Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Materials

Electronic Properties of the Layered Phosphorus Heterostructures

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Table S1. Calculated interfacial properties of the four phosphorus allotropes. *a* and *b* are the lattice constants of structures (denoted in Fig. S1), respectively. E_g is fundamental band gap. Both this work and reference[1] apply DFT-PBE methods but different basis sets. PW: plane wave; NAO: numerical atomic orbitals.

		phase	*a* (Å)	*b* (Å)	E_g (eV)
theo.	PW (This work)	*α*	4.62	3.35	1.05
		β	3.30	3.30	1.93
		γ	3.25	5.47	0.44
		δ	5.56	5.46	0.50
	NAO[1]	*α*	4.53	3.36	0.90
		β	3.33	3.33	1.98
		γ	3.41	5.34	0.50
		δ	5.56	5.46	0.45
expt.		*α*[2]	4.39	3.33	…
		β[3]	3.28	3.28	1.01

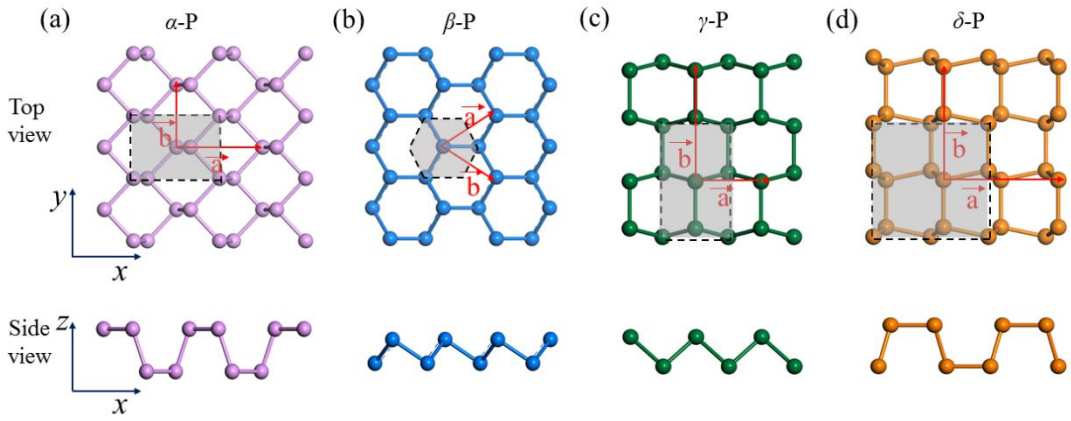

Fig. S1. Top and side views of the schematic structures of the monolayer (a) *α*-P, (b) *β*-P, (c) *γ*-P and (d) *δ*-P. The Wigner-Seitz cells are as shown as in gray shadows.

The size of bandgap changes when different lattice constants are applied, since the bandgap in the layered phosphorus is sensitive to tensile. However, the two key features remain: 1) direct band gap at the Γ point, 2) type-II band alignment with CBM comes from *β*-P and VBM comes from *α*-P.

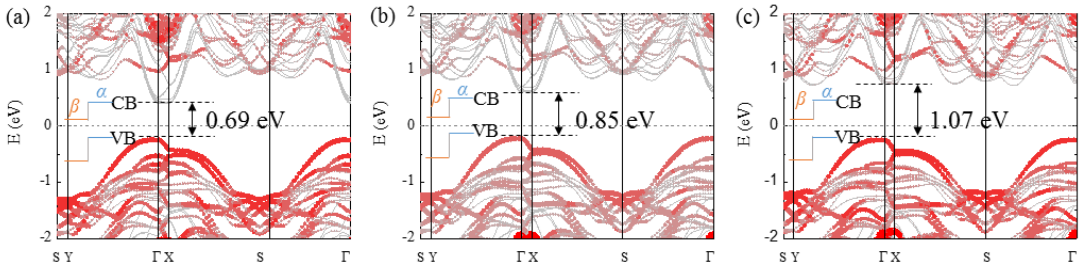

Fig. S2. Band structures of the α/β vdW heterostructures with the lattice constants fixed to that of (a) α-P, (b) averaged over α-P and β-P, and (c) β-P, respectively. The Fermi level is at zero energy. The gray line is the band structure of the whole system. The red color represents contribution from the α-P layer, and its size is proportional to the weight.

