Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for:

Semiconductor-to-Metal Transition from Monolayer to Bilayer Blue Phosphorous Induced by Extremely Strong Interlayer Coupling: A First-principles Study

Dan-Dong Wang,[†] Xin-Gao Gong,[†‡] Ji-Hui Yang[†‡*]
†Key Laboratory of Computational Physical Sciences (Ministry of Education), Institute of Computational Physics, Fudan University, Shanghai 200433, China
‡Shanghai Qi Zhi Institute, Shanghai 200230, China
*corresponding author
Email: jhyang04@fudan.edu.cn

1. The Slater-Koster parameters for bilayer blue-P structure with A_1B_{-1} stacking in the on-site and adjacent-sites unit cell.

	1-s	1-p_y	1-p_z	1-p_x	2-s	2-p_y
1-s	5.5213245	0	0	0	1.4450006	0.9566837
1-p_y	0	71.042139	0	0	-0.9566837	1.949396
1-p_z	0	0	16.296367	0	1.1466826	1.6121623
1-p_x	0	0	0	3.079527	1.6570244	2.3296701
2-s	1.4450006	-0.9566837	1.1466826	1.6570244	5.5213245	0
2-p_y	0.9566837	1.949396	1.6121623	2.3296701	0	71.042139
2-p_z	-1.1466826	1.6121623	1.3620916	-2.7923464	0	0
2-p_x	-1.6570244	2.3296701	-2.7923464	-0.7406743	0	0
3-s	0	0	0	0	0	0

Table S1. The Slater-Koster parameters in on-site unit cell (0,0,0). The '1-s' means the s orbit of the 1st atom, and the other ones could be derived similarly. The unit is eV.

	1-s	1-p_y	1-p_z	1-p_x	2-s	2-p_y
1-s	0	0	0	0	0	0
1-p_y	0	0	0	0	0	0
1-p_z	0	0	0	0	0	0
1-p_x	0	0	0	0	0	0
2-s	1.445001	1.913367	1.146683	-8.3E-07	0	0
2-p_y	-1.913367	-2.08571	-3.224324	2.35E-06	0	0
2-p_z	-1.146683	-3.224324	1.362092	1.41E-06	0	0
2-p_x	8.3E-07	2.35E-06	1.41E-06	3.294432	0	0
3-s	1.445001	0.808444	-1.536727	1.400265	0	0

Table S2. The Slater-Koster parameters in unit cell (0,1,0). The '1-s' means the s orbit of the 1st atom, and the other ones could be derived similarly. The unit is eV.

	1-s	1-p_y	1-p_z	1-p_x	2-s	2-p_y
1-s	0	0	0	0	1.445001	0.956683
1-p_y	0	0	0	0	-0.956683	1.949398
1-p_z	0	0	0	0	1.146682	1.612161
1-p_x	0	0	0	0	-1.657025	-2.32967
2-s	0	0	0	0	0	0
2-p_y	0	0	0	0	0	0
2-p_z	0	0	0	0	0	0
2-p_x	0	0	0	0	0	0
3-s	0	0	0	0	0	0

Table S3. The Slater-Koster parameters in unit cell (1,0,0). The '1-s' means the s orbit of the 1st atom, and the other ones could be derived similarly. The unit is eV.

	1-s	1-p_y	1-p_z	1-p_x	2-s	2-p_y
1-s	0	0	0	0	0	0
1-p_y	0	0	0	0	0	0
1-p_z	0	0	0	0	0	0
1-p_x	0	0	0	0	0	0
2-s	0	0	0	0	0	0
2-p_y	0	0	0	0	0	0
2-p_z	0	0	0	0	0	0
2-p_x	0	0	0	0	0	0
3-s	0	0	0	0	0	0

Table S4. The Slater-Koster parameters in unit cell (1,1,0). The '1-s' means the s orbit of the 1st atom, and the other ones could be derived similarly. The unit is eV.

	1-s	1-p_y	1-p_z	1-p_x	2-s	2-p_y
1-s	0	0	0	0	0	0
1-p_y	0	0	0	0	0	0
1-p_z	0	0	0	0	0	0
1-p_x	0	0	0	0	0	0
2-s	0	0	0	0	0	0
2-p_y	0	0	0	0	0	0
2-p_z	0	0	0	0	0	0
2-p_x	0	0	0	0	0	0
3-s	0	0	0	0	0	0

Table S5. The Slater-Koster parameters in unit cell (1, -1,0). The '1-s' means the s orbit of the 1st atom, and the other ones could be derived similarly. The unit is eV.

2. The total energy in Blue-P with A_1B_{-1} stacking.

Function	PBE	LDA	PBE+SCAN+rVV10	LDA+SCAN+rVV10
Metal	-5.472	-6.193	-10.288	-45.099
Semiconductor	-5.461	--	-10.300	-45.074

Table S6. Calculated total energies of semiconducting and metallic phases of bilayer blue-P with A_1B_{-1} stacking based on different functionals. The unit is eV/atom. Note that, the semiconducting phase is not stable using the LDA functional.

3. Molecular dynamics simulations in Blue-P with A_1B_{-1} stacking.

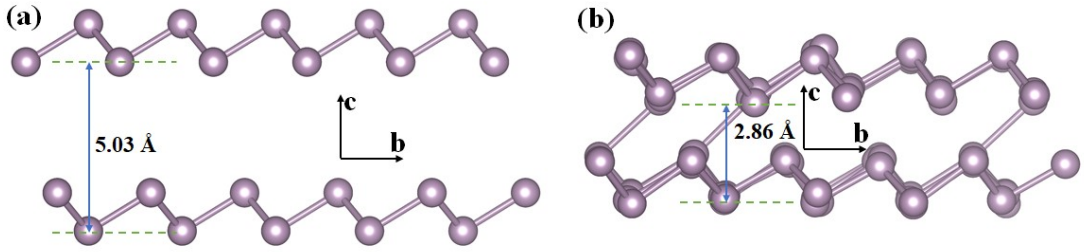

Figure S1. Structures of bilayer blue-P with A_1B_{-1} stacking before and after MD simulations at T=300 K. Note that, the semiconducting phase automatically transforms into the metallic phase after 5 ps. The MD simulations are performed using PBE+SCAN+rVV10 functionals. A 4x4 supercell is used and the lattice constants are allowed to relax.