Noncovalent Functionalization of 2D Black Phosphorus with Fluorescent Boronic Derivatives of Pyrene for Probing and Modulating the Interaction with Molecular Oxygen

Margherita Bolognesi, Salvatore Moschetto, Mariachiara Trapani, Federico Prescimone, Claudia Ferroni, Gabriele Manca, Andrea Ienco, Silvia Borsacchi, Maria Caporali, Michele Muccini, Maurizio Peruzzini, Manuel Serrano-Ruiz, Lucia Calucci, Maria Angela Castriciano, and Stefano Toffanin

Supporting Information

ABSTRACT: We studied the chemical-physical nature of interactions involved in the formation of adducts of two-dimensional black phosphorus (2D BP) with organoboron derivatives of a conjugated fluorescent molecule (pyrene). Time-resolved fluorescence spectroscopy showed a stabilization effect of 2D BP on all derivatives, in particular for the adducts endowed with the boronic functionalities. Also, a stronger modulation of the fluorescence decay with oxygen was registered for one of the adducts compared to the corresponding organoboron derivative alone. Nuclear magnetic resonance experiments in suspension and density functional theory simulations confirmed that only noncovalent interactions were involved in the formation of the adducts. The energetic gain in their formation arises from the interaction of P atoms with both C atoms of the pyrene core and the B atom of the boronic functionalities, with a stronger contribution from the ester with respect to the acid one. The interaction results in the lowering of the band gap of 2D BP by around 0.10 eV. Furthermore, we demonstrated through Raman spectroscopy an increased stability toward oxidation in air of 2D BP in the solid state (more than 6 months). The modification of the electronic structure at the interface between 2D BP and a conjugated organic molecule through noncovalent stabilizing interactions mediated by the B atom is particularly appealing in view of creating heterojunctions for optoelectronic, photonic, and chemical sensing applications.

KEYWORDS: phosphorene, black phosphorus, 2D materials, non-covalent functionalization, boron

INTRODUCTION

The ongoing technological race toward low-dimensional and high-performing nanodevices has opened the way for the study of nanostructured materials. In particular, the discovery of graphene in 2004, which resulted in the Nobel Prize in Physics in 2010, has drawn the attention of materials scientists toward two-dimensional (2D) materials. The exploration of new 2D materials starting from other elements of the periodic table led to the discovery of other semiconducting 2D materials, such as 2D black phosphorus (BP) whose single layer is named phosphorene. The most appealing property of 2D BP is surely the direct thickness-dependent band gap, which changes from 0.33 eV for...
the bulk to 2.26 eV for the single layer. Owing to the high optical absorbance efficiency, combined with a high anisotropy, and the direct band gap, this material is a promising candidate for optoelectronic and photonic applications in the near-mid infrared range.

One of the major drawbacks of 2D BP is its high instability due to oxidation under ambient conditions. The covalent and noncovalent functionalization of 2D BP with organic molecular materials is a very common approach that is used to protect its surface from air degradation and also to tailor its electrical properties. Till date, there are some reports in the literature dealing with the covalent functionalization of 2D BP, such as the covalent bonding of phenyl groups, of fluorine atoms and of C60 molecules or the reaction with metal-halide reagents.

Alternatively, the protection of 2D BP can be achieved through noncovalent interactions, which are particularly relevant to phosphorene, for which covalent bonds alter strongly the electronic structure. For example, literature reports on the adsorption of 7,7,8,8-tetracyano-p-quinodimethane and various perylene derivatives on 2D BP flakes. This strategy allowed to improve the performance of 2D BP-based devices and to implement heterojunctions in biophotonics or optoelectronics. Indeed, hybrid inorganic semiconductor (2D BP)/organic (molecular) systems combine the high carrier mobility and high excitation densities of inorganic semiconductors and the strong light–matter coupling featured by the organic compounds.

Molecular phosphines easily react with the suitable boron precursor leading to either phosphinoboranes (containing a covalent B=P double bond) or borylphosphines (having a covalent single B−P bond). Thus, 2D BP is expected to show a high affinity and/or a specific chemical reactivity with compounds containing B units. Moreover, 2D BP flakes display relevant interactions with planar and conjugated organic molecules on its surface by chemisorption. However, a detailed study on the functionalization of 2D BP by means of conjugated organo-boron compounds is still lacking. In this work, this two-fold approach is defined, implemented, and validated by using boronic derivatives (acid or ester) of pyrene (Py, PBA, and PBE, Figure 1). Pyrene derivatives have been selected because they are a class of largely investigated solvatochromic, conjugated, planar fluorophores, which find wide use in optoelectronic and sensing applications. They are characterized by a long excited-state lifetime, the values of which are affected by the chemical environment, such as the nature of the solvent and the presence of oxygen in solution. Furthermore, in concentrated solution and/or in the solid state, pyrene derivatives can lead to the formation of characteristic excimers. Thus, we used computational modelling, NMR and Raman spectroscopy, fluorescence emission, and microscopy to study the interactions of pyrene and/or its derivatives with 2D BP.

