Electronic Supporting Information

Electronic Properties of Red and Black Phosphorous: the Potential Application as Photocatalysts

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S1. Computational methods

In order to determine which functional can provide the best fit to experiment, several DFTs were used to optimize the geometry structure of bulk **rP** and **bP** systems, and our calculated lattice parameters can be found in Table S1 and Table S2, respectively. Considering the interlaminar van der Waals interactions in the layered systems, several DFT-D methods were adopted, including Grimme's[1] GGA/PBE (noted as PBEgrime in Table S1) and OBS[2] for GGA/PW91(noted as PW91obs in Table S1) and LDA(noted as LDAobs in Table S1). Further analysis the results of lattice parameters found that with correction of van der Waals interaction, the GGA/PBE method (PBEgrime) gives the best results, comparing with the experimental reports. Besides, we checked the layer distance of **bP** and found that the layer distances of 2D systems which corrected by van der Waals interaction are more close to the bulk **bP**. Thus, in this article, the geometry models our investigation all were optimized with GGA/PBE method.

Table S1 The lattice parameters based on different methods for the Hittorf's **rP**

Method	System	*a*	*b*	*c*	α	β
PBE	**rP**-Bulk	9.126	9.177	24.259	90.00	103.80
	rP-MonoL	9.229	9.164	29.416	90.00	90.00
PBEgrime	**rP**-Bulk	9.264	9.118	22.414	90.00	105.74
	rP-MonoL	9.257	9.121	29.396	90.00	90.00
PW91	**rP**- Bulk	9.141	9.159	24.089	90.00	103.78
	rP-MonoL	9.213	9.146	29.441	90.00	90.00
PW91obs	**rP**-Bulk	9.091	9.066	23.119	90.00	104.87
	rP-MonoL	9.184	9.103	29.423	90.00	90.00
RPBE	**rP**-Bulk	9.305	9.270	28.492	90.00	101.045
	rP-MonoL	9.375	9.211	29.395	90.00	90.00
LDA	**rP**-Bulk	8.889	8.794	21.576	90.00	105.904
	rP-MonoL	9.049	9.012	29.406	90.00	90.00
LDAobs	**rP**-Bulk	8.830	8.702	20.997	90.00	106.380
	rP-MonoL	9.105	9.110	29.145	90.00	90.00
Exp[a]	**rP**-Bulk	9.270	9.170	22.610	90.00	106.18

[a] Ref. 35

Table S2 The lattice parameters based on different methods for **bP** in the bulk form.

	a(Å)	*b*(Å)	*c*(Å)	α(°)	β(°)
PBE	3.331	11.175	4.521	90.00	90.00
PBEgrime	3.317	10.368	4.406	90.00	90.00
PW91	3.333	11.078	4.520	90.00	90.00
PW91obs	3.345	11.794	4.673	90.00	90.00
LDA	3.308	10.287	3.643	90.00	90.00
LDAobs	3.292	10.158	4.381	90.00	90.00
Exp[a]	3.314	10.478	4.376	90.00	90.00

[a] Ref. 46

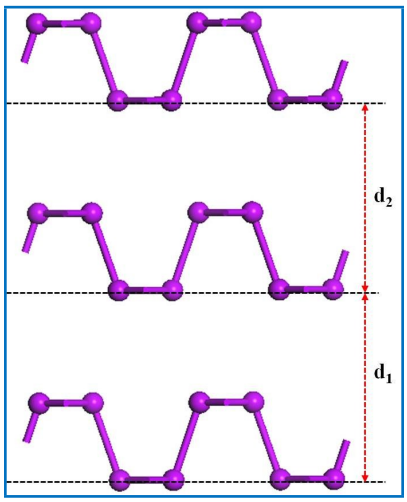

Figure S1. Schematic diagram of the layer distance of **bP**.

Table S3. The layer distance (**D**) of **bP** with and without van der Waals correction.

	bP-Bulk		**bP**-TriL		**bP**-BiL	
	d_1	d_2	d_1	d_2	d_1	d_2
$\mathbf{D}_{(DFT)}$[a]	5.179	5.179	5.500	5.382	5.432	-
$\mathbf{D}_{(DFT\text{-}D)}$[b]	5.180	8.150	5.235	5.240	5.179	-

[a] optimize without van der Waals correction. [b] optimize with van der Waals correction.

