Lattice Opening Upon Bulk Reductive Covalent Functionalization of Black Phosphorus

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Abstract: The first chemical bulk reductive covalent functionalization of thin layer black phosphorus (BP) beginning with BP intercalation compounds has been developed. Through effective reductive activation, covalent functionalization of the charged BP is achieved by organic alkyl halides. Functionalization was extensively demonstrated by means of several spectroscopic techniques, showing higher functionalization degrees than the neutral routes. Moreover, these results were complemented by means of DFT calculations.

Since 2014, two-dimensional (2D) Black Phosphorus (BP) has attracted enormous attention throughout the scientific community due to its high p-type charge carrier mobility up to ~6000 cm² V⁻¹ s⁻¹ and its tunable direct bandgap ranging from ~0.3 eV for bulk to ~2 eV for monolayers.[1–9] In contrast to graphene, BP exhibits a marked puckering of the sp³ structure, constituting a two dimensional α-only system, involving one lone electron pair at each P atom. Whereas its outstanding physical and materials properties have been intensively investigated, its chemistry remains almost unexplored.[10,11] Indeed, a first-series of non-covalent functionalization protocols has been reported, mainly focused on improving the intrinsic instability of BP against water and oxygen. The development of supramolecular hybrids of BP with perylenediimides (PDIs) and 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) lead to the formation of a protective layer all over the surface of the BP avoiding the oxygen and water penetration.[12,13] Similarly, supramolecular network formation has been achieved by solution deposition of trimesic acid and melamine cyanurate under ambient conditions.

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First, we investigated the in-situ treatment of a potassium-BPIC upon the addition of an electrophilic functionalization reagent followed by Raman Spectroscopy.[20] This extremely powerful technique allows the easy determination of small spectroscopic changes indicating a successful modification of the BP lattice. Therefore, we slowly evaporated hexyl iodide onto the previously synthesized BPIC KP$_6$, under ultra-high vacuum (UHV) conditions and measured constantly Raman spectra in order to monitor the course of the functionalization process in-situ. Here, we would like to emphasize that none of the used reagents were exposed to ambient conditions at any time. Indeed, the BP was intercalated in a glovebox under Argon atmosphere and transferred into the UHV-reaction chamber, which was equipped with a capillary filled with the hexyl iodide. The complete setup was assembled in an Ar-filled glovebox before its connection to the UHV setup for the in-situ Raman measurements (SI 1). As depicted in Figure 1, highlighted in grey, a series of new distinct Raman modes arise below 400 cm$^{-1}$ concomitantly with the increasing amounts of the evaporated electrophilic hexyl iodide. More specifically, a sharp peak at 145 cm$^{-1}$, a broad shoulder around 210 cm$^{-1}$, another broad feature between 260 cm$^{-1}$ and 285 cm$^{-1}$ and a small peak between the A$_2^+$ and B$_2^+$ peak at 405 cm$^{-1}$ can be clearly observed, strongly suggesting the modification of the 2D BP lattice. Bearing in mind the experimental UHV conditions, these spectroscopic changes should originate from the formation of a P–C bond between the BP lattice and the hexyl chain. For further understanding this very promising first hint towards a successful covalent modification of the BP lattice, we carried out DFT calculations simulating the covalent attachment of a methyl group to BP and calculating the expected Raman spectra. In this sense, the predicted Raman spectrum of a methylated BP monolayer saturated with potassium fits extremely well our experimentally obtained results. Moreover, we have investigated the effect of the alkali metal used for the preparation of the BPICs in the functionalization reaction. As can be observed in Figure SI 5, the in-situ experiment using Na-BPICs leads to the appearance of similar Raman features than in the case of potassium. This is in clear contrast with GICs chemistry, in which the Na-intercalation compounds cannot be achieved without using Na$^+$($\text{G}(\text{C}$_8$)$_n$)-complexes, where G accounts for linear ethylene glycol dimethyl ether homologues (“glymes”)[27], and therefore has not been used for reductive graphene covalent chemistry.

