Supporting information for

Stacking dependent electronic structure and optical properties of bilayer black phosphorus

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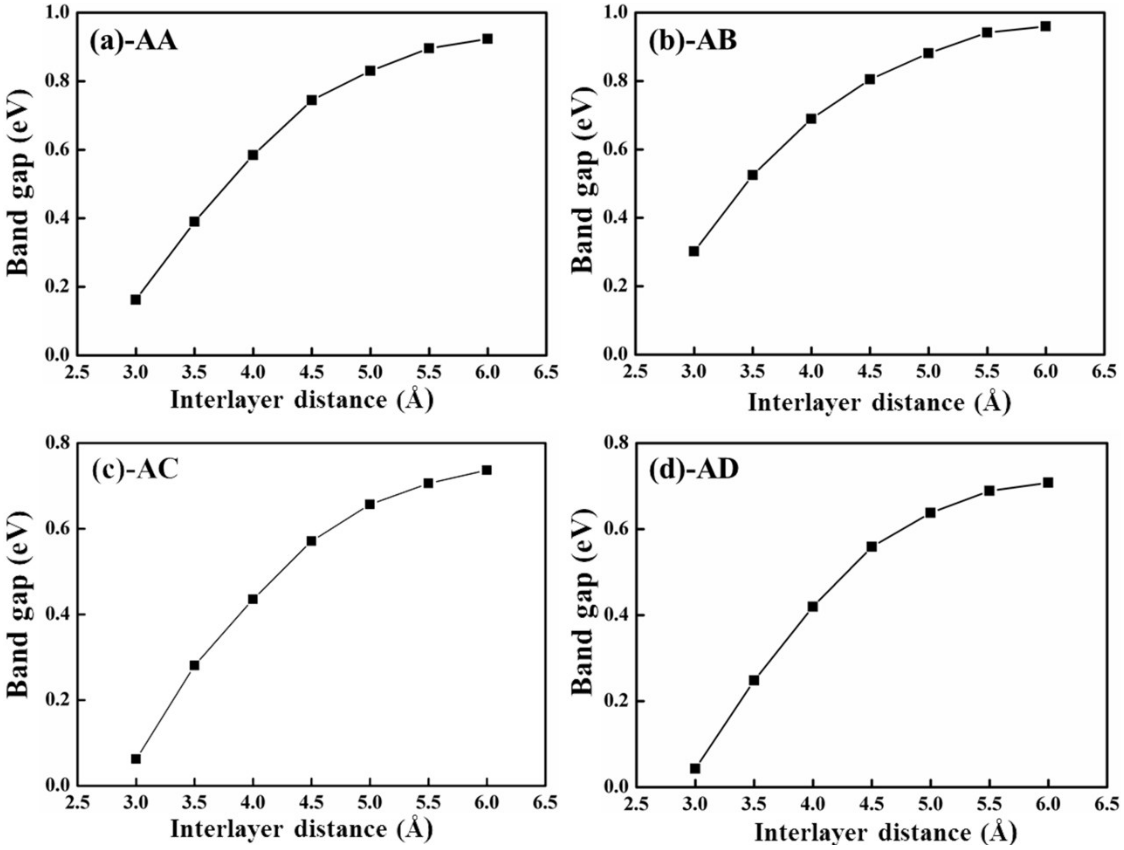

Figure S1. (a)-(d) The relation between the energy band gap and the interlayer distance for four stacked bilayer black phosphorus. These results are from DFT-PBE calculation.

