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

Supporting Information:

Robust Indirect Band Gap and Anisotropy of Optical Absorption in B-doped Phosphorene

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Supporting Figures:

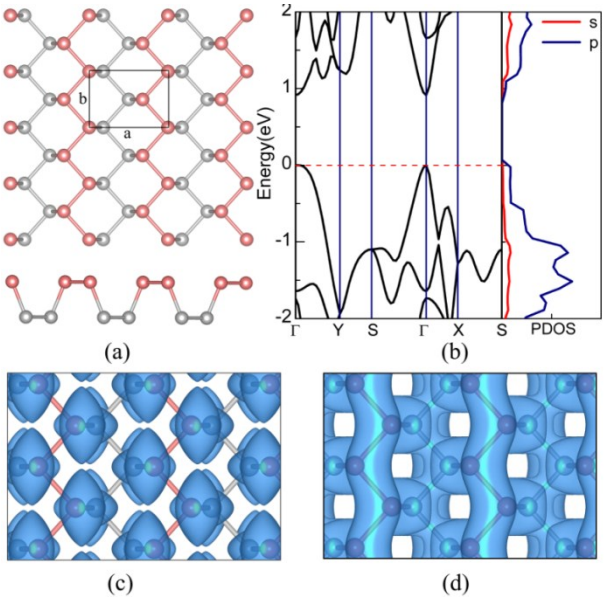

Fig. S1 Geometrical structure (a) electronic properties of pure phosphorene: (b) band structures and partial density of states (PDOS). (c) and (d) are charge density distributions of the VBM and

CBM. The Fermi level is set to zero. The isosurface is set to 0.02 e/Å^3.

Table S1. Binding energy E_b (eV) and band gap E_g (eV) of the corresponding phosphorenes. (d) or (in) denotes a direct or an indirect band gap. Due to the large calculations, the band gaps of certain B-doped phosphorenes are explored by using the HSE06 approach.

Phosphorenes		E_b	$E_{g\text{-DFT}}$	$E_{g\text{-HSE06}}$
Pure		-	0.909 (d)	1.592 (d)
$P_{47}B_1$		0.749	0.718 (in)	1.368 (in)
$P_{46}B_2$-(*m*-1)	$P_{46}B_2$-(2-1)	0.776	0.825 (in)	1.501 (in)
	$P_{46}B_2$-(3-1)	0.729	0.750 (in)	
	$P_{46}B_2$-(4-1)	0.737	0.711 (in)	
	$P_{46}B_2$-(5-1)	0.740	0.800 (in)	
	$P_{46}B_2$-(6-1)	0.779	0.681 (in)	
	$P_{46}B_2$-(7-1)	0.752	0.649 (in)	
	$P_{46}B_2$-(8-1)	0.760	0.659 (in)	
	$P_{46}B_2$-(9-1)	0.807	0.749 (in)	1.412 (in)
	$P_{46}B_2$-(10-1)	0.689	0.785 (in)	1.439 (in)
	$P_{46}B_2$-(11-1)	0.700	0.841 (in)	1.493 (in)
	$P_{46}B_2$-(12-1)	0.743	0.803 (in)	
$P_{45}B_3$-(*m*-*n*-1)	$P_{45}B_3$-(3-2-1)	0.818	0.695 (in)	1.350 (in)
	$P_{45}B_3$-(5-3-1)	0.703	0.799 (in)	1.487 (in)
	$P_{45}B_3$-(14-8-1)	0.733	0.636 (in)	
	$P_{45}B_3$-(13-12-1)	0.748	0.843 (in)	

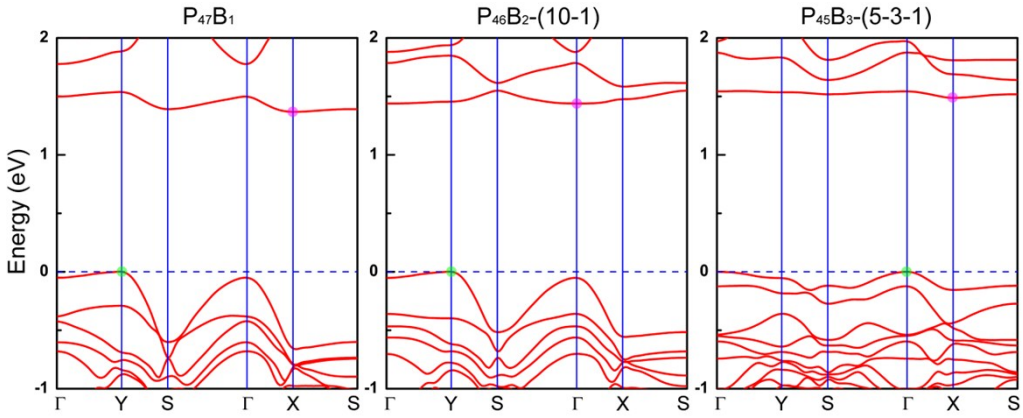

Fig. S2 Electronic band structures of the B-doped phosphorenes predicted by the HSE06 method. The highest occupied levels are set to 0 and denoted by blue dash lines. The VBM and CBM are marked out by light green and pink dots.