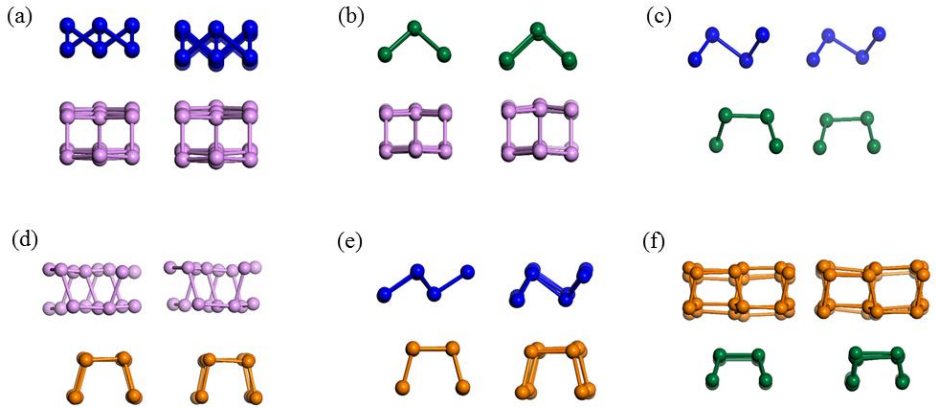

Fig. S3. Comparison of the geometry of the vertical heterostructures before (left) and after (right) the molecular dynamical simulations: (a) α/β, (b) α/γ, (c) β/γ, (d) α/δ, (e) β/δ, and (f) γ/δ. The purple, blue, green, and yellow balls represent α-P, β-P, γ-P, and δ-P, respectively.

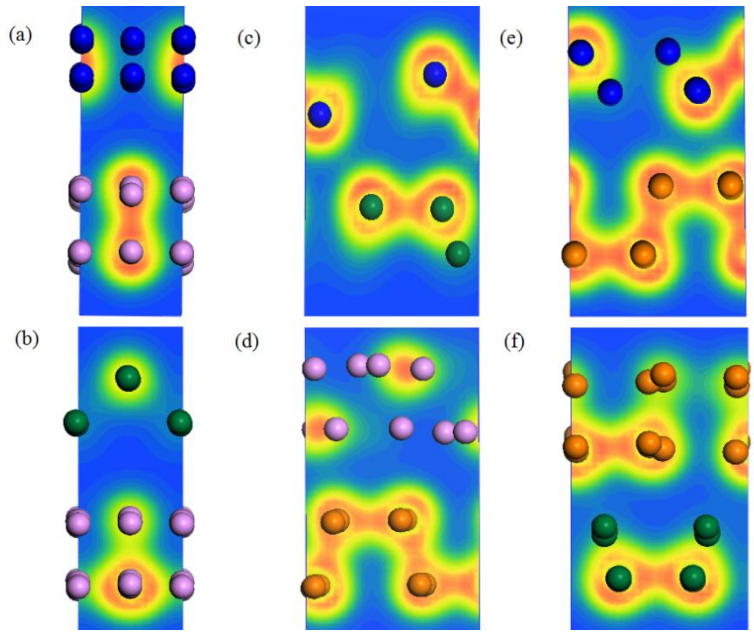

Fig. S4 Contour plots of total electron distribution of the (a) *α*/*β*, (b) *α*/*γ*, (c) *β*/*γ*, (d) *α*/*δ*, (e) *β*/*δ*, and (f) *γ*/*δ* vdW heterostructures. The purple, blue, green, and yellow balls represent the *α*-P, *β*-P, *γ*-P and *δ*-P atoms, respectively.