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Tight-binding models

We employed the tight-binding models for monolayer and bilayer black phosphorus proposed by Rudenko *et al.*[1,2] The Hamiltonian for monolayer black phosphorus is

$$H = \sum_{i \neq j} t_{ij}^{\text{P}} c_i^\dagger c_j \ , \tag{1}$$

where t_{ij}^{P} is the intra-layer hopping terms between site *i* and *j* and $c_i^\dagger$ (c_j) is the creation (annihilation) operator of electrons at site *i* (*j*). Note that equation (1) does not contain onsite terms, meaning that electrons at different sites have the same onsite energy.[2] For bilayer black phosphorus, additional interlayer hopping terms are included to account for the interlayer interaction, and the Hamiltonian is in the following form

$$H = \sum_{i \neq j} t_{ij}^{\text{P}} c_i^\dagger c_j + \sum_{i \neq j} t_{ij}^{\perp} c_i^\dagger c_j \ , \tag{2}$$

where $t_{ij}^{\perp}$ is the interlayer hopping term between site *i* and *j* at different layers.

We considered eleven intra-layer hopping terms for monolayer, namely t_1 to t_{11}, which corresponded to a maximum distance of 5.551 Å. It should be clarified that t_1 to t_5 and t_7 to t_{11} of our model are exactly the same ten hopping terms of by Rudenko's model[2] while t_6 is an additional term which seems to be omitted by the authors. t_1 and t_2 are shown in Figure S2 (a), while other terms are not shown for clarity. The initial guess for the hopping terms was taken from Rudenko's paper, while their final values were determined through least square fitting. The fitting took the data of the highest valence and the lowest conduction bands from density functional calculations as the reference, as demonstrated in Figure S2 (b), and was implemented with the optimization subroutines from the SciPy[3–5] package. The fitted hopping terms are summarized in Table S1. As we took band structure from density functional calculation for fitting while Rudenko *et al* chose *GW* band structure, the dominant hopping terms of our results, i.e. t_1 and t_2, have smaller absolute values than that of Rudenko's.

For bilayer black phosphorus, we fixed the eleven intra-layer hopping terms to that of monolayer black phosphorus and introduced six interlayer hopping terms, namely t'_1 to t'_6, for AA-, AC-and AD stacking pattern and four interlayer terms for AB-stacking pattern, as demonstrated in Figure S3 (a)-(d). The interlayer hopping terms were then optimized through least square fitting to band structure of the highest two valence bands and the lowest two conduction bands from density functional theory calculation, as demonstrated in Figure S3 (e)-(h). The fitted hopping terms are summarized in Table S2. It should be clarified that the physical meanings of the interlayer hopping terms in this work are different from that of Rudenko's due to the different stacking patterns.

To determine the dependence of tight-binding band structure on the interlayer hopping terms, we varied the dominant term from its half to its double for four stacking patterns, and plotted the corresponding band structures in Figure S4 (a)-(d). The dominant terms are t'_1 for AA-, AC- and AD- and t'_4 for AB-stacked bilayer black phosphorus respectively, which is obvious from Table S2.