In order to examine the structural stability of monolayer **rP**, the dynamics simulations in the CASTEP code were performed using a time step of 1 fs and total simulation time of 10 ps with the temperature controlled at 300 K. Snapshots for the monolayer **rP** and the numbered key band lengths are presented in Figure S2. As shown in Figure S3, the key bond lengths of monolayer rP, which obtained by extracting every other 200 steps during the dynamics simulations, tend to a stable value after 7000 steps. That is to say, the P-P bonds are stable in monolayer **rP** during

the dynamics simulations, indicating that monolayer **rP** is stable thermodynamically.

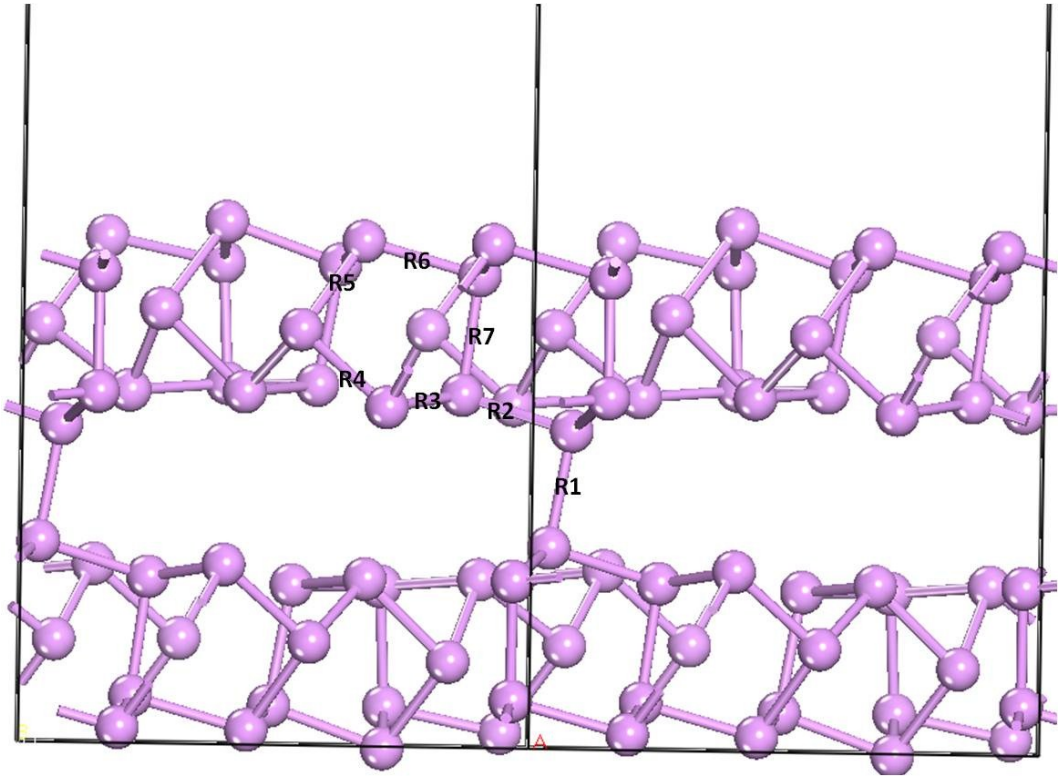

Figure S2. The snapshots for the monolayer **rP.**

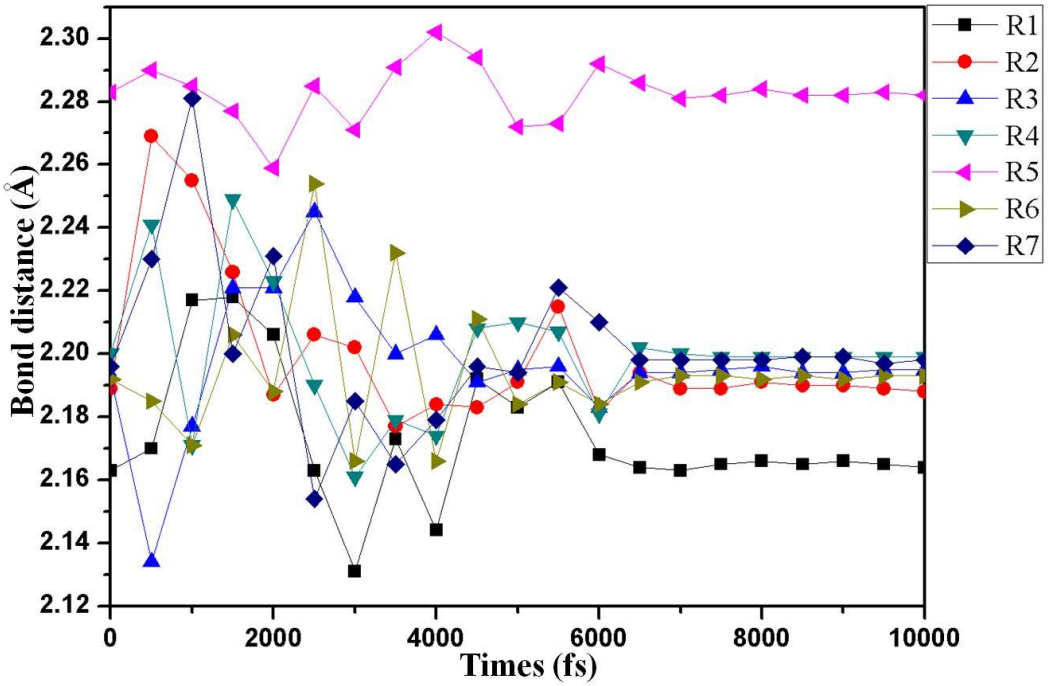

Figure S3. the distribution of key bond length of monolayer rP, which obtained by extracting every other 200 steps during the dynamics simulations.

In order to decide which is the most appropriate method to describe the electronic structure of the **rP** systems, several DFT calculations were performed to calculate the band gap of those systems and the band gaps from different calculations are listed in Table S3. The results show that GGA/PBE (1.25 eV) and LDA/CAPZ (1.15 eV) have obviously underestimated the band gap compared with the experimental value of 1.8 eV[3] due to the well-known shortcoming in these two functionals. While the band gap produced from HSE03 and PBE0 is 0.22 and 0.79 eV larger than the experimental value, respectively. Finally, the results calculated by HSE06 are quite comparable to the experimental reports[3] .