In the next step, we focused on the bulk reductive covalent functionalization of BP using the wet chemical approach.[17,28] For this purpose, pristine BP was intercalated with sodium or potassium to yield the respective BPICs (NaBP$_6$, K BP$_6$), which afterwards was dispersed in purified THF. By applying ultrasonication a better separation of the negatively charged BP sheets can be achieved before the electrophilic trapping reagent – alkyl halide – was added and reacted for 1 hour under magnetic stirring (Scheme 1). After filtration in the glovebox, the reaction product was obtained in form of a dark grey powder, which could then be used for further characterization. SRS using an excitation wavelength of 633 nm revealed the appearance of a new band at around 145 cm$^{-1}$, which was also observed in the in-situ experiment, and new Raman modes in the 250–300 cm$^{-1}$ region. Interestingly, these new fingerprints fit well with the calculated Raman spectra for a methylated BP monolayer without saturation. One could have expected that the electrophilic trapping with hexyl iodide will lead to the formation of 2D-BP phosphonium sites incorporated in an otherwise intact
heagonal P-lattice, with a formal positive charge in the alkylated P-atoms. However, our DFT calculations point towards a P–P bond cleavage. Indeed, we only obtain data for the phosphonium if a whole positive charge is included on the BP sheet. In this scenario we found a Raman fingerprint at 315 cm⁻¹, which seems to be absent in the experimental data. To further check the suitability of the DFT calculations, we also developed the functionalization reaction with methylidiole, showing an excellent agreement with the predictions (Figure S1 4&10). According to our calculations, we assume that the occurrence of these distinct peaks is related to P–P vibrations originating from lattice distortions in the BP sheet, which are caused by the covalent attachment of the alkyl chains (see Supporting Information Videos XX for further details). In this sense we discard the assignment of these new Raman modes to P–C bonds[7] because they exhibit an asymmetric vibration and consequently should not be Raman active. Moreover, the peaks at around 195 cm⁻¹ and 230 cm⁻¹ can be associated to turbostratic disordering of individual layers or edge phonons in the BP lattice and can even be measured in pristine micromechanically exfoliated BP with a certain thickness.[4,6] We would also like to emphasize that SRM of covalently functionalized BP can lead to slight variations in the Raman spectra (SI 6). One explanation might be that no potassium or iodine is coordinated to the modified BP sheet, as it was already outlined by our DFT calculations (SI 3). Also, one could consider that different addition patterns of the covalently bound addend might result in diverse lattice distortions leading to P–P vibrations with varying energies. Furthermore, our DFT calculations suggest that depending on the coverage of the addend, the intensity of the new Raman modes may change (SI 7).

Moreover, we have checked the suitability of the reaction using both Na- and K-BPICs as the starting activated material, and methyl- and hexylidiole as benchmark electrophiles. Mean Raman spectra (at least 50 single point spectra) collected for all the samples repeatedly exhibit the same behavior with clear Raman spectra (at least 50 single point spectra) collected for all the samples repeatedly exhibit the same behavior with clear Raman spectra (SI 11) indicating the de-functionalization reaction. Therefore, we conducted Raman mappings of the functionalized flakes deposited on Si/SiO₂ wafers increasing the temperature from 20 °C up to 220 °C. The resulting mean spectra are visualized in Figure 2b and SI13. The three main vibrational Raman modes of BP can be clearly seen as well as the characteristic peaks below 300 cm⁻¹ related to the covalent functionalization, which are highlighted in grey. When heating the sample, the intensity of these modes start to decrease at temperatures above 160 °C, until they nearly vanish at 200 °C. This result correlates very well with the observed mass loss in the TGA-MS analysis indicating the de-functionalization of the BP lattice. Here, it should be mentioned that also the three main Raman modes of BP decrease in absolute intensity with increasing temperature, which is explained by the thermal instability of the sample (SI 11). Moreover, it is remarkable that neither hexylidiole (m/z = 212), I₂ (m/z = 254), nor its monoatomic equivalent m/z = 127 have been detected (SI 10). This observation points towards the formation of the side product KI between the leaving group iodide and the K from the intercalation compound, which has a melting point of 723 °C and thus cannot be detected in the measurement. As a matter of fact, the residual mass loss in the functionalized sample is ca. 30%, which could be related to the presence of KI due to its poor solubility in THF during the work-up (vide infra), as well as the formation of graphicarbon from the carbon addends. These assumptions can be confirmed by the solubilization of KI in silver nitrate as well as the presence of benzene mass fragments, typically associated to nanocarbon degradation.[28] Moreover, the formation of these carbon nanoflakes was corroborated by Raman spectroscopy (SI 12). Finally, the abrupt mass at around 480 °C may be related with trapped alkyl moieties between the layers, the formation of more stable P-based nanoflakes like nanoribbons or the decomposition of cluster-like phosphorus species, taking into account the smaller bond energy between P–P compared to P–C.

