Difluorophosphorane-Flattened Phosphorene through Difluorination

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S Supporting Information

ABSTRACT: We computationally showed that by difluorination of phosphorene we can make a new material difluorphosphorane (DFP) with perfectly planar honeycomb structure out of phosphorus atoms with fluorine atoms attached to every phosphorus atom from above and below. The structure is dynamically stable. It is a semiconductor with a direct band gap of 4.51 eV and an indirect band gap of 3.88 eV. We hope that with the passivation this new DFP material if made could find many applications in nanoelectronics.

Phosphorene → Difluorophosphorane
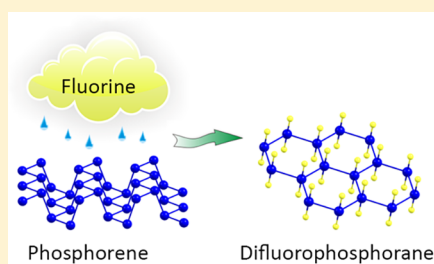
Black phosphorus (BP), the most stable allotrope of the phosphorus element, was discovered in 1914 at Harvard University by Professor Bridgman, who was studying the effects of high pressure.[1] BP is a layered semiconductor that consists of corrugated planes of phosphorus atoms with strong intralayer bonding and weak interlayer interactions. In 2014, the 2D black phosphorus, phosphorene, was prepared.[2−4] This material immediately attracted a lot of attention because, unlike graphene, which has zero band gap, phosphorene has a band gap of ~2 eV in addition to highly anisotropic charge-transport and optical-response properties,[2−7] which differentiate it from previously studied two-dimensional (2D) nanomaterials. The BP favorable field-effect hole mobility of ~1000 cm^2 V^{-1} s^{-1} [3,4,8] exceeds those of transition-metal dichalcogenides[9,10] and makes it attractive for high-performance electronic devices, as well as for optoelectronic,[11−13] energy storage,[14] and molecular sensing applications.[15] In spite of these good properties, BP has one big disadvantage. It chemically degrades in the presence of ambient oxygen and water when exfoliated to nanoscale dimensions,[16,17] which results in the rapid loss of semiconducting properties.[16] Thus, it is an important goal to find a way to passivate BP. One of the ways to passivate BP was proposed through making a covalent aryl diazonium functionalization, which suppresses the chemical degradation of exfoliated BP even after 3 weeks of ambient exposure.[18−21]

In this work, we propose a new way to passivate BP through its diflorination. It is well-known in chemistry that the PF$_5$ molecule has a trigonal bipyramid geometry, with the central atom, phosphorus, having formally sp^{3}d hybridization. We speculated that, if we attach two fluorine, hydrogen, or chlorine atoms to every phosphorus atom in phosphorene from above and below, we might get a new material with a perfectly planar structure of a phosphorus monolayer with every phosphorus atom in the formal sp^{3}d hybridization. Such a planar phosphorus structure could be well protected by fluorine, hydrogen, or chlorine atoms from above and below and could make the new material stable toward reactions with oxygen and water. We also hoped that the new material would be a semiconductor. In order to test our hypothesis, we performed density functional calculations with imposing periodic boundary conditions for the PF$_2$, PH$_2$, and PCl$_2$ stoichiometries.

The calculations have been performed using the program VASP (Vienna Ab initio Simulation Package)[22−25] with PAW pseudopotentials[26,27] and the PBEsol functional.[28] The planewave cutoff energy of 850 eV for PF$_2$ and PH$_2$ and 600 eV for PCl$_2$ of the associated pseudopotentials was used. The Brillouin zone has been sampled by the Monkhorst−Pack method[29] with an automatically generated k-mesh of 15 × 15 × 1. The convergence criterion for energy minimization of the wave function was set to 1.0 × 10^{-10} eV. The phonon spectrum was calculated using the Phonopy program[30] using a 5 × 5 × 1 supercell and 3 × 3 × 1 k-mesh. It is well-known that GGA functionals tend toward underestimation of the band gap. The HSE06 functional is known to yield accurate predictions of electronic bandgaps in semiconductors.[31] The single-point calculations based on the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06)[32,33] were performed to obtain the electronic band structure. Due to more expensive HSE06 calculations, the cutoff energy for the plane-wave basis was set to 490 eV. The convergence criterion for energy minimization of the wave function was set to 1.0 ×
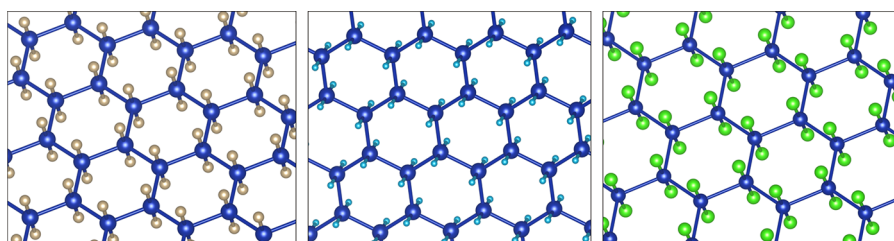
Figure 1. Schematic view of a two-dimensional structure consisting of PX$_2$ units where (a) X = F, (b) X = H, and (c) X = Cl.

10^{-5} eV, and the Brillouin zone was sampled by a k-mesh of 21 × 21 × 1.