**EXPERIMENTAL SECTION**

**General.** Pyrene (Sigma-Aldrich, 98% purity), pyren-1-boronic acid (Sigma-Aldrich, 95% purity), and all reagents and solvents employed for the synthesis and preparations reported below were used as received, without further purification.

**Synthesis of BP.** BP was synthesized following a procedure described in the literature. Red phosphorus was used as a starting material, and Sn and SnCl4 were used as catalysts. The solids were heated in a quartz vial at a temperature of 650 °C for 3 days and then cooled down to room temperature very slowly to obtain high quality crystals of BP.

**Synthesis of 4,4,5,5-Tetramethyl-2-pyren-1-yl-1,3,2-dioxaborolane.** 4,4,5,5-Tetramethyl-2-pyren-1-yl-1,3,2-dioxaborolane (PBE) was synthesized as reported in the literature. Briefly, to a well degassed solution of 1-bromopyrene (180 mg, 0.64 mmol) in anhydrous 1,4-dioxane (1.6 mL) were added bis(pinacolato) diboron (245 mg, 0.96 mmol), potassium acetate (KOAc, 138 mg, 1.41 mmol), and 7 mg of [1,1’-Bis(diphenylphosphino)ferrocene]-dichloropalladium(II) (Pd(dppf)Cl2). The resulting mixture was stirred at 90 °C for 5 h under N2. After cooling, the solution was removed under pressure, and CH2Cl2 was added. The organic layers were washed with H2O, dried over Na2SO4, filtered, and concentrated. The crude was purified on a silica gel column, eluting with 0%–10% CH2Cl2 in cyclohexane, affording a yellowish solid (148 mg, 0.45 mmol, yield = 70%). The 1H and 13C NMR spectra were recorded on a Varian spectrometers (500 MHz for 1H and 125 MHz for 13C) at 298 K. Deuterated chloroform was used as the solvent for NMR experiments. Abbreviation for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; quin., quintet; m, multiplet; br., broad. Flash chromatography was performed on Teledyne Isco CombiFlash RF 200 using RediSep Normal-phase Silica Flash Columns (230–400 mesh). Thin-layer chromatography was performed on silica gel 60 F254 plastic sheets. Purity of PBE was determined by high-performance liquid chromatography (HPLC)–ultraviolet (UV) analysis (Waters 600 HPLC instrument connected to a photodiode array detector 996).

**BNMR** (500 MHz, CDCl3): 6 (s, 12H), 8.01–8.25 (m, 7H), 8.60 (d, J = 9.5 Hz, 1H), 9.14 (d, J = 12.0 Hz, 1H). 13C NMR (125 MHz, CDCl3): 6 25.03, 83.85, 124.04, 124.36, 124.58, 125.15, 125.30, 125.65, 127.44, 127.74, 128.00, 128.49, 130.74, 131.09, 133.43, 133.84, 136.42.

**BP Exfoliation in Solution.** Five milligrams of BP crystals were suspended in a vial with 5.0 mL of dry dimethylsulfoxide, and deoxygenated distilled water (3–5 μL) was added. The vial was sealed under an inert atmosphere and sonicated in an ultrasonic bath (200 W, 37 KHz) for 120 hours. The Raman spectrum of the 2D BP flakes drop-casted onto a freshly cleaved silicon substrate is reported in the Supporting Information (Figure S1).

**Preparation of the Adducts on Solid Substrates.** BP was mechanically exfoliated with a blue foil tape on freshly cleaved quartz substrates to produce supported 2D BP. The samples were functionalized with dip coating in anhydrous THF solutions of either Py, PBA, or PBE 10 mM. Both exfoliation and functionalization steps were performed in a glovebox with an inert N2 environment (O2 < 0.1 ppm, H2O < 0.1 ppm).

![Figure 1. Chemical structure of Py, PBA, and PBE.](image-url)
Scanning Electron Microscopy. The morphology of the adducts prepared on quartz, as described above, was studied by scanning electron microscopy (SEM) using a dual beam instrument, Gaia 3 TESCAN. The elemental analysis on the surface of the samples was carried out by an energy-dispersive X-ray (EDAX) system interfaced with SEM (AMETEK, Mahwah NJ, USA, software TEAM EDS Basic Suite).

Atomic Force Microscopy. The morphology of the adducts supported on solid quartz substrates, as described above, was studied also by atomic force microscopy (AFM) in the PeakForce Tapping mode on a Bruker MultiMode 8 microscope with a NanoScope V controller and a J scanner.

Raman Spectroscopy. The Raman spectra on liquid exfoliated samples deposited on silicon substrates were studied using a Renishaw inVia confocal Raman microscope equipped with a 532 nm laser and a motorized stage for 2D mapping of samples. A laser spot size of approximately 2 μm in diameter was used. Confocal micro-Raman spectroscopy of the samples prepared with mechanical exfoliation and functionalized by dip coating was performed on single flakes of approximately the same thickness, for better comparison, by using a Renishaw micro-Raman 1000 system equipped with a 488 nm laser and a motorized stage for 2D mapping of samples. The laser beam was focused through a 20x objective.

