Electronic Supplementary Information

Edge stabilities and growth kinetics of graphene-like two dimensional monolayers composed with Group 15 elements

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Contents

1 Tests of other possible basic edges.

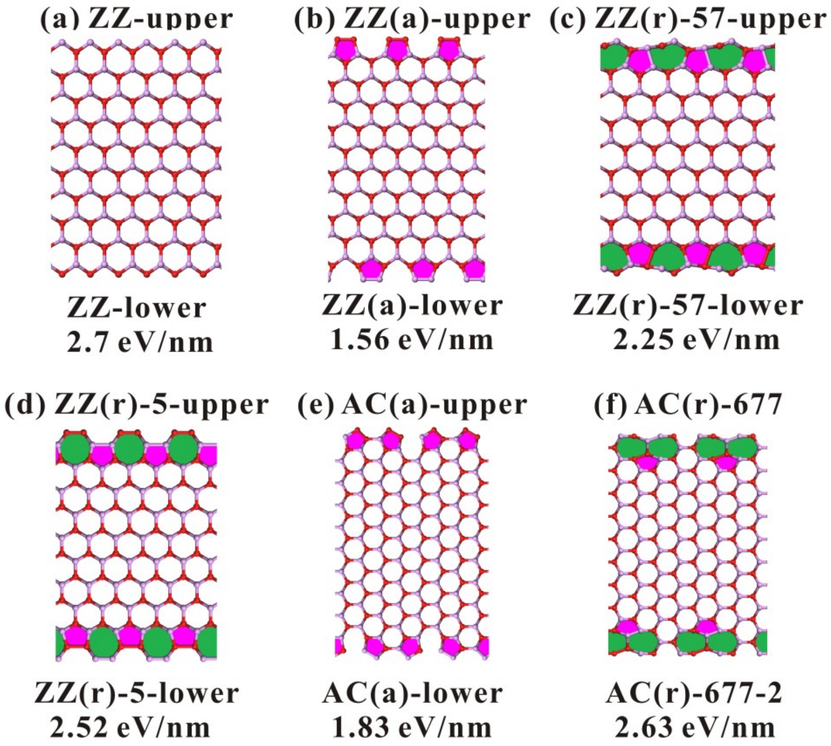

Fig. S1 Top view of various edges of free-standing β-structured P films. The formation energies are also listed under each panel. The upper/lower atoms are shown in light pink/red, the 5- and 7-member rings are highlighted with purple and green, respectively.

Quite different from graphene, there is a buckle ranging from 1.24 Å to 1.65 Å in two dimensional (2D) films constituted with β-structured Group 15 elements. To examine the possible influence of the buckle on the edge configurations and stabilities, here, we carefully examined the edges terminated with upper/lower atoms and calculated their formation energies. Take β-P as an example, the pristine zigzag edge can be terminated with upper or lower P (named as ZZ-upper and ZZ-lower, respectively, see Fig. S1a), which can be reconstructed by adding lower or upper atoms (named as ZZ(a)-upper and ZZ(a)-lower, respectively, see Fig. S1b). Edges can be reconstructed by adding atoms (Fig. S1b, e) or rotating bonds clockwise/anti-clockwise (Fig. S1c, d and f). There is no difference induced by adding upper/lower atoms (see Fig. S1b for zigzag type and Fig. S1e for armchair type). The rotation operation induces two different zigzag edges, ZZ(r)-57 and ZZ(r)-5, in which the difference lies in the distribution of the upper/lower atoms in the 5- and 7-membered rings. In ZZ(r)-57, the upper/lower atoms lie between 5- and 7-membered rings while in ZZ(r)-5 the atoms only lie in 5- or 7-membered rings. For the reconstructed armchair edges, there is no difference formed by bond rotation. In a word, ZZ-upper, ZZ(a)-upper, ZZ(r)-57-upper, ZZ(r)-5-upper, AC(a)-upper, and AC(r)-677 should be exactly the same as ZZ-lower, ZZ(a)-lower, ZZ(r)-57-lower, ZZ(r)-5-lower, AC(a)-lower, and AC(r)-677-2 because there is no constriction in direction perpendicular to the film plane. The identical edges can also be verified by their formation energies. Therefore, only seven basic edges are considered in the main text (Fig. 1c).