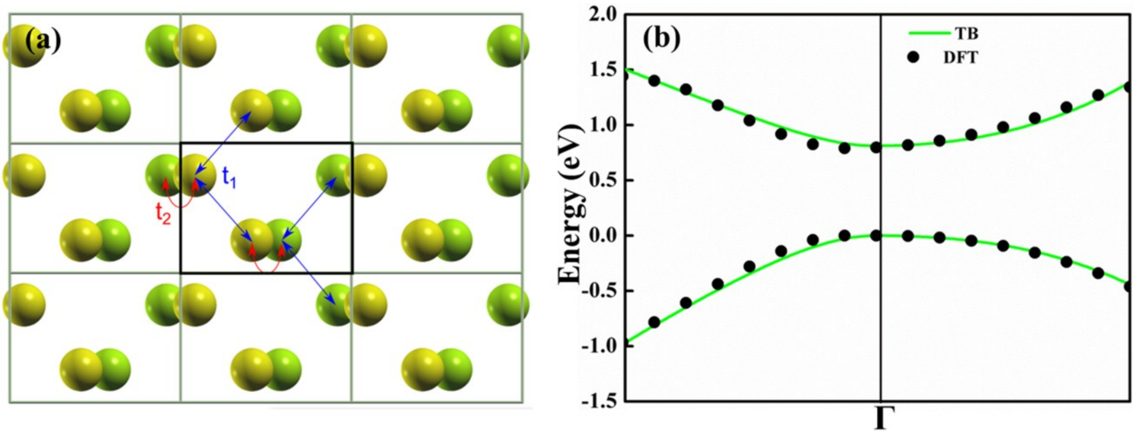

Figure S2. (a) Illustration of the intra-layer hopping terms for monolayer black phosphorus. Atoms belonging to different sublayers are colored in yellow and green respectively, while chemical bonds are not depicted for clarity. A 3×3 supercell is shown in order to demonstrate the hopping terms between atoms from different primitive cells. Only the t_1 and t_2 terms are given, with blue and red arrows respectively. For clarity, hopping terms of higher orders or are equivalent to t_1 and t_2 are not shown. (b) Band structures calculated within tight-binding model (TB) and density functional theory (DFT). The k-points are sampled in the vicinity of the Γ point along the X→Γ→Y k-path in the first Brillouin zone.