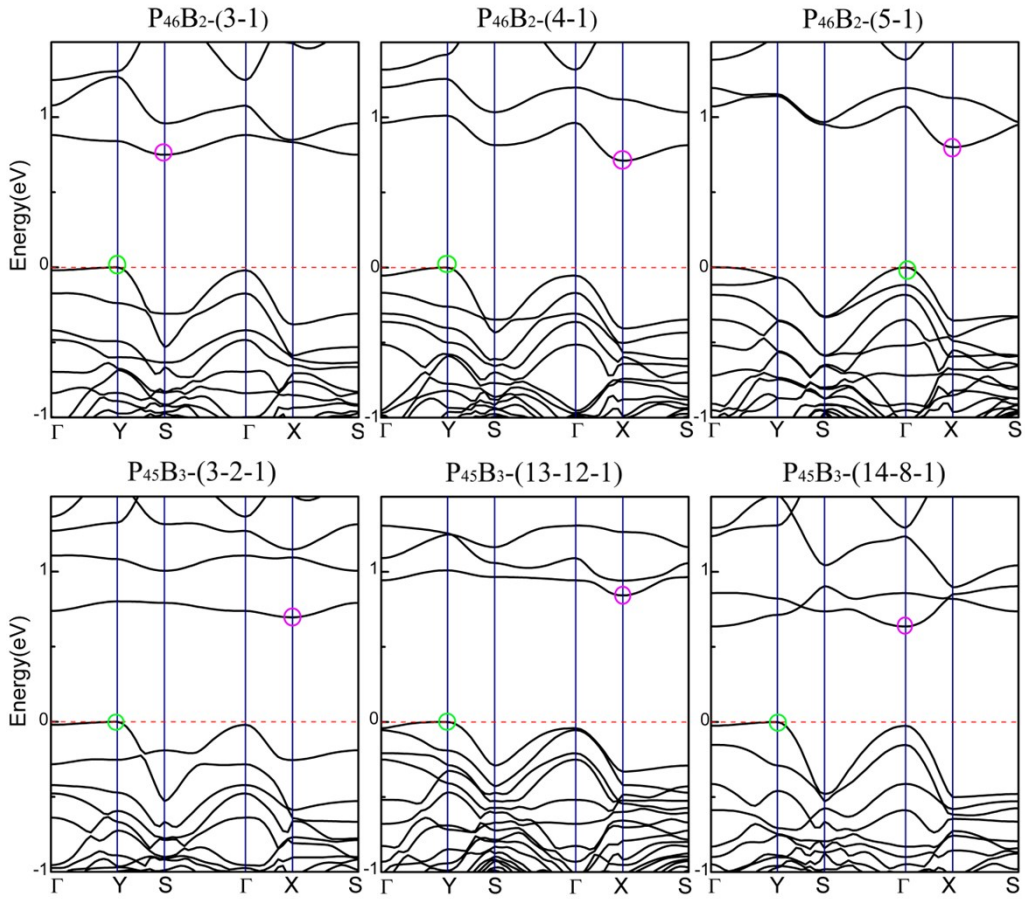

Fig. S3 Electronic band structures of the $P_{46}B_2$-(*m*-1) and $P_{45}B_3$-(*n*-*m*-1). The highest occupied levels are set to 0 and denoted by red dash lines. Light green and pink circles represent the VBM and CBM.