Ultraviolet–Visible and Fluorescence Spectroscopies. Ultraviolet–visible (UV–vis) spectra were obtained with a Hewlett-Packard mod. 8453 diode array spectrophotometer. Static and time-resolved fluorescence emission measurements were performed on a Jobin Yvon-Spex Fluoromax 4 spectrophotometer using time-correlated single-photon counting technique. A NanoLED (λ = 390 nm) has been used as the excitation source. Emission spectra were not corrected for the absorbance of the samples. The fluorescence decay profiles were analyzed using iterative fitting algorithm (Levenberg–Marquardt, simplex), achieving an instrumental resolution (corresponding to the minimum measurable time value) of about few tens of picoseconds. Spectroscopy was done on adduct suspensions, in anhydrous and degassed THF, prepared as described above.

DFT Calculations. To understand the nature of the interaction between 2D BP and pyrene (Py) or its boronic derivatives (PBA or PBE), we carried out a detailed solid-state DFT computational analysis. All efforts to optimize a covalent adduct involving the boron center and phosphorene failed because of electronic and steric reasons, recently deeply illustrated from a computational viewpoint. Hence, we focused our attention on the noncovalent possible interaction between the organic moiety and the material. Therefore, we were led to optimize a noncovalent adduct involving the pyrene moiety and in between 1.37 and 1.44 Å in the adduct. Indeed, the C–C distances of pyrene are slightly lengthened, being in between 1.35 and 1.42 Å in the pristine pyrene moiety and in between 1.37 and 1.44 Å in the adduct.

RESULTS AND DISCUSSION

DFT Calculations. To understand the nature of the interaction between 2D BP and pyrene (Py) or its boronic derivatives (PBA or PBE), we carried out a detailed solid-state DFT computational analysis. All efforts to optimize a covalent adduct involving the boron center and phosphorene failed because of electronic and steric reasons, recently deeply illustrated from a computational viewpoint. Hence, we focused our attention on the noncovalent possible interaction between the organic moiety and the material.

The formation of the first adduct, phosphorene/Py in Figure 2a, was estimated to be favored by −2.2 eV. The P–C distances between the organic moiety and the 2D material are within 3.20–3.40 Å, confirming the noncovalent nature of the involved interactions. Although noncovalently bonded, the structures of both phosphorene and pyrene are rearranged in the phosphorene/Py adduct. Indeed, the C–C distances of pyrene are slightly lengthened, being in between 1.35 and 1.42 Å in the pristine pyrene moiety and in between 1.37 and 1.44 Å in the adduct.
the P−P nonbonding distances of phosphorene are shortened, especially the ones directly interacting with the organic moiety, passing from an estimated medium value of 3.5 Å for pristine phosphorene to 3.2 Å for the first and fourth channels of phosphorene in the adduct (indicated as first ch. and fourth ch. in Figure 2).

The favourable noncovalent P−B interaction gives a relevant contribution to the further stabilization of the other two adducts, phosphorene/PBA in Figure 2b and phosphorene/PBE in Figure 2c. Indeed, the interaction energy between phosphorene and the organic molecules increases by −0.30 eV in the case of PBA and by −0.50 eV in the case of PBE, compared to Py. This occurs even though a noncovalent P−B bond is formed, the calculated P−B distance being as long as 3.00 Å. This is in perfect agreement with NMR results (see the following section). However, the main contribution to the stabilization energy of the moieties of the adduct has still to be ascribed to the noncovalent interaction between the conjugated core of pyrene and the phosphorus atoms. The slight increase (−0.1 eV) in the stabilization energy of phosphorene/PBE compared to phosphorene/PBA could be attributed to the dependence of the dispersion interaction on the number of involved atoms. Therefore, the phosphorene/PBE adduct is the most stable within all, even though the optimized P−B and H···P distances in this adduct are longer than in phosphorene/PBA likely due to the higher steric hindrance of the ester around the B atom in PBE with respect to the OH groups in PBA. In addition, for phosphorene/PBA and phosphorene/PBE adducts, the interaction leads to a geometrical rearrangement of the two organic moieties, evidenced by a variation of the interatomic distances (Figure S3b,c in the Supporting Information).

From an electronic viewpoint, the band gap calculated for the phosphorene/PBA and phosphorene/PBE adducts with the PBE-D3 functional decreases by 0.10 and 0.08 eV with respect to bare phosphorene. The corresponding density of state (DOS) plots of the adduct (Figure 3) reveal that the band gap lowering is due to a contribution of the organic molecules in the DOS region next to the top of the valence band. This contribution arises from a partial mixing of the π* of the pyrene moiety with the 2p orbitals of the lone pairs of phosphorene, as observed in the DOS plots (Figure 3). This is in accordance with the structural data of the optimized adducts, which, as described above, feature an elongation of the C−C bonds of the pyrene moiety and a shortening of the P−P distances within the channels of phosphorene.

**NMR Spectroscopy.** To confirm the DFT predictions, the interaction between 2D BP and PBA was investigated by means of multinuclear NMR spectroscopy directly on the 2D BP/PBA suspension. To the best of our knowledge, this is the first time that NMR has been applied on suspensions of exfoliated BP, allowing chemical features and interactions of BP nanoflakes to be characterized directly in the dispersed state. Figure 4 reports the 31P NMR spectra of pristine 2D BP in suspension, both under static and MAS conditions.