So far, various approaches (including the tight-bonding method[4], self-consistent pseudopotential method[5] and local-orbital method[6]) has been performed to determine the electronic structure of black phosphorus with different results. In our DFT calculations, GGA, LDA and hybridization functional were adopted to determine the electronic properties of the bulk **bP**. Table S3 lists the calculated band gap using different methods. As usual, PBE and LDA calculations underestimate the electronic band gap, as the results from these two functionals are smaller than those determined by HSE03, HSE06 and PBE0. Herein, we have obtained 0.40 eV band gap for the bulk **bP** using HSE06 hybrid functional, while HSE03 and PBE0 give an overestimated band gap 0.76 and 0.90 eV, respectively. The previous HSE06 computational result reported by Qiao[7] is 0.36 eV, and the experimentally measured value is 0.31-0.36 eV[8-10]. So we considered the HSE06 is a reliable method to examine the electronic properties of **bP**. Hence, in this article, we will display only the electronic and optical properties of systems our investigation calculated by HSE06 functional.

Table S4 The band gap of **rP** and **bP** calculated with different methods.

	rP-Bulk	**rP**-MonoL	**bP**-Bulk	**bP**-TriL	**bP**-BiL	**bP**-MonoL
PBE	1.25	1.68	0.10	0.44	0.37	0.80
LDA	1.15	1.43	0.10	0.42	0.33	0.74
HSE03	2.02	2.44	0.77	0.73	1.12	1.61
HSE06	1.99	2.39	0.40	0.74	1.08	1.67
PBE0	2.59	3.11	0.90	1.36	1.69	2.24
Exp	1.7[a]	-	0.31-0.36[b]	-	-	1.45[c]
Other theory	1.8[d]	-	0.36[e]	0.78[e]	1.05[e]	1.4-1.6[e]

[a] Ref. S3. [b] Ref. S8. [c] Ref. 18. [d] Ref. S3. [e] Ref. 19.

S2. Geometry Structure of bulk rP

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Title bulk **rP** after geometry optimization using GGA-PBE method incorporating Grimme correction.