2 Relaxed geometries of free-standing and Au(111)-surface supported triangular β-P flakes.

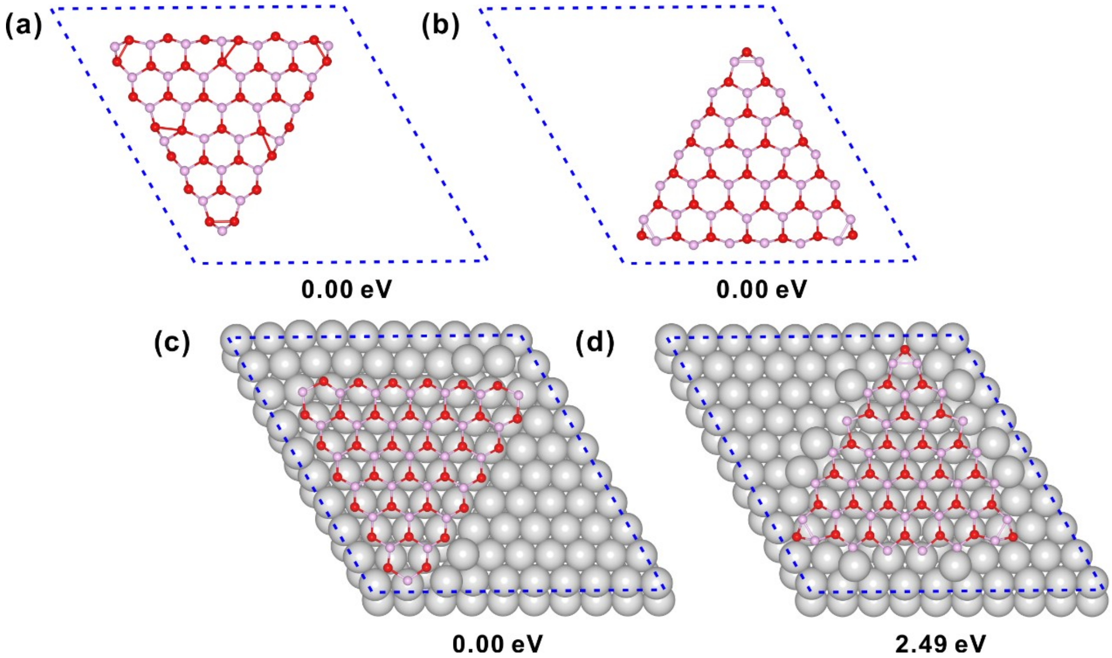

Fig. S2 Relaxed geometries of free-standing and Au(111)-surface supported triangular β-P flakes. The flakes are terminated with lower (a, c) and upper (b, d) P atoms, respectively. The metal substrate is modeled with double-layered Au(111) with the bottom one fixed. The upper/lower P and Au atoms are shown in purple/red and grey, respectively. The relative energies are also shown under each panel.

To further study the possible influence of the metal substrate and the buckle on edge stabilities, both freestanding and Au(111)-surface supported triangular β-P flakes are constructed. The flakes are terminated with lower (Fig. S2a,c) and upper (Fig. S2b,d) P atoms, respectively. The relative energies are also shown under each panel. No energy difference can be observed in free-standing P flakes. For metal supported flakes, the energy is 2.49 eV lower in the flake terminated with lower P atoms.

3 Chemical potential of hydrogen as function of temperature and partial pressure.

The chemical potential of hydrogen is highly dependent on the temperature and partial pressure, which can be written as,[1,2]

$$2\mu_{H} = E_{H2} - kTln(kT/p \times g \times \zeta_{trans} \times \zeta_{rot} \times \zeta_{vib}) \qquad (1)$$

where E_{H2} is DFT calculated energy of H_2 (-6.76 eV), k is Boltzmann constant, p is partial pressure of H_2, and g is the degeneracy degree of the electron energy level. ζ_{trans}, ζ_{rot} and ζ_{vib} are the partition functions for translational, rotational, and vibration motions, respectively. Suppose the temperature equals to 1000 K, the pressure of H_2 varies from 10^{-4} mbar to 10^{2} mbar, μ_{H} falls in the range [-4.74 eV, -4.15 eV]. To mimic the real experiment, we substitute -4.74 eV into equation 2 in the main text to calculate formation energies of H-terminated edges.