In order to unambiguously demonstrate the covalent binding of the alkyl chains, we performed a temperature-dependent SRS analysis, which is a powerful characterization technique for observing the detachment of covalently bound addends from a 2D-lattice, like previously developed for graphene. This technique allows to investigate the reversibility of the functionalization reaction. Therefore, we conducted Raman mappings of the functionalized flakes deposited on Si/SiO₂ wafers increasing the temperature from 20 °C up to 220 °C. The resulting mean spectra are visualized in Figure 2b and SI13. The three main vibrational Raman modes of BP can be clearly seen as well as the characteristic peaks below 300 cm⁻¹ related to the covalent functionalization, which are highlighted in grey. When heating the sample, the intensity of these modes start to decrease at temperatures above 160 °C, until they nearly vanish at 200 °C. This result correlates very well with the observed mass loss in the TGA-MS analysis indicating the de-functionalization of the BP lattice. Here, it should be mentioned that also the three main Raman modes of BP decrease in absolute intensity with increasing temperature, which is explained by the thermal instability of the FL-BP.[12]
In Figure 3, the narrow region scan of the P 2p region of pristine BP (bottom) displays the P 2p region. Indicated by black, orange and red are the P 0, P-C and oxidized P 0 species.

In Figure 3 the narrow region scan of the P 2p region of pristine BP and the covalently modified analogue can be seen. The fitted model comprises three spin-orbit split doublets (splitting of 0.8 eV) assigned to pristine BP P 0 (black), oxidized phosphorous P + (red), and carbon-bound phosphorus (orange). The P 0 peak core level signal of the P 0 species was set to 130.1 eV, which is the value determined from the measurement of the pristine BP sample, and is in perfect agreement with a value of 130.06 eV reported in literature for crystalline BP. For all samples the chemical shift between P 0 and P + is constrained to be 4.1 eV, in accordance to the pristine sample. Our applied fitting suggests that for the hexyl-functionalized sample a carbon-bound species with a chemical shift of +2.7 eV relative to the P 0 signal can be observed. Although, the assignment of peaks in the P 2p region has to be handled cautiously, as chemical shifts for stable POx structures at the surface of black phosphorus crystals reportedly are very similar, this gives experimental evidence for the successful covalent modification of the BP lattice. Additionally, the related survey spectrum (SI 16) shows contributions of potassium iodide (KI), which as previously mentioned is formed as side product due to the chosen reaction route, thus further confirming the successful covalent functionalization of BP.

Additionally, we have evaluated the stability of the final functionalized flakes versus exposure to oxygen and moisture by measuring the SRM immediately after functionalization and after 15 days showing the typical exponential decay of the Raman modes, reflecting its degradation (SI 17). Furthermore, we have evaluated with XPS the influence of water on the covalent functionalization procedure. For this, we have submitted the sample to a final aqueous washing step during the work-up process. Interestingly, the spin-orbit split doublets assigned to the formation of P-C bonds dramatically decreases, while the peaks associated to the formation of KI almost completely disappeared, in accordance to the high solubility of KI in water (SI 18). These results point towards a water assisted de-functionalization of the BP lattice.

The crystallinity of the flakes functionalized with both methyl and hexyl moieties was investigated by X-ray diffraction in SAXS configuration under vacuum without exposing the samples to ambient conditions. The samples preserved the in-plane crystallinity with a substantial decrease in the (0 02) and (0 40) layer peaks, indicative of turbostratic disorder. In comparison to pristine BP, new peaks arise in hexylated BP (SI 19). The dashed gray lines are peak positions calculated for an orthorhombic system, which is slightly compressed (lattice parameters a=0.3308 nm, b=1.0481 nm, and c=0.4236 nm in comparison to values of pristine BP, a=0.3313 nm, b=1.0473 nm, and c=0.4374 nm). The peaks for methylated BP are rather broad, which indicates a lower order in comparison to the hexyl sample, and are described by a model with separated planes (two or few layer model), where the Cmca symmetry of BP has been lost. It is proposed that the lack in symmetry in the b-axis leads to an additional reflecting plane in b-axis and the structure is described with lattice parameters a=0.3518 nm, b=0.2478 nm, and c=0.4127 nm (dashed red lines). The indices of the identified reflections are also found in the supporting information. Differently, the hexyl functionalized sample cannot be described successfully with one single lattice structure, thus two phases are used, the distorted (compressed) phase and the separated phase (two or few layer model). These results are related to the presence of randomly restacked nanosheets, and therefore to the presence of turbostratic disorder, as previously stated by Raman spectroscopy.
≈7% of the total P atoms.