Lattice type P

Space group name P 2/c

Space group number 13

Setting number 1

Lattice parameters

a	b	c	alpha	beta	gamma
9.06420	9.01810	22.41400	90.0000	105.7380	90.0000

Unit-cell volume = 1763.478133 ?^3

Structure parameters

		x	y	z	Occ.	U	Site	Sym.
1 P	P1	0.30399	0.20076	0.18098	1.000	1.000	4g	1
2 P	P2	0.17717	0.03174	0.11625	1.000	1.000	4g	1
3 P	P3	0.05155	-0.05503	0.17960	1.000	1.000	4g	1
4 P	P4	-0.07098	-0.22174	0.11464	1.000	1.000	4g	1
5 P	P5	-0.20261	-0.32320	0.17236	1.000	1.000	4g	1
6 P	P6	-0.31481	-0.48613	0.10179	1.000	1.000	4g	1
7 P	P7	-0.43311	-0.55363	0.17080	1.000	1.000	4g	1
8 P	P8	-0.57147	-0.72741	0.11519	1.000	1.000	4g	1
9 P	P9	0.04108	0.39383	0.07193	1.000	1.000	4g	1

10 P	P10	-0.00218	0.16032	0.04474	1.000	1.000	4g	1
11 P	P11	-0.21394	0.13949	0.07391	1.000	1.000	4g	1
12 P	P12	-0.25046	-0.09006	0.04318	1.000	1.000	4g	1
13 P	P13	-0.46344	-0.12419	0.06885	1.000	1.000	4g	1
14 P	P14	-0.49309	-0.35057	0.03177	1.000	1.000	4g	1
15 P	P15	-0.69806	-0.36405	0.06556	1.000	1.000	4g	1
16 P	P16	-0.74882	-0.59757	0.04204	1.000	1.000	4g	1
17 P	P17	0.14788	0.39234	0.17225	1.000	1.000	4g	1
18 P	P18	-0.14160	0.10039	0.17451	1.000	1.000	4g	1
19 P	P19	-0.40282	-0.17188	0.16971	1.000	1.000	4g	1
20 P	P20	-0.58770	-0.35533	0.16744	1.000	1.000	4g	1
21 P	P21	-0.05479	0.32512	0.20086	1.000	1.000	4g	1

Number of polygons and unique vertices on isosurface = 0 (0)
84 atoms, 0 bonds, 0 polyhedra; CPU time = 65 ms

S3. Geometry Structure of bulk bP

Title bulk **rP** after geometry optimization using GGA-PBE method incorporating Grimme correction.

Lattice type C
Space group name Cmca
Space group number 64
Setting number 1

Lattice parameters

a	b	c	alpha	beta	gamma
3.34110	10.35620	4.36020	90.0000	90.0000	90.0000

Unit-cell volume = 150.867715 ?^3

Structure parameters

		x	y	z	Occ.	U	Site	Sym.
1 P	P1	0.00000	0.10198	0.08302	1.000	0.010	8f	m..

Number of polygons and unique vertices on isosurface = 0 (0)
12 atoms, 0 bonds, 0 polyhedra; CPU time = 13 ms

S4. Electronic Structure of rP

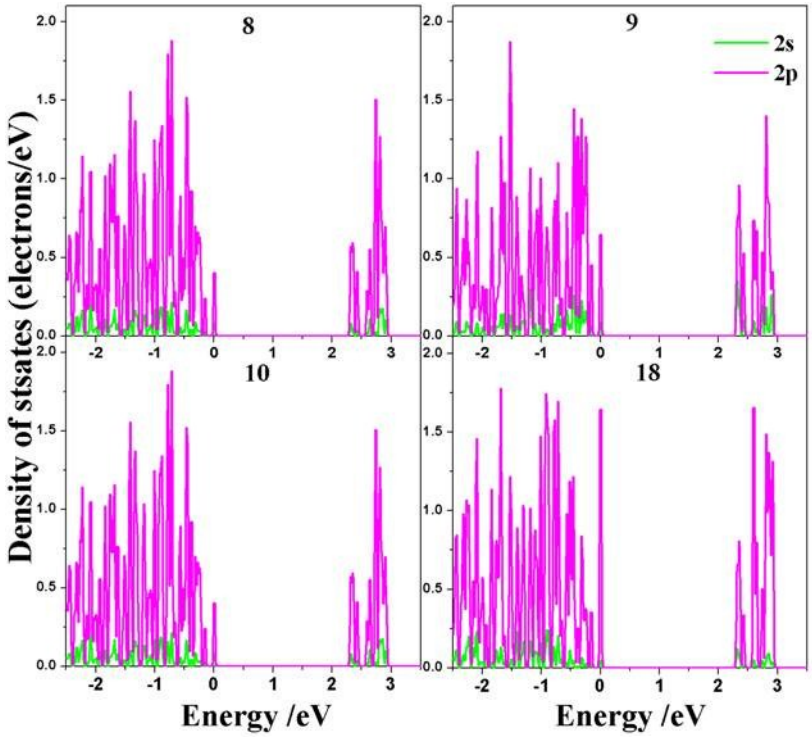

Figure S4: The partial density of states for **rP** in bulk form, and 8, 9, 10, and 18 are the numbered atoms on the tube being consistent with that in Figure 1.