4 Formation energies of β-P NRs calculated with PBE and vdw-D3 functionals.

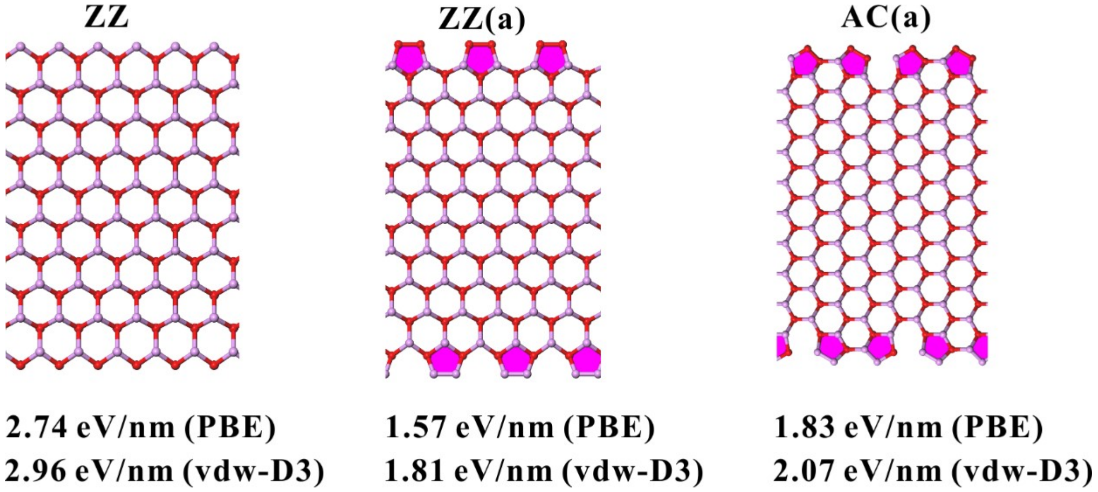

Fig. S3 Edge energies of β-P NRs calculated with PBE and vdw-D3 functionals. The β-P NRs are terminated with ZZ, ZZ(a) and AC(a), respectively.

Three β-P NRs terminated with ZZ, ZZ(a) and AC(a) were constructed. Their formation energies calculated with PBE and vdw-D3 functionals were also listed under each ribbon. The edge energy difference calculated with both functionals is 0.22, 0.24, and 0.24 eV/nm, respectively, indicating both functionals can be used to characterize the relative stabilities of β-P NRs terminated with various edges. Therefore, PBE functional was adopted in this work to save calculation cost.