The calculated geometric characteristics of the studied systems were visualized using the Vesta program.[34]

Geometries of the calculated structure for the PF$_2$, PH$_2$, and PCl$_2$ stoichiometries are presented in Figure 1.

We optimized 2D crystal lattices, which have honeycomb structures with fluorine, hydrogen, or chlorine atoms attached above and below every phosphorus atom. The calculated P–P bond length was found to be 2.379 Å in PF$_2$, 2.284 Å in PH$_2$, and 2.880 Å in PCl$_2$, which is in the first two cases close to a sum of two atomic phosphorus atoms, 2.22 Å.[35] However, the calculated phonon spectra indicate the dynamic stability only for the PF$_2$ 2D material, difluorophosphorane (DFP), since it does not have low-frequency branches entering the imaginary region (see Figure 2). The other two PH$_2$ and PCl$_2$ 2D
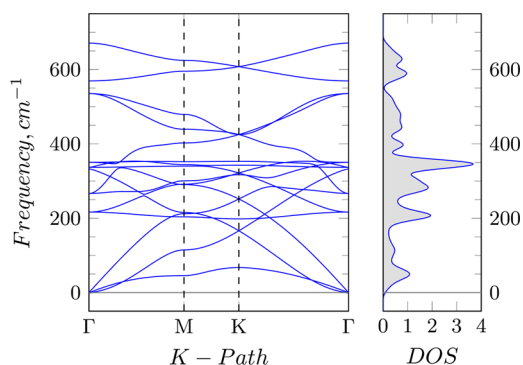

Figure 2. Calculated dispersion curves along paths Γ-M-K-Γ (left) and the density of states (right) of the phonon spectrum for an infinite 2D structure consisting of PF$_2$ units.

materials have low-frequency branches entering the imaginary region (see Figures S1 and S2 in the Supporting Information). Thus, we will discuss further only DFP in more detail. We chose the name difluorophosphorane, in order to preserve similarity with the pairs of graphene/graphane[36−38] and borophene/borophane.[39−41]

These results show that by difluorination of phosphorene we can get a new 2D material, DFP, which has a perfectly planar phosphorus honeycomb structure with a good protection of phosphorus atoms from above and below. The next important goal is to check if DFP is a semiconductor or not. From the calculations of the band electronic structure of the system shown in Figure 3, it follows that DFP is indeed a semiconductor with a direct band gap of 4.51 eV and and an indirect band gap of 3.88 eV. Results for the direct and indirect gaps with the PBEsol functional can be found in the Supporting Information (Figure S3).
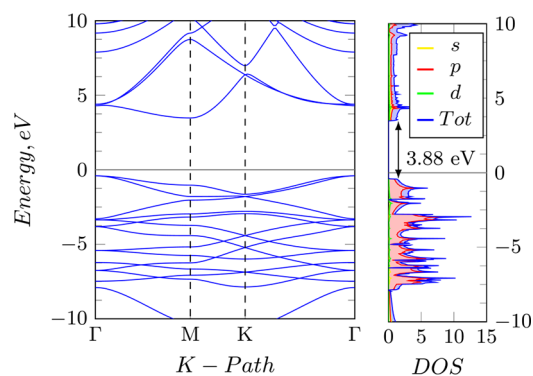

Figure 3. Electronic band structure of an infinite 2D structure consisting of PF$_2$ units calculated by the DFT PAW HSE06 method (left) and the density of partial and total states (right).

Thus, the DFP is a semiconductor and could be used in nanoelectronics.

In order to evaluate the mechanical properties of DFP, we calculated elasticity constants c_{ij}. Table 1 shows the calculated

Table 1. Calculated Values of the Elasticity Constants (c_{ij}, in N·m^{-1}), the Young's Modulus (Y_{2D}, in N·m^{-1}), and Poisson's Ratio ν

structure	c_{11}	c_{12}	c_{66}	Y_{2D}	ν
PF$_2$ (DFP)	57.4	44.5	6.4	22.9	0.78

elastic constants, Young's modulus, and Poisson's ratio, which characterize the plastic and elastic properties of the material under study. In view of the fact that the monolayers under study are isotropic, the table presents only two elastic constants (c_{11} and c_{12}) as well as Young's modulus (Y_{2D}) and Poisson's ratio (ν), which are calculated according to formulas 1 and 2.

$$Y_s = \frac{c_{11}{}^2 - c_{12}{}^2}{c_{11}} \qquad (1)$$

$$\nu = \frac{c_{12}}{c_{11}} \qquad (2)$$

Summarizing, we computationally showed that, by difluorination of phosphorene, we made a new material, DFP, which has a perfectly planar honeycomb phosphorus lattice with two fluorine atoms attached to every phosphorus atom from above and below. This material is dynamically stable, since it does not have low-frequency branches entering the imaginary region. It is still a semiconductor with a direct band gap of 4.51 eV and an indirect band gap of 3.88 eV. We hope that fluorine atoms can protect phosphorus from rapid reactions with oxygen and water and make this material suitable for nanoelectronics.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b02918.

Calculated dispersion curves along paths Γ-M-K-Γ and the density of states of the phonon spectrum for an infinite 2D structure consisting of PH_2 or PCl_2 units; the electronic band structure of an infinite 2D structure consisting of PF_2 units calculated by the DFT PAW PBEsol method and the density of partial and total states; Cartesian coordinates of atoms and translation vectors of Bravais lattice for PF_2, PH_2, and PCl_2 structures (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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