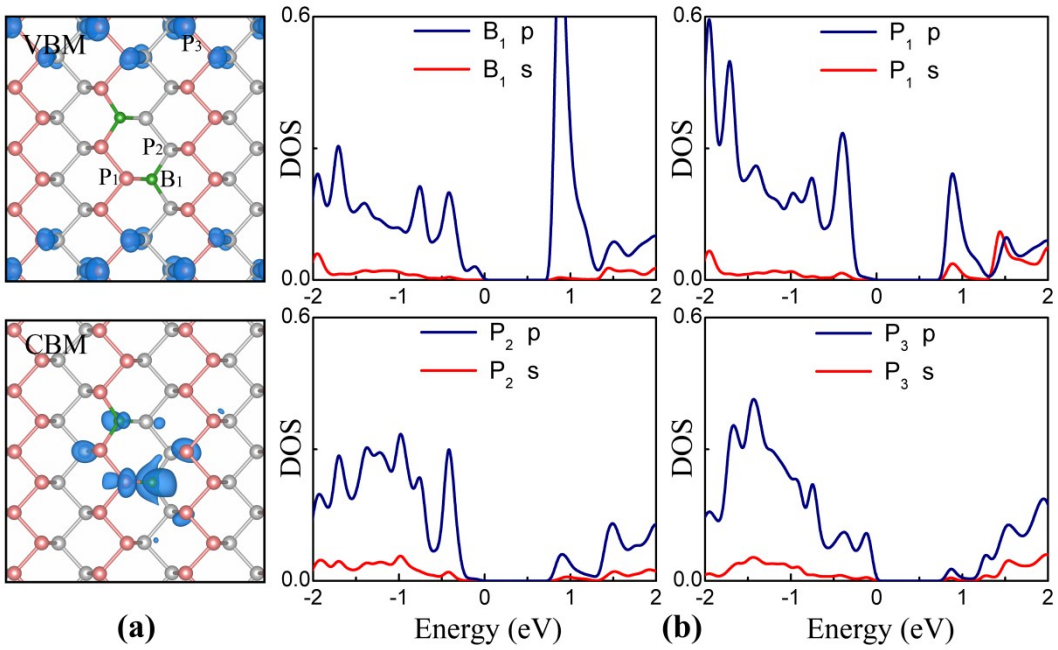

Fig. S4 (a) Spatial charge densities at the VBM and CBM, and (b) partial density of states of the $P_{46}B_2$-(11-1). The isosurface is set to 0.02 e/Å^3.

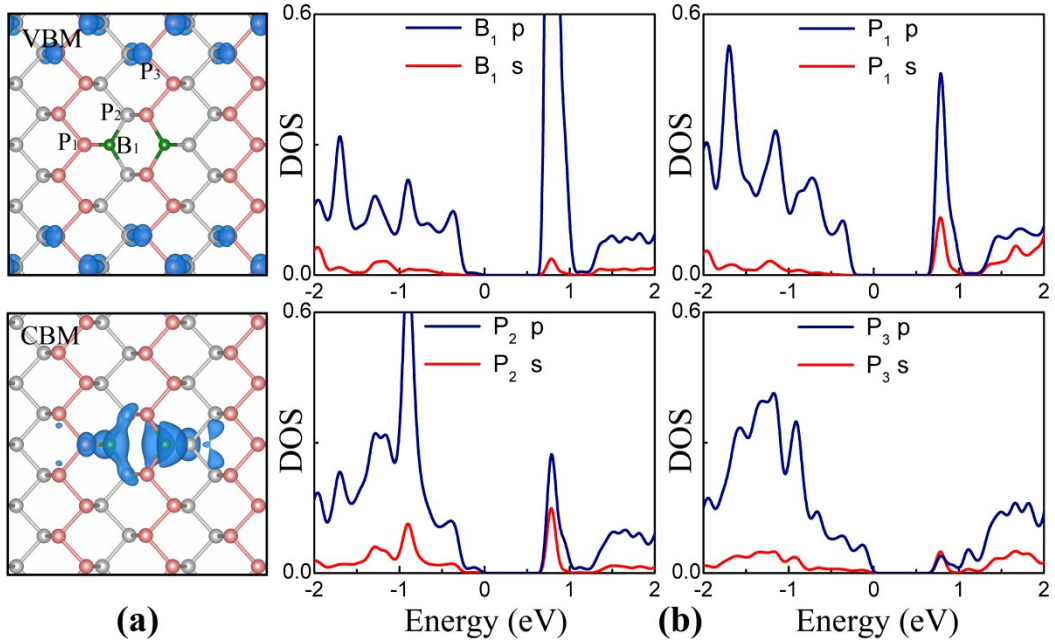

Fig. S5 (a) Spatial charge densities at the VBM and CBM, and (b) partial density of states of the $P_{46}B_2$-(9-1). The isosurface is set to 0.02 e/Å^3.