5 Phonon band dispersions and densities of vibrational states of β-P NRs terminated with ZZ and ZZ(a) edges.

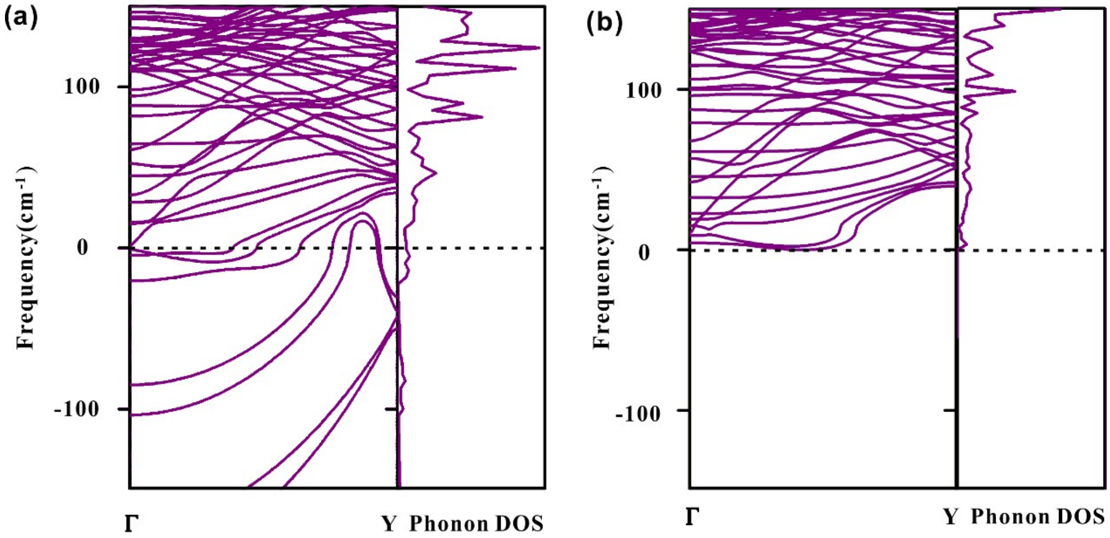

Fig. S4 Phonon band dispersions and densities of vibrational states of β-P NRs terminated with ZZ (panel a) and ZZ(a) (panel b) edges. The absence of imaginary frequency in ZZ(a)-terminated nanoribbons illustrate its kinetics stability.

6 Edge energy and charge distribution comparisons between graphene and β-structured Group 15 elements.

To explore the possible influence of buckle on edge stabilities, we present the comparison of edge energy and charge distributions of graphene and β-structured Group 15 elements in Fig. S3. From Fig. S3a, we can see that all the edge energies of graphene are much larger than those of Group 15 elements. What's more, the types of edges with the lowest-energy in graphene and Group 15 elements are different: the edge ZZ(r)-57 is the most stable one in graphene, while in films constructed with Group 15 elements, ZZ(a) is the most stable one in P, As, Sb film and pristine AC is the most stable one in Bi film. From the charge distribution in graphene and β-P (Fig. S3b) we can see that π bonds can be formed on the edges of ZZ(r)-57, AC and AC(r) in graphene (the upper row in panel b), however, in β-P nanoribbons, obvious π bonds can only be observed on ZZ(a) and AC(a) (see the lower row in panel b). Such difference in charge distribution can only be attributed to the lateral buckle difference.

Therefore, both the formation of π bonds and the buckle influence the edge stabilities of Group 15 element films.