![Figure 3. Band structure and DOS for the adduct between phosphorene and PBA. In the DOS plot, the contribution highlighted in blue is due to the PBA moiety.](image)

The static spectrum (Figure 4a) is constituted by a broad signal, similar to that observed for pristine solid bulk BP, which arises from the anisotropic spin interactions of 31P nuclei. The anisotropy is partially averaged out by MAS, and indeed in the 31P MAS spectrum (Figure 4b), it is possible to observe an intense signal of 2D BP at an isotropic chemical shift of about 18.5 ppm, similar to that observed for bulk BP crystals and 2D BP, mechanically exfoliated or embedded in polymer hybrids, together with spinning sidebands arising from the residual anisotropy of the spin interactions. In the 31P NMR spectrum of the 2D BP/PBA suspension (Figure 4c), the signal of 2D BP does not show any modification, suggesting that substantial chemical functionalization of 2D BP with PBA did not occur. Two weak narrow peaks, ascribable to minor amounts of oxidized (phosphate and phosphite) species, appear between 0 and 10 ppm.

31P NMR spectra of the 2D BP/PBA suspension (Figure 5), under static and MAS conditions, confirm the substantial absence of covalent functionalization of 2D BP. The static spectrum (Figure 5a) shows only one approximately Lorentzian peak at a chemical shift of about 30.5 ppm typical of boronic acids in solution. As expected, this peak slightly narrows in the MAS spectrum (Figure 5b), in which, on the other hand, no
additional signals appear. Analogous results were obtained from $^{13}$C and $^1$H NMR spectra (Figure S4 in the Supporting Information).

Photophysical Investigation. Photophysical investigation has been carried out, thanks to the presence of luminescent probes. The interactions between 2D BP and pyrene-based molecules have been explored in a medium polarity solvent (THF) to have a good compromise between the solubility of the fluorophores and a good dispersion of 2D BP. For comparison with NMR, the dye concentration for photophysical investigation has been fixed at $3 \times 10^{-5}$ M. In any case, control experiments have been performed on more dilute samples ($3 \times 10^{-6}$ M), and no difference in photophysical behavior has been observed.

The extinction spectrum of pristine 2D BP in THF suspension is broad and featureless, except for a peak at 275 nm, and covers the whole UV–vis region. It is worth noting that, working with suspensions, in Figure 6, we report the “extinction spectra” measured by a conventional spectrophotometer as the sum of the absorption and scattering contributes, whereas absorbance is typically reported for the electronic spectra of the pure fluorophores in solution (see Figure S5 in the Supporting Information). The three pristine pyrene derivatives show, in the electronic spectra, absorption bands with a characteristic vibronic fine structure between 300 and 350 nm. According to the literature, the absorption maxima of PBA and PBE present a slight red shift compared to Py. Thus, the optical band gaps ($E_{g}^{opt}$) of the three samples, calculated from the $\lambda$ onsets of the absorption spectra, vary in the trend Py > PBA > PBE.

The electronic spectra of the three adducts present profiles corresponding to the sum of the spectra of the single components (Figures 6a and S5 in the Supporting Information). This excludes the formation of absorbing charge transfer (CT) electronic states. According to the literature, the emission spectra of the three pure fluorophores (Figure 6b), taken as a reference, show structured bands spanning from 380 to 500 nm typical for this class of compounds. For Py, the most intense vibronic band is III, whereas the presence of the boronic functionalities in PBA and PBE causes a significant enhancement of the higher energy vibronic bands (I) at the expense of the lower ones. The II vibronic band is slightly detectable.

The emission spectra of the adducts were taken by exciting the suspensions in the UV region, where both 2D BP and the investigated fluorophores absorb. However, no emission in the red–NIR range, characteristic of 2D BP, was observed. In the presence of 2D BP, the emission spectra of all pyrenes show a slight bathochromic shift of the bands (by +2 nm) and an evident change in the intensity ratio of the first to third vibronic emission bands (I/IVI ratio), more evident for PBA and PBE. Since for this class of compound, the I/III intensities ratio is very sensitive to the solvent polarity,

Figure 6. (a) UV–vis extinction spectra of pristine 2D BP in suspension (green line) and of the adducts of 2D BP with Py (black line), PBA (red line), and PBE (blue line) in a suspension of THF, $3 \times 10^{-5}$ M. (b) Fluorescence spectra of the pristine fluorophores Py (black dotted line), PBA (red dotted line), and PBE (blue dotted line) and their adducts with 2D BP in THF suspensions (same colors, continuous lines); $\lambda_{ex}$ = 260 nm.