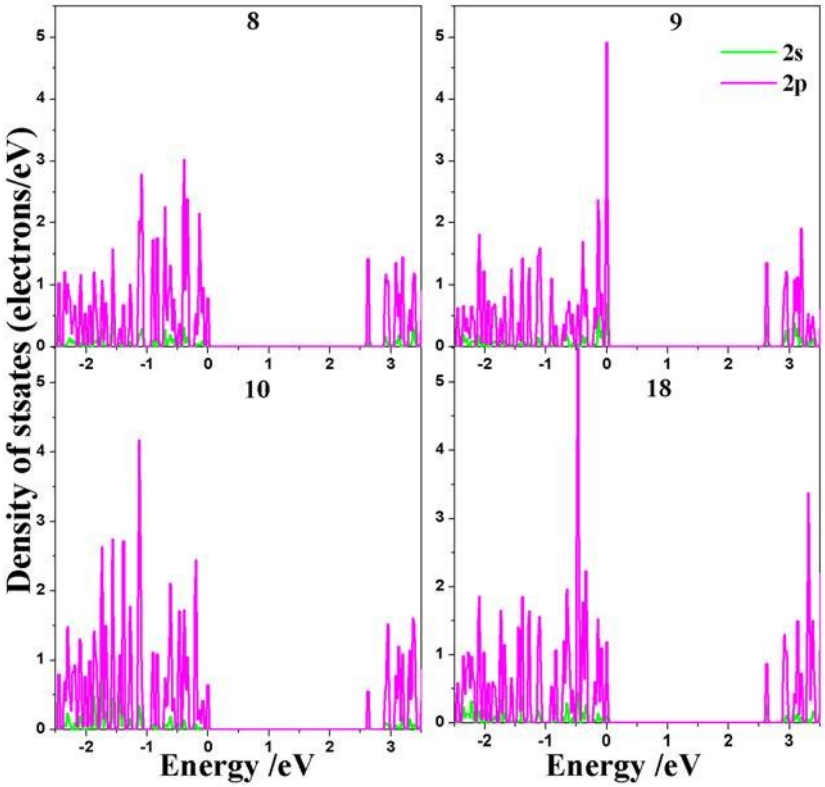

Figure S5: The partial density of states for **rP** monolayer, 8, 9, 10, and 18 are the numbered atoms on the tube being consistent with that in Figure 1.

S5. Effective Mass of rP

Table S4 The effective mass of electrons (m_e^*) and holes (m_h^*) in the unit of free-electron mass for rP in bilayer and thilayer systems along different directions in the reciprocal space.

	System	Γ-X	Γ-Y	Z-Γ
m_e^*	**rP**-ThiL	0.587	0.569	-
	rP-BiL	0.625	0.612	-
m_h^*	**rP**-ThiL	1.070	1.800	-
	rP-BiL	1.442	1.495	-
D	**rP**-ThiL	0.549	0.316	-
	rP-BiL	0.433	0.409	-