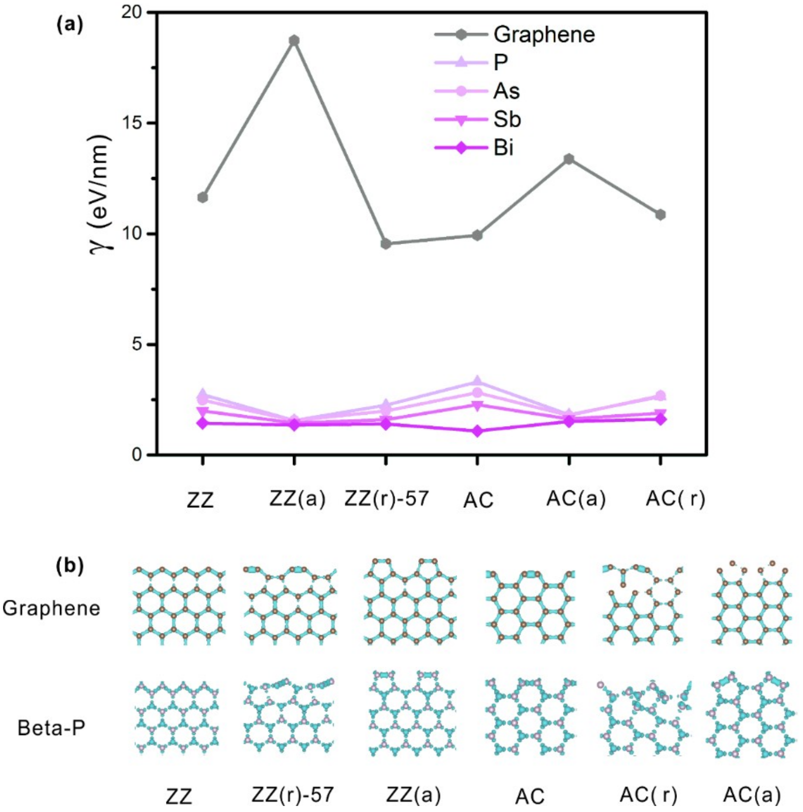

Fig. S5 (a) Edge energies (γ) of graphene (hexagon), P (up triangle), As (circle), Sb (down triangle) and Bi (diamond). (b) Comparison of charge distributions in graphene and β-P nanoribbons constructed with different bare edges. The isosurfaces for graphene and β-P are 0.28 e/Å^3 and 0.11 e/Å^3, respectively.

7 Charge distributions on possible stable edges of bare and H-terminated P and Bi.

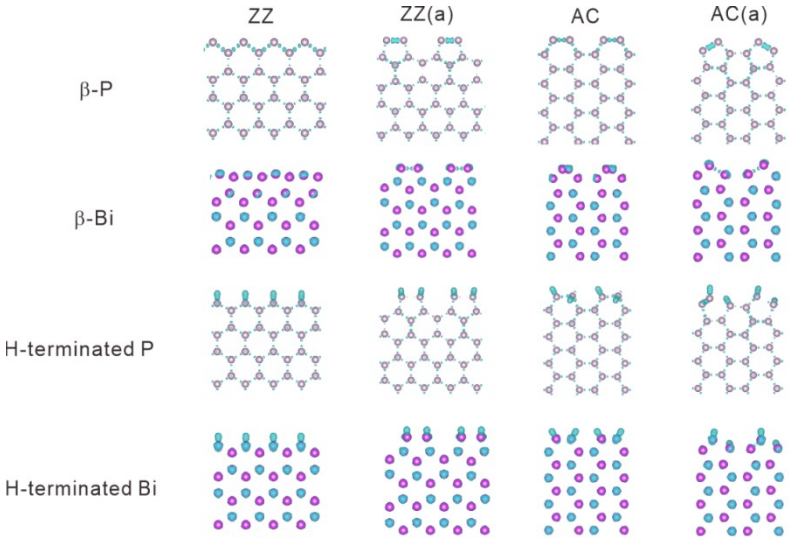

Fig. S6 Charge distributions on possible stable edges of bare and H-terminated P and Bi. The isosurfaces for P and Bi are 0.12 e/Å^3 and 0.053 e/Å^3, respectively.

8 Possible atomistic structures, the binding energy and free energy in growth of ZZ(a) and AC(a) edge of β-P film.

The relative binding energies (E_b) and formation free energy, ΔG can be calculated from $E_{m+1} - E_m$ and $E_m - E_0 - m\mu_P$, respectively.[3] E_0, E_m and E_{m+1} is the energies of original nanoribbon and nanoribbons with m and (m+1) atoms added, μ is the chemical potential of β-P film.