As well explained in literature,[4] the commonly used vdW correction functional can be classified into 3 types: 1) PBE+D2; 2) D3 and TS; and 3) vdw-optB86b and vdw-DF2. To estimate the effects of applying different vdW correction methods, we compared the optimized geometry and electronic properties of the *α*/*β* vdW heterostructure using PBE+D2, D3 and vdw-optB86b functionals. The formation energy of the *α*/*β* vdW heterostructures calculated using these three functionals are -0.028, -0.032, -0.046 eV/atom, respectively. The vdw-optB86b functional gives the strongest binding feature in the checked system. The optimized geometries of the *α*/*β* vertical structure are overall similar, with interlayer distances of 3.32, 3.37, and 3.42 Å respectively. As shown in Fig. S5, the size of the band gap of the α/β vdW heterostructure varies with different functionals, ranging from 0.56 ~ 0.69 eV. However, the direct band gap (Γ point) and the type II band alignment remain. Therefore, we believe that the key electronic structure features of the checked system are not sensitive to different approaches to treat vdW interaction.

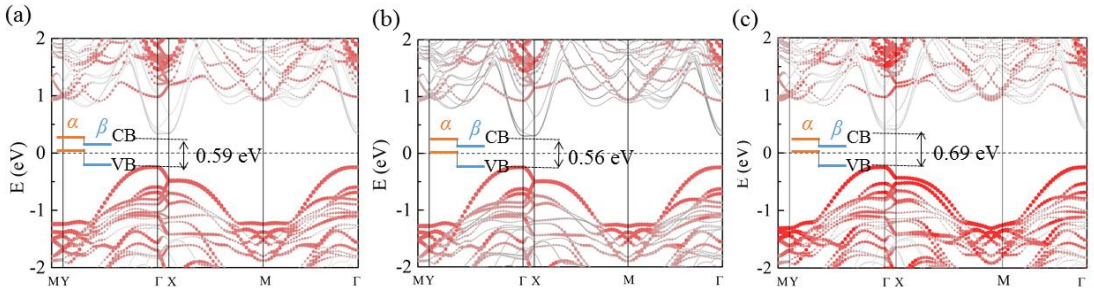

Fig. S5 Band structures of the α/β vdW heterostructure based on (a) PBE+D2, (b) D3, (c) vdw-optB86b approaches. The Fermi level is at zero energy. The gray line is the band structure of the whole system. The red color represents contributions from the α-P layer and its size is proportional to the weight.

The calculated work function of α-P, β-P, γ-P, and δ-P is 4.58 eV, 5.79 eV, 4.82 eV, and 4.37 eV, respectively. In the Fig. S6, we find that the band alignments in (c) and (e) are conflict with those from the band structures in Fig. 3(b) and (e), while the other four in (a), (c), (d) and (f) are in agreement with front calculations. The difference of band alignment decided by work function and band structure comes from the coupling between the adjacent layers is not included in the former. Thus, using the work function of isolated 2D layers to decide the band match of their heterostructures is not reliable.