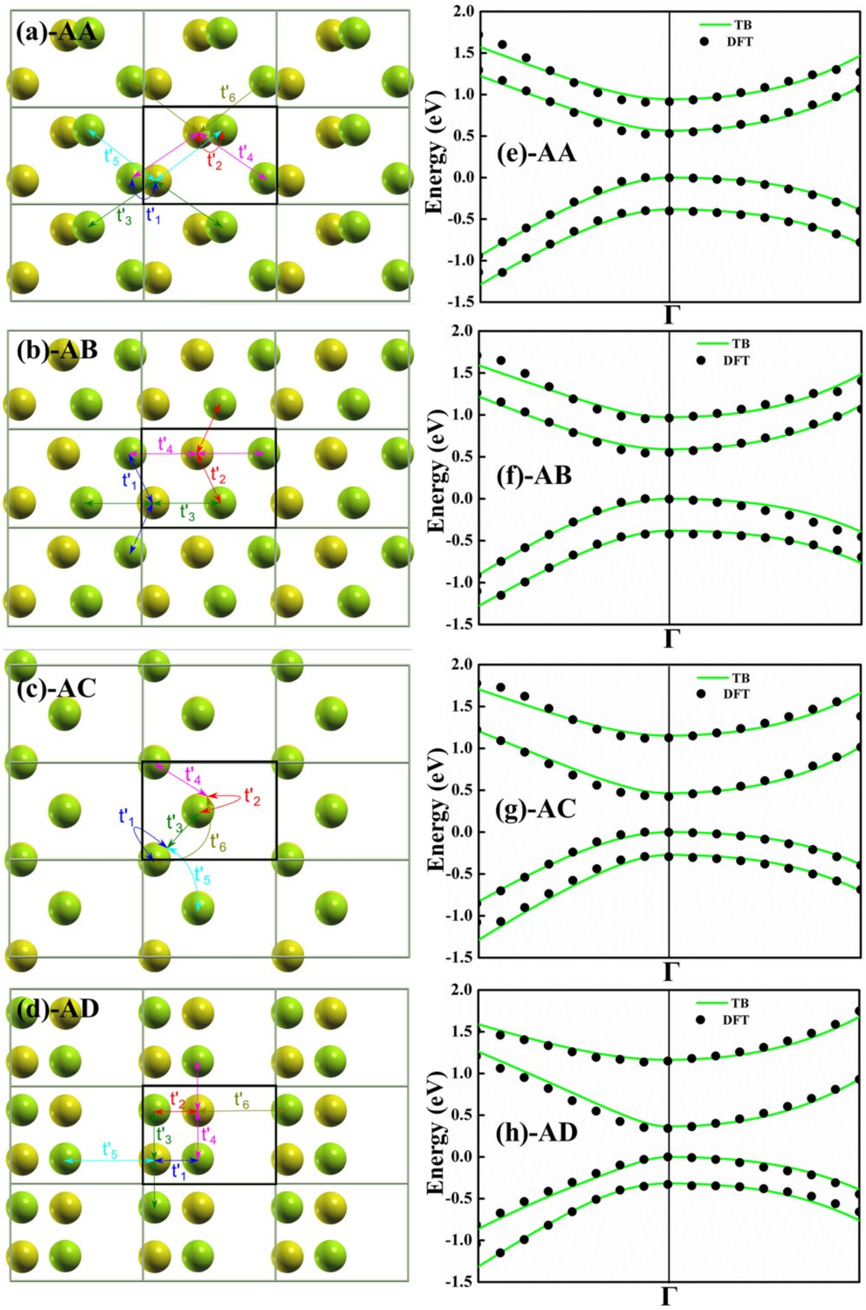

Figure S3. (a)-(d) Illustration of interlayer hopping terms for AA-, AB-, AC- and AD-stacked bilayer black phosphorus, respectively. For clarity, only the atoms near interface of the two layers, i.e. the upper sublayer of the bottom layer and the lower sublayer of the top layer, are shown and colored in yellow and green respectively. (e)-(h) Band structures calculated within tight-binding model (TB) and density functional theory (DFT). The k-points are sampled in the vicinity of the Γ point along the X→Γ→Y k-path in the first Brillouin zone.