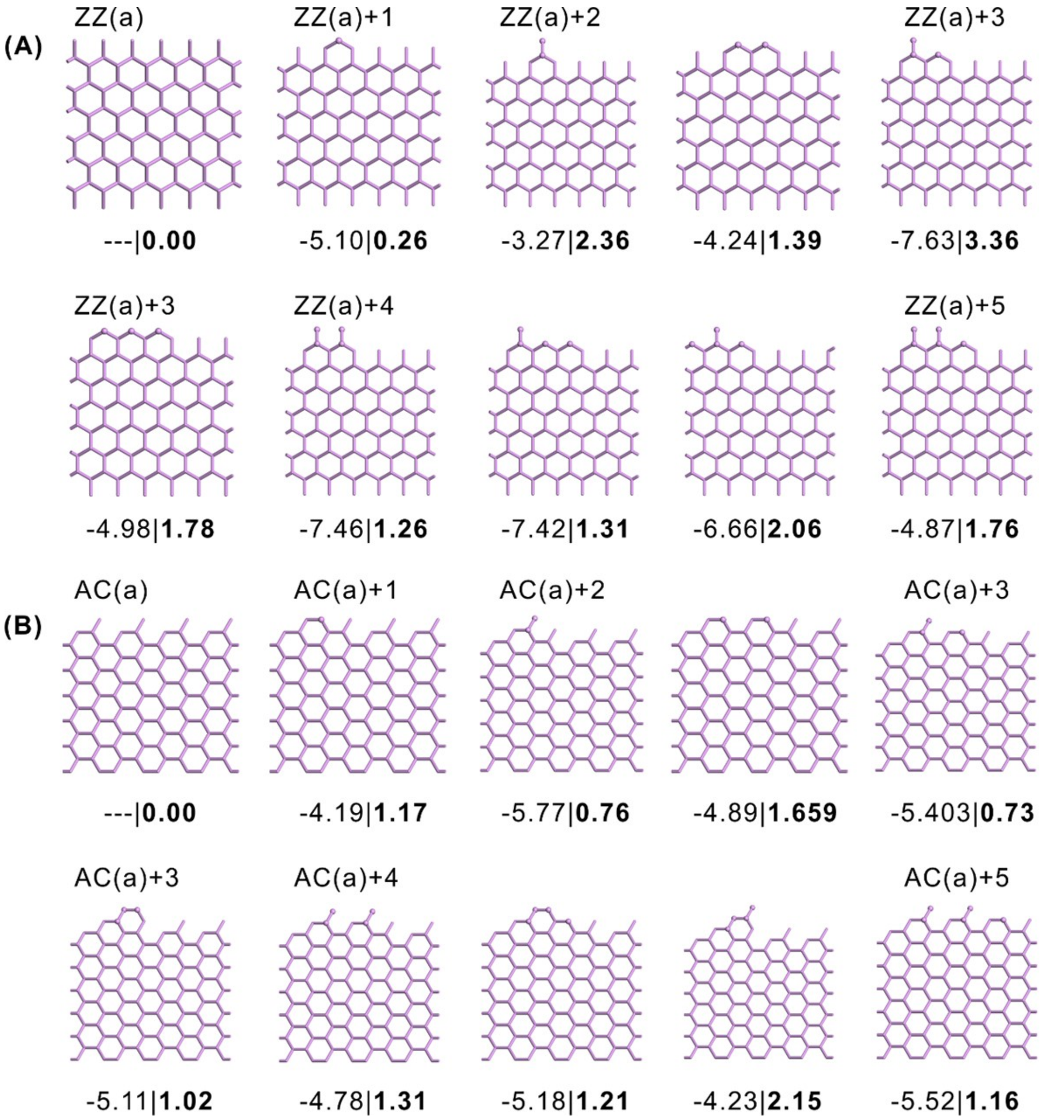

Fig. S7 Possible atomistic structures, the binding energy E_b (eV) and formation free energy ΔG (bold, eV) of ZZ(a) and AC(a) edge as newly P atom incorporates into the front edge.

9 Band structures and density of states of monolayer β-P film.

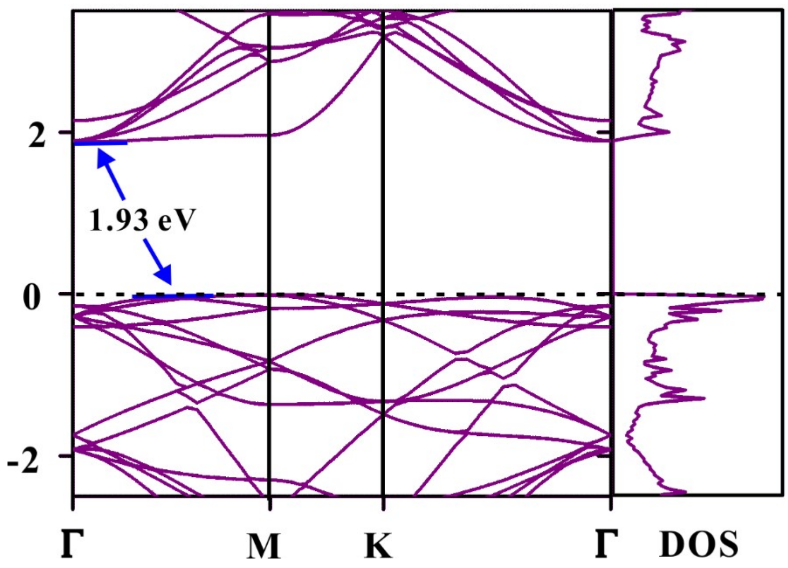

Fig. S8 Band structures and density of states of monolayer β-P.

