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

Supporting information for:

Two-dimensional exciton states in monolayer semiconducting phosphorus allotropes

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I. STRUCTURAL PARAMETERS

The relaxed lattice parameters and atomic coordinates, in Bohr units, for blue and black phosphorus are presented. For the reproducibility of our results the reader should consider an atomic mass of 30.97 and the pseudo-potential P.pbe-hgh.UPF, available in the Quantum-Espresso project webpage [1].

A. Blue Phosphorene

Cell Parameters:

a_1	6.181	0.000	0.000
a_2	3.091	5.353	0.0000
a_3	0.000	0.000	37.201

Atomic Positions:

P	6.1811406168	3.5686831906	20.9403459486
P	3.0905703084	1.7843415984	18.6006200000

B. Black Phosphorene

Cell Parameters:

a_1	8.628	0.000	0.000
a_2	0.000	6.243	0.000
a_3	0.000	0.000	51.930

Atomic Positions:

P	0.0010552522	0.0000356586	29.9470289674
P	2.8030439932	3.1217420556	29.9470395784
P	4.3153452296	3.1217421076	25.9662853800
P	7.1173323694	0.0000357105	25.9662777203

II. SUBSTRATE EFFECTS

Performing accurate GW-BSE simulations of the phosphorus allotropes taking into consideration the underlying substrate can result computationaly expensive or even prohibitive. Nevertheless, the proposed symplified models result useful in order to assess such effects. In the main text we define the effective dielectric constant κ in equation (7). For the monoloayer in vaccum $\kappa = 1$ as we considered throught the work, but it is also possible to include the effects of a substrate by considering

$$\kappa = \frac{(\epsilon_1 + \epsilon_2)}{2} = \frac{(1 + \epsilon_{sub})}{2} \ , \tag{1}$$

where $\epsilon_1 = 1$ and $\epsilon_2 = \epsilon_{sub}$ represent the dielectric constant of the two media: vacuum and substrate, respectively.

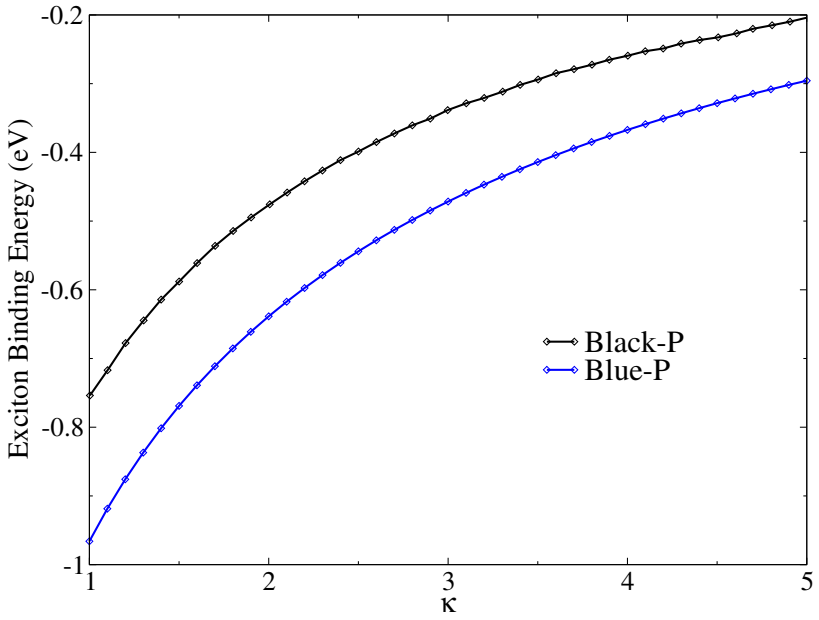

FIG. S1. Exciton binding energy as a function of the effective dielectric constant for blue and black phosphorus allotropes.

In Fig. (S1) we present the binding energy of blue and black Phosphorene as a function of the effective dielectric constant. In the figure, we observe that the absolute values of the binding energy for both, blue and black phosphorene, decreases as the dielectric constant increases. The reduction of the binding energy is expected since the effect of the dielectric

is to gradually enhance the screening of the system. Notice that for $\kappa = 1$, the free standing case studied in the main manuscript, the binding energies provide values of 0.96 and 0.75 for blue and black, respectively.

If we consider, for instance, the phosphorus allotropes deposited on SiO_2, for which $\kappa \approx 2.45$, our model predicts a binding energy for the first excitonic peak of 0.4 and 0.56 eV for black and blue phosphorus, respectively. Note that the predicted exciton binding energy of Black phosphorus on top of SiO_2 is in good agreement with the measured value of 0.38 eV [2].

Finally, we can also predict the exciton binding energy of phosphorene on Au - the substrate on which blue phosphorene was recently obtained [3]. Thus, considering $\epsilon_{Au} = 6.9$ ($\kappa \approx 4$) for nanometer thick Gold [4], the binding energies for black and blue phosphorene are 0.26 and 0.368 eV, respectively.

REFERENCES

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