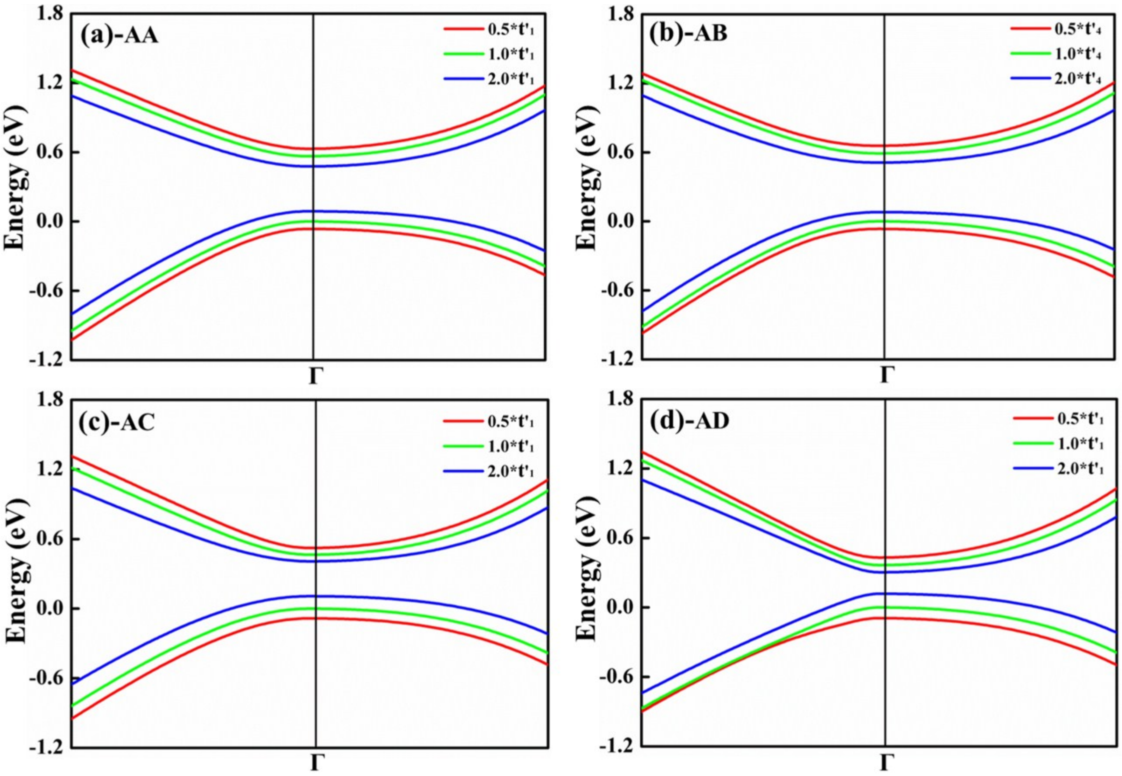

Figure S4. (a)-(d) Band structures from tight binding model calculations by varying the dominant interlayer hopping term from the half to the double of its original value for AA-, AB-, AC- and AD-stacked bilayer black phosphorus, respectively. The dominant interlayer hopping terms are t'_1 for AA-, AC- and AD- and t'_4 for AB-. The k-points are sampled in the vicinity of the Γ point along the X→Γ→Y k-path in the first Brillouin zone.

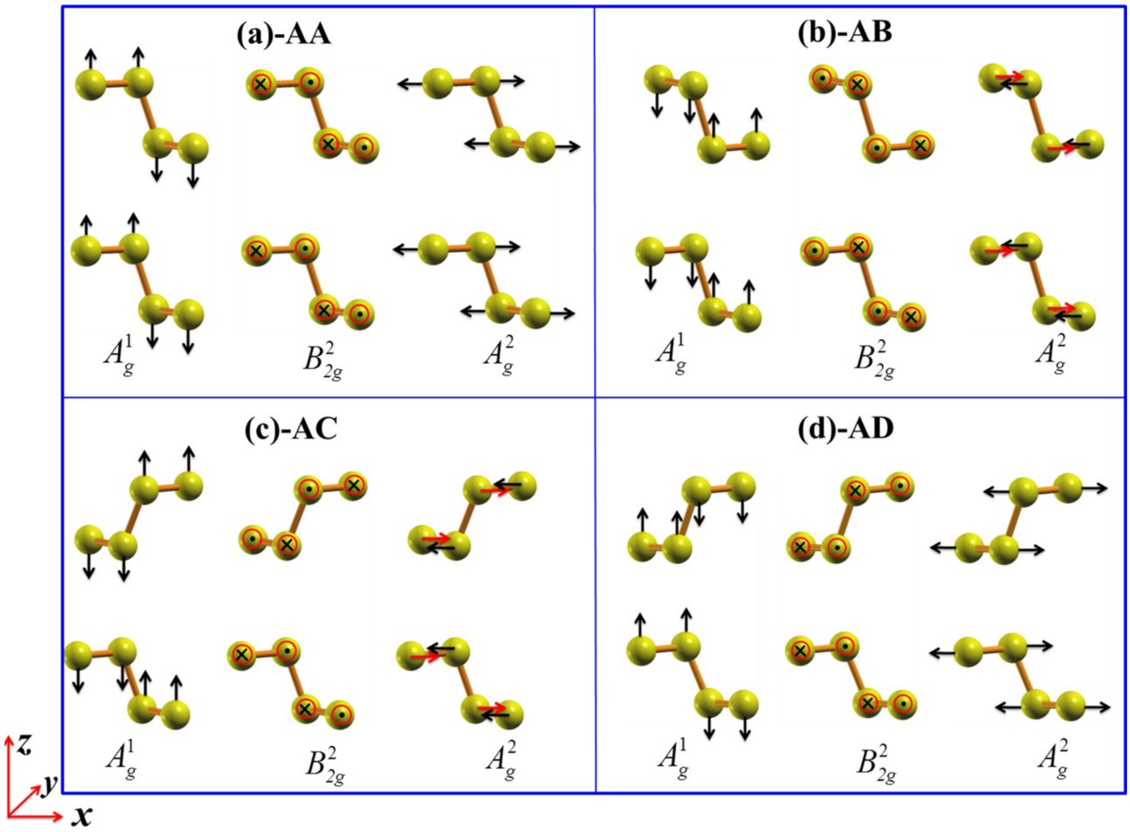

Figure S5. Demonstration of vibration modes A_g^1, B_{2g}^2 and A_g^2 in the AA-, AB-, AC- and AD-stacked bilayer black phosphorus. The "⊗" sign denotes the atomic displacement along the +*y* direction, following the convention in electrodynamics theory.