10 Electronic and magnetic properties β-P nanoribbons constructed with different bare edges

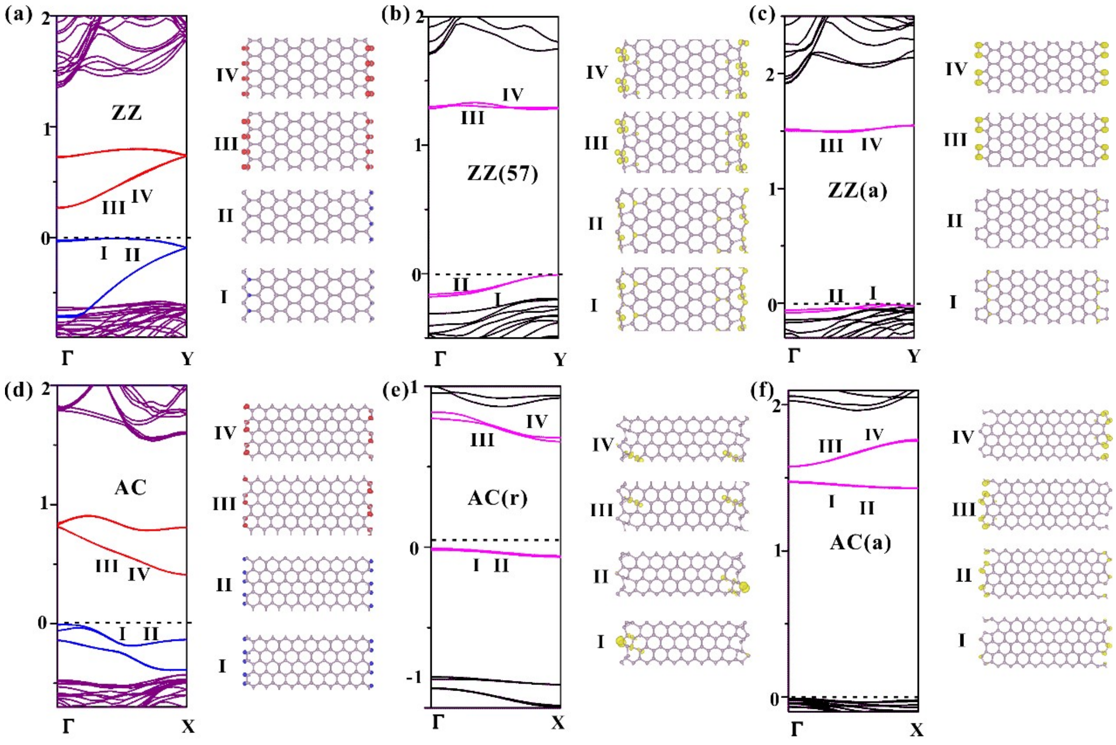

Fig. S9 (a-f) Band structures of β-P NRs and partial charge density of specific bands at the Γ point. The Fermi level (dashed lines) is set to zero. Γ and X/Y denotes the center and the boundary of the first Brillouin zone, respectively. The isosurface is 0.005e/Å^3. It clearly presents that the variations in electronic and magnetic properties can be attributed to the edge states in β-P NRs.

References

1. C. G.Van de Walle and J. Neugebauer, *Phys. Rev. Lett.* **2002,** 88, 066103.

2. K..Reuter and M.Scheffler, *Phys. Rev. B* **2001,** 65, 035406.

3. V. I. Artyukhov, Y. Liu and B. I. Yakobson, *P. Natl. Acad. Sci.* **2012**, 109, 15136-15140.