These high-fielded P atoms nicely bear a localized negative charge and that corresponds to ppm, which can be assigned to axially coordinated P atoms functionalized with methyl moieties showing the appearance of a new signal at 22 ppm confirming the presence of P-CH$_3$ species. Accordingly, the $^{31}$P MAS NMR spectrum acquired in $^1$H-$^{31}$P cross-polarization mode shows the disappearance of the original phosphorene signal at 18.2 ppm strongly supporting the formation of a covalent P–CH$_3$ bond.

Figure 4. a) $^{31}$P MAS NMR spectra of pristine and intercalated BP (KP$_6$) featuring the signal for single black phosphorus at 18.2 ppm as well as a signal at -117 ppm, which can be assigned to axially coordinated P atoms bearing a localized negative charge. b) $^{31}$P MAS NMR spectrum of BP functionalized with methyl moieties showing the appearance of a new signal at 22 ppm confirming the presence of P-CH$_3$ species. Accordingly, the $^{13}$C MAS NMR spectrum acquired in $^1$H-$^{31}$P cross-polarization mode shows the disappearance of the original phosphorene signal at 18.2 ppm strongly supporting the formation of a covalent P–CH$_3$ bond.

Last but not least, to gain unambiguous evidence on the covalent bond formation we conducted quantitative magic angle spinning $^{31}$P solid nuclear magnetic resonance ($^{31}$P MAS NMR). Figure 4A shows the spectra of pristine BP, the intercalated KP$_6$, as well as the methylated reaction product. In the case of KP$_6$, it can be clearly observed the expected signal for phosphorene at 18.2 ppm (Ref. Nat. Mater.) plus a single new signal at -117 ppm, which can be assigned to axially coordinated P atoms bearing a localized negative charge and that corresponds to ≈7% of the total P atoms.$^{[31]}$ These high-fielded P atoms nicely agree the proposed P atoms popping out from the 2D framework after receiving electronic density from K in the BPIC structure (Figure SI 3). Following this, the $^{31}$P MAS NMR spectrum of the methylated BP shows the complete disappearance of the negatively charged P atoms, and the appearance of a new signal at 22 ppm, a value that fits very precisely to that expected for a P–CH$_3$ and not for a P+–CH$_3$ bond, and that integrates for ≈7% of the total P atoms after deconvolution (Figure 4B).

Moreover, $^{13}$C MAS NMR also supports the formation of new P–CH$_3$ bonds (and not the corresponding phosphonium species), and in order to further confirm the covalent functionalization, the spectrum was acquired in $^1$H-$^{31}$P cross-polarization mode, in such a way that only the P atoms having H atoms at 1 or 2 atom bond distance will be detected (Figure 4B). The inset shows the persistence of the signal at 22 ppm and the complete disappearance of the original phosphorene signal at 18.2 ppm, which strongly supports the formation of a covalent P–CH$_3$ bond. These NMR results, together, indicate that the KP$_6$ BPIC possesses a ≈7% of localized and negatively charged P atoms that react quantitatively in a substitution reaction with methyl iodide to give new covalent P–CH$_3$ bonds and KI. In accordance with this, and as previously shown with other characterization techniques, other iodides such as the hexyl derivative can be used to covalently functionalize, with a lower degree of functionalization (hexylated BP, Figure S20), probably due to the reduced reactivity and higher steric hindrance compared to methyl iodide, but in any case with comparable values to that of related hexyl-functionalized graphene.$^{[28]}$ Moreover, in terms of solubility, the alkylated BP exhibits a similar behaviour to that of hexyl functionalized graphene in o-DCB, indicative of improved processability (SI 21).

These results point towards a P–P bond breakage caused by the covalent addition, and fostered by the strong polarization induced by the alkali-metal doping. This suggest that phosphonium sites are not involved in the reaction, leaving behind P atoms still bound to two neighbouring P atoms and one C atom, while a lone pair of electrons remains, thus limiting the environmental stability of the final material, as previously discussed.

In conclusion, we demonstrated that intercalating BP with alkali metals prior to the reaction with alkyl halides result in remarkably higher degree of functionalization compared to the neutral route. These results pave the way for the development of the reductive covalent chemistry of black phosphorus, opening new pathways for the finely tuning of the BP interface and its physical properties. Taking into account the rich chemistry develop for graphene, one can envision the synthesis of complex hybrid materials endowed with functional molecules like precursors of click chemistry such as alkynes, magnetic macrocycles, or optically active dyes, to name a few.

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Keywords: black phosphorus • covalent functionalization • reductive • Raman spectroscopy • $^{31}$P NMR

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