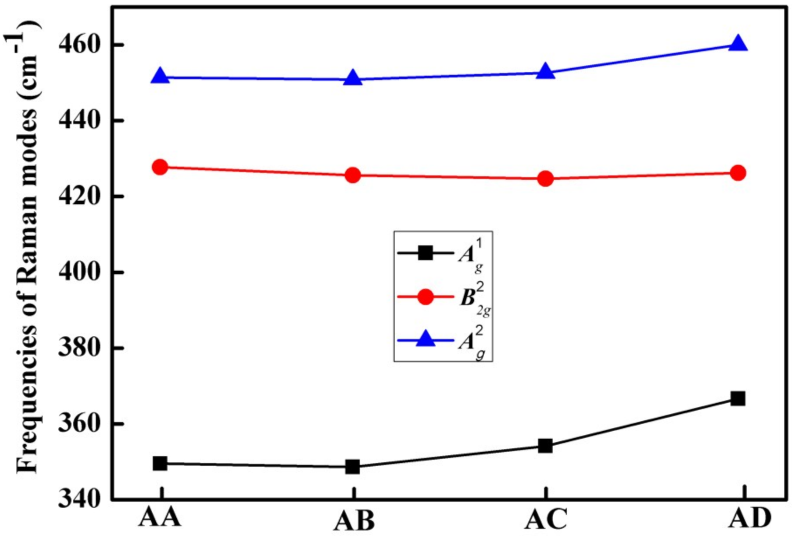

Figure S6. Stacking-dependent Raman frequency in bilayer black phosphorus with different stacking orders.

Table S1. Intra-layer hopping terms (t_i) for monolayer black phosphorus. d and N denotes the distances between the corresponding atoms and the coordination number at the given distance, respectively. t_1 and t_2 of the hopping terms are shown in Figure S2. Hopping terms are in eVs and distances are in angstroms.

NO.	t_i	d	N
1	-1.162	2.232	4
2	2.826	2.246	2
3	-0.210	3.351	4
4	-0.119	3.393	4
5	-0.015	3.492	8
6	-0.047	4.034	4
7	0.097	4.253	2
8	-0.058	4.425	4
9	0.176	5.238	2
10	-0.018	5.415	4
11	0.091	5.551	8

Table S2. Interlayer hopping terms (t'_i) for AA-, AB-, AC- and AD-stacked bilayer black phosphorus. d and N denotes the distances between the corresponding atoms and the coordination number at the given distance, respectively. The hopping terms are shown in Figure S3. Hopping terms are in eVs and distances are in angstroms.

	AA			AB			AC			AD		
NO.	t'_i	d	N	t'_i	d	N	t'_i	d	N	t'_i	d	N
1	0.719	3.897	1	-0.128	4.023	2	0.956	4.033	1	0.979	4.021	1
2	0.065	3.894	1	0.128	4.023	2	0.012	4.033	1	0.501	4.027	1
3	-0.177	4.712	2	0.071	4.233	2	0.099	4.577	1	0.130	4.097	2
4	0.163	4.712	2	-0.448	4.233	2	0.099	4.590	1	0.130	4.096	2
5	-0.014	4.768	2	——	——	-	0.132	4.627	1	-0.021	4.839	1
6	0.026	4.768	2	——	——	-	0.132	4.640	1	-0.335	4.829	1

Table S3. Frequencies (cm-1) of Raman modes of bilayer black phosphorus with AA-, AB-, AC-, AD-stacked.

Mode	AA	AB			AC	AD
			Exp.[6]	*Theo.*[7]		
A_g^1	349.5	348.6	362.0	346.7	354.1	366.6
B_{2g}^2	427.7	425.6	438.5	419.9	424.7	426.2
A_g^2	451.4	450.9	467.0	450.3	452.6	460.0

References

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