S6. optical property of bP

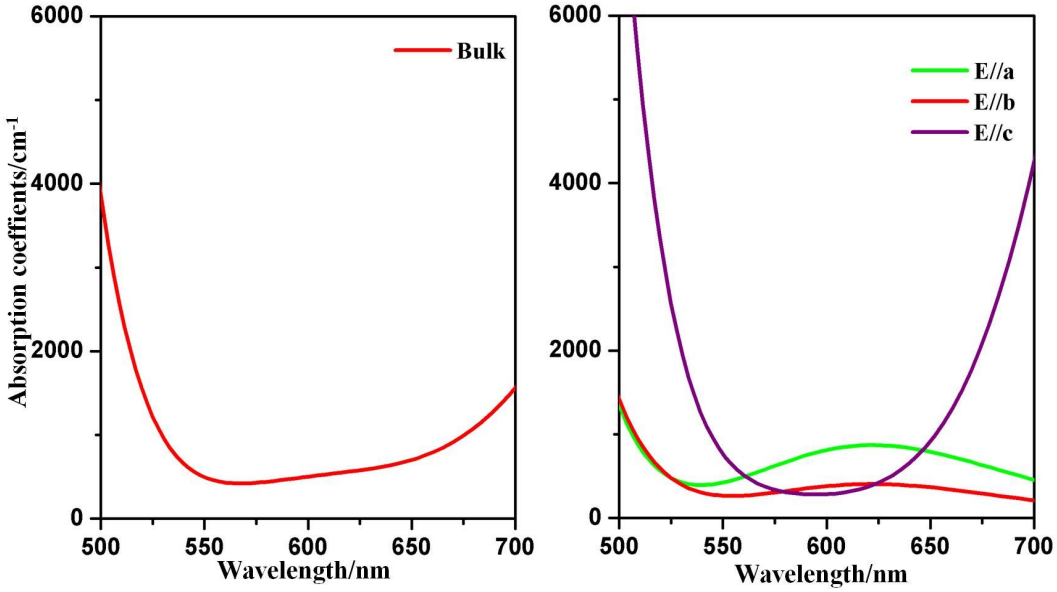

Figure S6: The detail with enlarged scale absorption spectra of **bP** in bulk at 500 - 700 nm being consistent with that in Figure 13a and 13b: (a) for direction-averaged; (b) for light incident polarized along the (100), (010), and (001) directions.

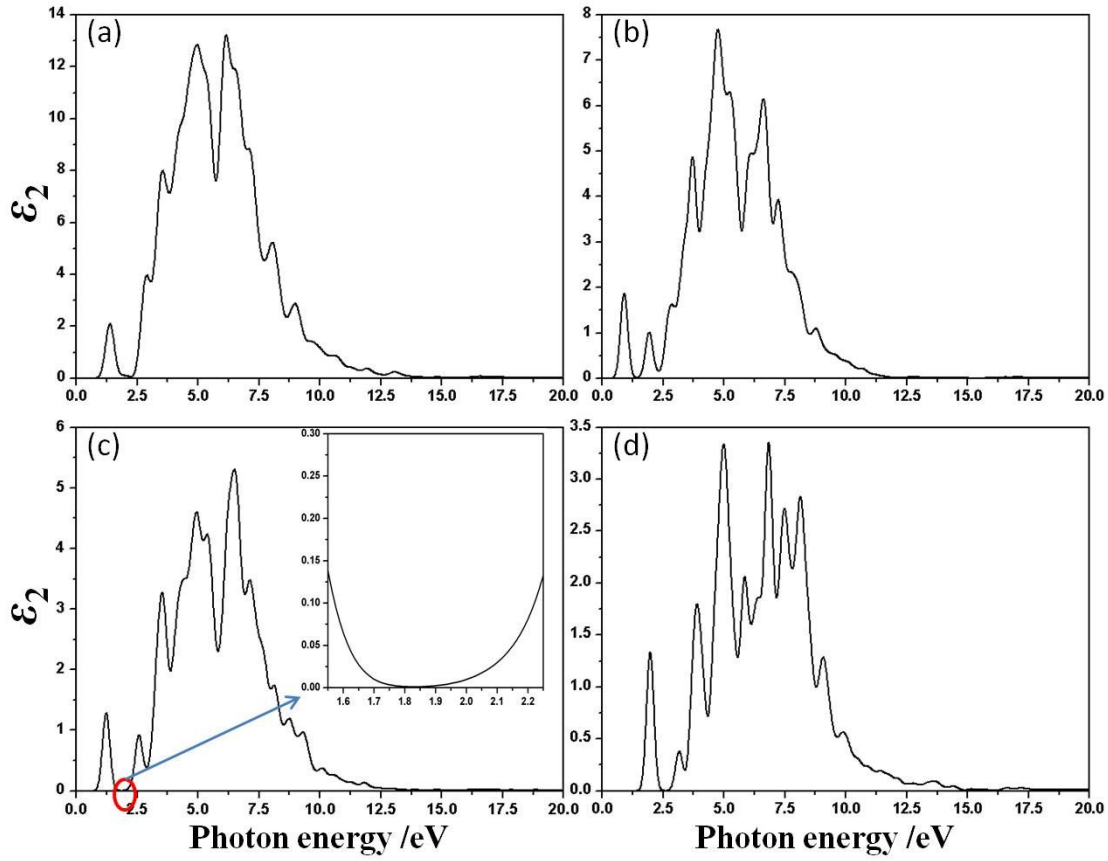

Figure S7. The calculated imaginary parts of dielectric function of the bulk (a), trilayer (b), bilayer (c), monolayer (d) **bP**. The inset shows a detail with enlarged scale in the photon energy range from 1.55 to 2.25 eV.

References

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