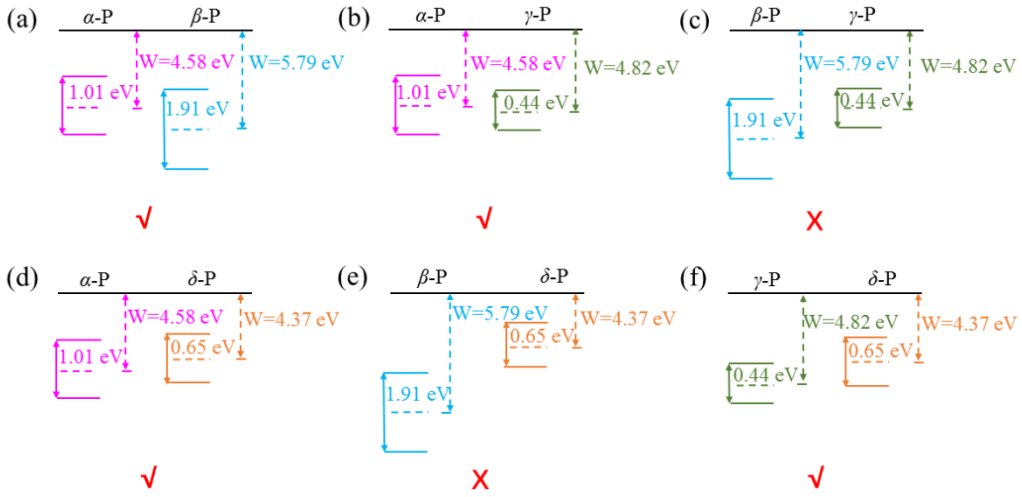

Fig. S6. Band alignments of the four structural phases of layered phosphorus decided by the work functions. *W* is the work function. The purple, blue, green, yellow colors represent α-P, β-P, γ-P, and δ-P, respectively.

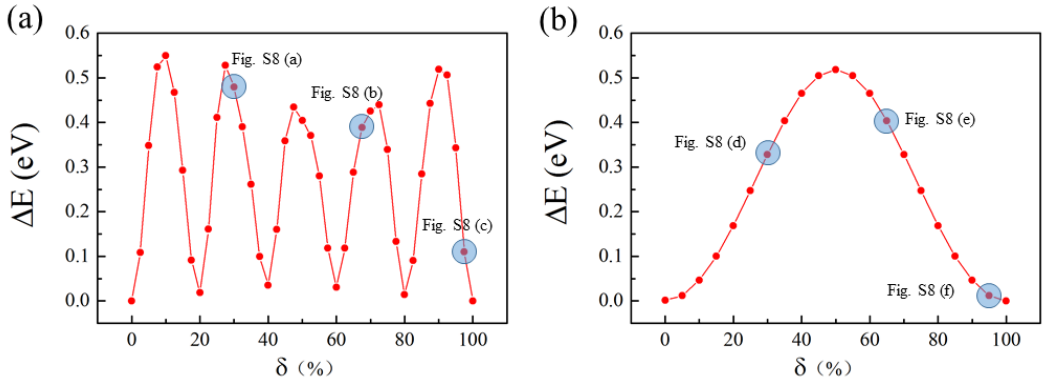

Fig. S7 Evolution of the total energy as a function of displacement $\delta_{x/y}$ of α-P layer relative to β-P layer in (a) *x* and (b) *y* direction, taking the origin at the lowest energy configuration.

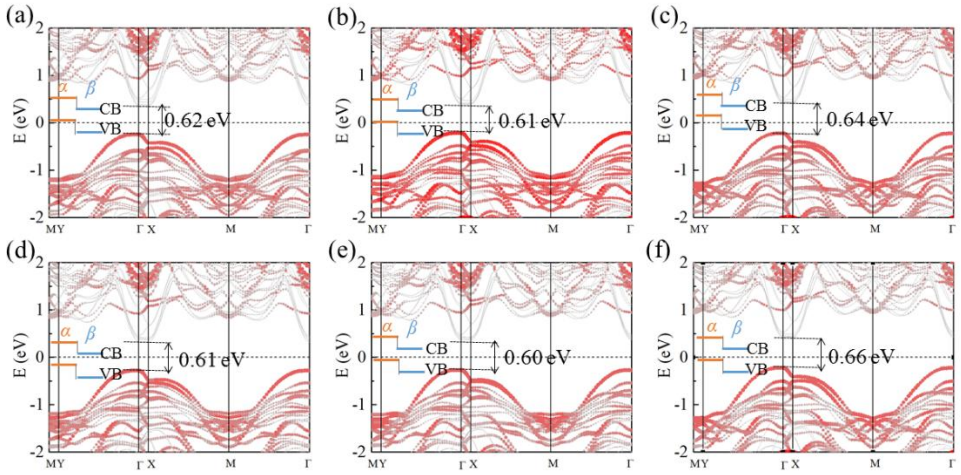

Fig. S8 Band structures of the α/β vdW heterostructure with displacement of α-P layer relative to β-P layer in (a-c) *x* direction and (d-f) *y* direction, as denoted in Fig. S7. The Fermi level is at zero energy. The gray line is the band structure of the whole system. The red color represents contributions from the α-P layer and its size is proportional to the weight.

References:

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