The fluorescence emission decay of pristine Py presents a biexponential behavior with a long lifetime value of about 7.1 ns and a shorter one of about 1.2 ns with almost equal amplitudes (Table 1). Differently, the PBA and PBE fluorescence decay profiles are well-fitted by triexponential curves (Table 1). Decays of both PBA and PBE present a short (2.1 and 1.6 ns) and long (8.8 and 5.0 ns) component, similar to those of Py; but differently from Py, they also present a third and longer lifetime value. In detail, pristine PBA has a $\tau_1$ of 53.3 ns with 0.19 of amplitude, and PBE has a $\tau_2$ of 40.1 ns with an amplitude as high as 0.61 (Table 1). A similar lifetime (around 50–60 ns) is reported in the literature for the fluorescence decay of molecular Py in solution. As already reported, the apparent discrepancy in lifetime values can be due to the nature of the solvent and the presence of excimers. To confirm the absence of excimers in solution, emission spectra at various sample concentrations and excitation spectra at different emission conditions were collected.
To note, the alignment of the energetic levels of 2D BP with Py, PBA, and PBE would favor a quenching of the emission of the organic molecules by energy or CT process to 2D BP.\textsuperscript{59,60} However, this did not occur.

Pyrene derivatives and their nanohydrs are used in the literature as simple, cheap biocompatible fluorescent compounds for the detection of molecular oxygen.\textsuperscript{61} Moreover, 2D BP has attractive physical properties for high-performance chemical sensing applications, such as a high molecular adsorption energy and surface-to-volume ratio.\textsuperscript{62–64} In addition, by exploiting the remarkable attitude to fast oxidation in the presence of oxygen, 2D BP can be used as an efficient getter like other molecular compounds containing phosphorus.

In this scenario, we investigated the possibility to use the as-designed heterosystem as an efficient fluorescent chemosensor for molecular oxygen. As a feasibility test, we performed time-resolved fluorescence spectroscopy on the pyrene derivatives and the corresponding 2D BP-based heterosystem in solution with and without exposition to air. We first carried out time-resolved fluorescence experiments on the PBA and PBE solutions exposed to air. In both cases, fluorescence decays show after exposure to air overnight a biexponential behavior with lifetime values, which are shorter compared to PBA and PBE in the degassed solution. According to the literature, the decrease of the fluorescence lifetime is ascribable to the presence of oxygen dissolved in the system.\textsuperscript{65} Moreover, the fluorescence of the 2D BP/PBA and 2D BP/PBE adducts in solution exposed to air under the same conditions presents shorter lifetime components in the case of a triexponential decay with respect to the corresponding adducts in an inert atmosphere.

For a quantitative comparison between the pyrenic compounds alone and on 2D BP-based adduct, the weighted average lifetimes ($\tau_{av}$) are calculated as

$$\tau_{av} = \sum_{i=0}^{n} \tau_i \cdot a_i$$

In detail, $\tau_{av}(\text{PBA} + \text{O}_2)$ is shorter by 1.7 times compared to $\tau_{av}(\text{PBA})$, whereas $\tau_{av}(2\text{D BP}/\text{PBA} + \text{O}_2)$ is shortened by 2.6 times compared to $\tau_{av}(2\text{D BP}/\text{PBA})$ (Table 1). Therefore, the signal variation due to the flux of oxygen, passing from a ratio of 1.7 to 2.6, is amplified by 1.5 times in the system containing 2D BP. Such amplification is even higher (2.6) for the 2D BP/PBE system with respect to PBE alone.

By degassing again the suspensions of the adducts, the fluorescence decays do not recover their initial state. Moreover, the fluorescence decays of the suspensions of the adducts, prepared with a 2D BP suspension previously exposed to air, show the same behavior as the pristine suspensions of the adducts then exposed to air. Thus, the observed variation of the lifetimes of the 2D BP/PBA and 2D BP/PBE adducts in the presence or absence of oxygen is predominantly due to the interaction of PBA and PBE with the oxidized sites of 2D BP. DFT modelling on the 2D BP/PBA system confirmed that the interaction energy between PBA and oxidized 2D BP increases by $-0.22$ eV compared to pristine 2D BP. This is due to the formation of hydrogen bonds between the acid group of PBA and the PO$_4$ sites on the surface of 2D BP, as also evidenced by the much shorter O·····H distances compared to the P·····H ones (2.88 vs 1.95 Å, see DFT section and Figure S2 in the Supporting Information). Analogous considerations can be

### Table 1. Fitting Parameters of the Time-Resolved Fluorescence Decays; $\lambda_{exc} = 390$ nm $\lambda_{em} = 450$ nm