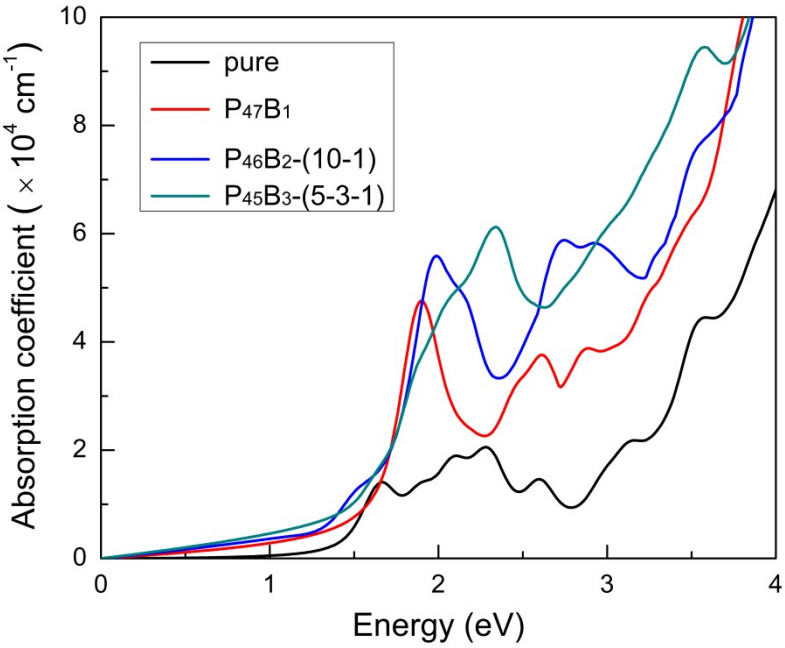

Fig. S6 Total optical absorption spectra of pure and B-doped phosphorenes.

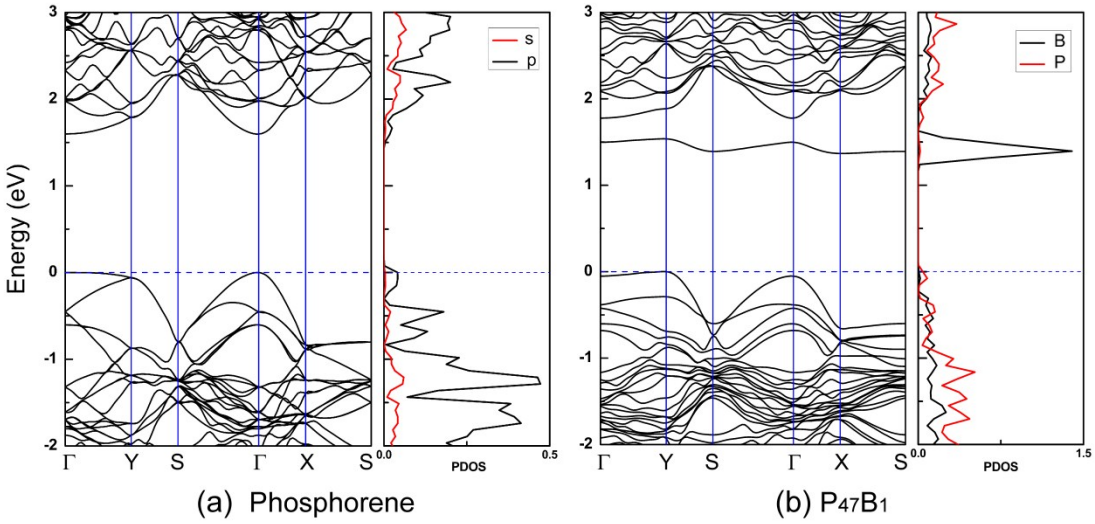

Fig. S7 Band structure and partial density of state (PDOS) for (a) pure phosphorene and (b) $P_{47}B_1$. The highest occupied level is set to zero. The PDOS averaged to one P or B atom is displayed in the right panel.

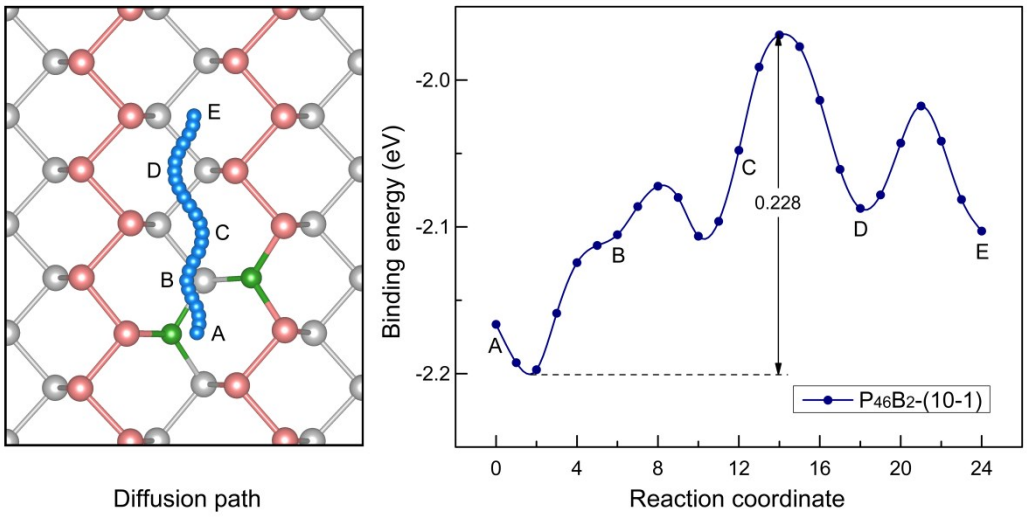

Fig. S8 Diffusion path of Li atom on $P_{46}B_2$-(10-1) and corresponding binding energy along the given diffusion path A→B→C→D→E.