$, $\beta$, $\gamma$, and $\delta$-P) in combination with the lately reported low-energy defects in phosphorene, we extend the structural diversity in phosphor-
ene with new energetically competitive (and elastically stable)
flexagon structures. The calculated STM images of these new
flexagon structures show interesting electron density patterns, very much mimicking symmetry patterns that one may typically see in a kaleidoscope. Given the advent of new large-scale molecular gas-phase synthesis methods, these low-dimen-
sional phosphorene flexagons can be potential 2D templates where electron-density-guided nanopatterning and nanofabri-
cation in complex organized nanoarchitectures are important.

Acknowledgements

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**Supporting Information**

**Assembling Phosphorene Flexagons for 2D Electron-density-guided Nanopatterning and Nanofabrication**

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**Brief computational setup**

We perform first-principles density-functional theory (DFT) calculations with the projector-augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP). In our DFT calculations, periodic boundary conditions are enforced with a vacuum region of 15 Å along the out-of-plane direction for all 2D models used in this work. A planewave kinetic energy cutoff of 500 eV is employed, and for geometry optimization, the semi-local approximation to the exchange-correlation functional due to Perdew, Burke, and Ernzerhof (PBE) is used. To achieve a higher precision in our electronic band structure calculations, we have adopted the HSE06 hybrid DFT functional instead. A Γ-centered k-point grid of a reciprocal space sampling distance of 0.2 Å⁻¹ and 0.15 Å⁻¹ are used for all geometry optimization and electronic band structure calculations, respectively. All geometries are relaxed until the forces do not vary more than and 0.02 eV Å⁻¹.

**TABLE S1. The calculated elastic stiffness constants (in GPa) of selected phosphorene flexagons.**

<table>
<thead>
<tr>
<th>Structure</th>
<th>C_{11}</th>
<th>C_{12}</th>
<th>C_{22}</th>
<th>C_{44}</th>
<th>Born-Huang criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>he-2F-t</td>
<td>17.10</td>
<td>-1.33</td>
<td>61.75</td>
<td>16.03</td>
<td>○</td>
</tr>
<tr>
<td>he-3F-t</td>
<td>27.08</td>
<td>12.25</td>
<td></td>
<td></td>
<td>○</td>
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<tr>
<td>he-4F-t</td>
<td>63.29</td>
<td>-7.42</td>
<td></td>
<td></td>
<td>○</td>
</tr>
<tr>
<td>ho-6F-t</td>
<td>27.71</td>
<td>18.51</td>
<td></td>
<td></td>
<td>○</td>
</tr>
<tr>
<td>α-P</td>
<td>24.31</td>
<td>17.48</td>
<td>103.95</td>
<td>22.65</td>
<td>○</td>
</tr>
</tbody>
</table>

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FIG. S1. (Color online) Atomic structure of unit phosphorene nanoflakes with different symmetry (2-, 3-, 4-, and 6-fold) and shape (flat- \((t)\) and bowl-shaped \((s)\)), which used to build phosphorene flexagons.
FIG. S2. (Color online) Calculated band structures, density-of-states, and partial electron densities at valence band edge (bottom-left) and conduction band edge (bottom-right) of he-flexagons: (a) he-2F-t, (b) he-2F-s, (c) he-3F-t, (d) he-3F-s, (e) he-4F-t, and (f) he-4F-s. Red and blue lines are to show different vertical arrangement of adjacent flakes.
FIG. S3. (Color online) Calculated band structures, density-of-states, and partial electron densities at valence band edge (bottom-left) and conduction band edge (bottom-right) of ho-flexagons: (a) ho-2F-t, (b) ho-2F-s, (c) ho-4F-t, (d) ho-4F-s, (e) ho-6F-t, and (f) ho-6F-s. Blue lines are to show same vertical arrangement of adjacent flakes.
FIG. S4. (Color online) Calculated band structures, density-of-states, and partial electron densities at valence band edge (bottom-left) and conduction band edge (bottom-right) of $\beta$-P combination flexagons; (a) $he$-6F-$\beta^1$, (b) $he$-6F-$\beta^2$, and (c) $he$-6F-$\beta^3$. Red, blue, and purple lines are to show different vertical arrangements and consisting phases of adjacent flakes.

FIG. S5. (Color online) Calculated strain energy of phosphorene flexagons with respect to the applied strain; (a) $he$-2F-$t$, (b) $he$-3F-$t$, (c) $he$-4F-$t$, and (d) $ho$-6F-$t$. 
FIG. S6. (Color online) Simulated STM images and corresponding atomic positions of normal phosphorene phases; (a) \( \alpha \)-, (b) \( \beta \)-, (c) \( \gamma \)-, and (d) \( \delta \)-P.