| sample    | $\tau_1$ (a) (ns) | $\tau_2$ (a) (ns) | $\tau_3$ (a) (ns) | $\tau_{av}$ (ns) |
|-----------|-------------------|-------------------|-------------------|------------------|
| Py        | 1.2 ± 0.1 (0.55)  | 2D BP/Py          | 3.1 ± 0.2 (0.64)  | 2D BP/PBA        |
|           | 7.1 ± 0.2 (0.45)  |                   | 12.0 ± 0.4 (0.36) |                  |
| PBA       | 2.1 ± 0.1 (0.42)  | 2D BP/PBA         | 2.2 ± 0.1 (0.48)  | 2D BP/PBA        |
|           | 8.8 ± 0.3 (0.39)  |                   | 8.7 ± 0.3 (0.36)  |                  |
| PBE       | 1.6 ± 0.1 (0.18)  | 2D BP/PBE         | 2.0 ± 0.2 (0.21)  | 2D BP/PBE        |
|           | 5.0 ± 0.2 (0.21)  |                   | 7.0 ± 0.2 (0.17)  |                  |
|           | 40.1 ± 0.5 (0.61) |                   | 62.2 ± 0.1 (0.62) |                  |
| PBA + O$_2$ | 2.0 ± 0.1 (0.17)  | 2D BP/PBA + O$_2$ | 1.0 ± 0.1 (0.22)  | 2D BP/PBA + O$_2$ |
|           | 9.6 ± 0.3 (0.83)  |                   | 4.0 ± 0.1 (0.43)  |                  |
|           |                   |                   | 15.0 ± 0.3 (0.25) |                  |
| PBE + O$_2$ | 2.3 ± 0.1 (0.04)  | 2D BP/PBE + O$_2$ | 0.7 ± 0.2 (0.24)  | 2D BP/PBE + O$_2$ |
|           | 9.6 ± 0.2 (0.96)  |                   | 3.3 ± 0.2 (0.52)  |                  |
|           |                   |                   | 15.2 ± 0.1 (0.24) |                  |

\textsuperscript{a}Data were fitted through bi- or triexponential decays where $\tau_i$ and $a_i$ are the resulting lifetimes (in ns) and relative amplitudes, respectively. For each fitting, $\chi^2 = 1$. \textsuperscript{b}Weighted average lifetimes ($\tau_{av}$) are $\tau_{av}(\text{PBA}) = 14.4$ ns; $\tau_{av}(\text{PBA} + \text{O}_2) = 8.3$ ns; $\tau_{av}(2\text{D BP}/\text{PBA}) = 14.0$ ns; $\tau_{av}(2\text{D BP}/\text{PBA} + \text{O}_2) = 5.7$ ns; $\tau_{av}(\text{PBE}) = 25.7$ ns; $\tau_{av}(\text{PBE} + \text{O}_2) = 9.3$ ns; $\tau_{av}(2\text{D BP}/\text{PBE}) = 40.2$ ns; $\tau_{av}(2\text{D BP}/\text{PBE} + \text{O}_2) = 5.5$ ns.

wavelengths have been performed. In any case, no evidence of the characteristic excimer bands has been observed. Considering these evidences, the bi- or triexponential decay fitting curves are clearly indicative of the presence in solution of two or three different species that we can justify by only speculating on the monomeric, dimeric, or oligomeric nature of the fluorophore, as previously reported for pyrene sulphonate derivatives.\textsuperscript{58}

The fluorescence decays of the three adducts were fitted with biexponential decay for Py and triexponential decays for PBA and PBE, respectively. In all three cases, the presence of 2D BP leads to an increase in the fluorescence lifetime values. In particular, for Py, both $\tau_1$ values increase ($\tau_1$ passing from 1.2 to 3.1 ns and $\tau_2$ passing from 7.1 to 12.0 ns), whereas the relative amplitudes are not very much affected. For PBA and, even more, for PBE, the stabilization effect is evidenced as an increase in the long lifetime component, $\tau_2$, which increases from 5.33 to 61.3 ns for PBA and from 40.1 to 62.2 ns for PBE, whereas $\tau_1$ and $\tau_2$ and the relative amplitudes remain almost constant. This stabilization, which becomes stronger with the trend Py < PBA < PBE, is in perfect accordance with theoretical calculations, with optical and fluorescence microscopy, and with Raman spectroscopy experiments (see following sections).

Overall, the interaction of the pyrene derivatives with 2D BP has a stabilization effect on their emissive electronic excited states. This could be due to a decrease in the nonradiative constant of deactivation of the S$_1$ excited state through the suppression of some vibrational modes (see the Raman spectroscopy section). In detail, the stabilization effect becomes stronger when passing from Py to PBA and to PBE. This could be due either to the different energetic displacement and geometry of the vibronic levels of Py, PBA, and PBE or to a different coupling of these vibronic states with those of 2D BP. Indeed, while in the 2D BP/Py adduct, the coupling occurs only through the pyrene conjugated core, in 2D BP/PBA and 2D BP/PBE adducts, the coupling is also mediated by the boronic functionality and, in particular, is stronger through the ester group of PBE than through the acid group of PBA.

Data were fitted through bi- or triexponential decays where $\tau_i$ and $a_i$ are the resulting lifetimes (in ns) and relative amplitudes, respectively. For each fitting, $\chi^2 = 1$. Weighted average lifetimes ($\tau_{av}$) are $\tau_{av}(\text{PBA}) = 14.4$ ns; $\tau_{av}(\text{PBA} + \text{O}_2) = 8.3$ ns; $\tau_{av}(2\text{D BP}/\text{PBA}) = 14.0$ ns; $\tau_{av}(2\text{D BP}/\text{PBA} + \text{O}_2) = 5.7$ ns; $\tau_{av}(\text{PBE}) = 25.7$ ns; $\tau_{av}(\text{PBE} + \text{O}_2) = 9.3$ ns; $\tau_{av}(2\text{D BP}/\text{PBE}) = 40.2$ ns; $\tau_{av}(2\text{D BP}/\text{PBE} + \text{O}_2) = 5.5$ ns.
done for the oxidized 2D BP/PBE system, where stabilization probably occurs through favorable boron–oxygen interactions. The properties of 2D BP as an oxygen getter, the tunable interaction of PBA and PBE with either pristine and oxidized 2D BP, and the fluorescent properties of the pyrenic derivatives allow to envisage the potential use of the proposed heterostructures as fluorescent active materials in the chemo-sensor for oxygen detection with amplified dynamic range and possibly enhanced sensitivity with respect to the pyrenic derivatives alone.

**Optical and Fluorescence Microscopies.** To get insight into the quality of the 2D BP flakes and their surface and to analyze the amount and coverage of Py, PBA, and PBE molecules on the surface of the functionalized samples, we performed optical and fluorescence microscopies on mechanically exfoliated 2D BP functionalized with either Py, PBA, or PBE by dip coating.

The optical microscopy images of pristine and functionalized 2D BP collected under backscattering conditions have very similar contrast (Figure 7a,c,e,g).

![Figure 7](image)

**Figure 7.** Optical (a,c,e,g) and fluorescence (b,d,f,h) microscopy images of the pristine and functionalized 2D BP flakes mechanically exfoliated on quartz: pristine 2D BP flakes (a,b), 2D BP/Py (c,d), 2D BP/PBA (e,f), and 2D BP/PBE (g,h). The scale bar is 50 μm.

The excitation light is efficiently reflected by the surface of the 2D BP flakes made of atomically flat superimposed sheets, whereas it is transmitted through the transparent substrate (quartz). The same areas of the samples, excited with UV light, give fluorescence images (Figure 7b,d,f,h). The fluorescence microscopy image of pristine 2D BP flakes is almost completely dark (Figure 7b), with the only contrast on the flakes given by the reflection of the residual excitation light passing through the long-pass filter.

The fluorescence images of 2D BP flakes functionalized with either Py, PBA, or PBE show almost the same contrast with respect to the background when the images are collected under the same experimental conditions (Figure 7d,f,h). The fluorescence emission of the heterostructures is weak either due to the low-thickness functional layer, which is probably limited to a single or few molecular layers, or to the lower fluorescence quantum yield of the pyrene-based adducts in the solid state compared to that in solution. However, the increase in the collected-light intensity is evaluated in a factor 1.5–2 going from bare to functionalized 2D BP flakes. To note, the fluorescence signal from the surface of the functionalized 2D BP flakes is substantially homogeneous, suggesting a homogeneous distribution of the Py, PBA, and PBE molecules on the 2D BP flakes. This was further confirmed by both SEM analysis, correlated with EDAX analysis on the same samples (Figure S6 in the Supporting Information), and by AFM analysis. AFM gave very low root-mean-square roughness values, comprised between 1.20 and 1.50 nm, in the three cases (Figure S7 in the Supporting Information), which is nonetheless slightly higher than the roughness of bare 2D BP (0.2 nm) that is atomically flat.11

**Raman Spectroscopy and Aging Studies.** Simulations describe that the coupling between 2D BP and pyrene derivatives is energetically favored and mediated by the boronic functionalities, with a stabilization energy that follows the trend 2D BP/Py < 2D BP/PBA < 2D BP/PBE. In addition, the spectroscopic data above discussed evidence that the excited state of the pyrene derivatives is stabilized by 2D BP with the same trend. In this scenario, Raman spectroscopy can shed light on the stabilization of 2D BP when terminated by a layer of Py, PBA, or PBE.

The Raman spectra of 2D BP/Py, 2D BP/PBA, and 2D BP/PBE samples show the three typical peaks of 2D BP at 360, 435, and 460 cm$^{-1}$ attributed to the A$_g$, B$_{2g}$, and A$_g$ vibrational modes, respectively (Figure 8). For all three samples, the relative intensity of the A$_g$ peak, which corresponds to out-of-plane atomic vibrations, decreases with functionalization, as compared to the relative intensity of the B$_{2g}$ and A$_g$ peaks. Interestingly, the A$_g$ peak decreases with the trend 2D BP > 2D BP/Py > 2D BP/PBA > 2D BP/PBE.

This confirms that the interaction forces involved in the formation of the adducts increase in strength following the trend 2D BP/Py < 2D BP/PBA < 2D BP/PBE, in parallel with the gradual suppression of the vibrational modes of both the organic moiety (as evidenced by time-resolved fluorescence emission) and the inorganic moiety (as evidenced by Raman spectroscopy).

Notably, the position and relative intensity of the peaks in the Raman spectra of freshly prepared and aged samples of functionalized 2D BP remain constant in time even after 6 months of exposure to air. On the contrary, the spectrum of a 3 month-aged sample of bare 2D BP is flat and featureless. Thus,
while pristine 2D BP undergoes severe degradation in air, its crystalline structure in the adducts is preserved from oxidation in air for over 6 months.66 Interestingly, the optical images of the 6 month-aged sample reveal that while many of the functionalized 2D BP flakes are preserved, some of them seem to have suffered degradation from the edges. Edges are indeed presumably less covered by the organic layer and thus more prone to air oxidation (Figure S8 in the Supporting Information).

This indicates that the organic layer, acting as a physical barrier for water/oxygen and as an energy stabilizing agent, has a strong protecting functionality. To note, in suspension, the intimate interaction between 2D BP flakes and organic compounds, which is at the basis of the protecting functionality, is reasonably much weaker compared to the solid state because of scavenging solvent molecules.

In solid state, the protecting functionality seems equal for all three investigated samples. However, the optical and fluorescence microscopy images of the adducts, taken over a period of 1 week, reveal the condensation of droplets of atmospheric water on the surface of the functionalized flakes. The images also reveal that the pyrene derivatives partially solubilize into droplets (Figure S9 in the Supporting Information). In detail, a more rapid condensation of atmospheric water is observed on the surface of the 2D BP/Py and 2D BP/PBA adducts (1–2 days) as compared to 2D BP/PBE (1 week). The condensation of atmospheric water, in the case of bare 2D BP, accelerates the degradation processes through the dissociation of oxidized P atoms from the surface of 2D BP (Figure S10 in the Supporting Information).

Therefore, the higher wettability/solubility of the PBA and Py layers with/in atmospheric water, compared to the PBE layer, combined with the slightly lower stabilization energy of their adducts with 2D BP, could cause a lower long-term stability of the corresponding 2D BP/Py and 2D BP/PBA samples compared to the 2D BP/PBE samples. However, the stability in air for at least 6 months is demonstrated for all functionalized 2D BP samples by Raman spectroscopy, which is in good accordance with the most relevant literature up to date.68

■ CONCLUSIONS
The aim of this work was to study the chemical—physical nature of the interactions involved in the formation of adducts of 2D BP and boronic derivatives of a conjugated organic fluorescent molecule (pyrene). DFT simulations predicted a favorable coupling between 2D BP and pyrene derivatives. The main contribution to the stabilization energy arises from the noncovalent interactions between the conjugated core of pyrene and the phosphorus atoms of 2D BP. A smaller but still relevant contribution (up to 0.5 eV) arises from the noncovalent P–B interaction, which is stronger in the boronic ester than in the boronic acid group of the pyrene derivatives. NMR spectra in suspension confirmed the noncovalent nature of the interactions involved in the formation of the adducts. Although noncovalently bonded, modelling showed that both the atomic and electronic structures of 2D BP and of the pyrene derivatives are rearranged in the adducts, resulting in a lowering of the band gap of 2D BP by around 0.10 eV. Time-resolved fluorescence emission data evidenced that, in the adducts, the pyrene derivatives are stabilized in their excited state by 2D BP, with a stabilization effect that is again stronger for the pyrene derivative bearing the boronic ester rather than the boronic acid group, thus following the theoretically predicted trend. Moreover, further investigation in the excitonic dynamics of the 2D BP-based heterostructures indicated that the 2D BP/PBA and 2D BP/PBE systems can be implemented as active materials in a fluorescent chemosensor for oxygen detection. Indeed, the two systems show relevant modulation of their fluorescence decay time constants with respect to the pyrenic derivatives alone. Finally, Raman spectroscopy and fluorescence microscopy showed that 2D BP also is stabilized in the adducts in solid state. Specifically, 2D BP when terminated with a layer of pyrene derivatives forms heterostructures, which are stable in air for more than 6 months. The presented study represents an innovative contribution to the understanding of the chemistry at the interface between 2D BP and organoboron compounds. The band gap tailoring and the modulation of the reactivity of 2D BP by means of pyrene derivatives are interesting tools for designing heterosystems with multifunctional applications, from passivation and protection of 2D semiconductors to the sensing of analytes of interest such as molecular oxygen.

■ ASSOCIATED CONTENT

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Pathways for the heteroatomic π-π stacking in conjugated polymers: A DFT and experimental investigation

Supporting Information

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Raman spectrum of liquid exfoliated 2D BP, absorption spectra of pyrene derivatives in solution, optimized geometry and energy parameters and bond lengths from DFT simulations, 13C and 1H NMR spectra of the adducts, SEM and EDAX analysis of the adducts, and optical, fluorescence and AFM microscopy of the oxidized adducts and oxidized 2D BP (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

E-mail: maria.castriciano@cnr.it (M.A.C.).
E-mail: s.toffanin@bo.ismn.cnr.it (S.T.).

ORCID

Margherita Bolognesi: 0000-0003-0080-3279
Claudia Ferroni: 0000-0002-7386-1624
Gabriele Manca: 0000-0003-2068-1731
Andrea Ienco: 0000-0002-2586-4943
Maria Caporali: 0000-0001-6994-7313
Lucia Calucci: 0000-0002-3080-8807
Maria Angela Castriciano: 0000-0002-1514-8820
Stefano Toffanin: 0000-0003-4099-8664

Notes

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