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Supporting Information

Interface Amorphization of Two-Dimensional Black Phosphorus upon Treatment with Diazonium Salts

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SI 1: SRM of covalently functionalized BP *via* a neutral route on Si/SiO₂

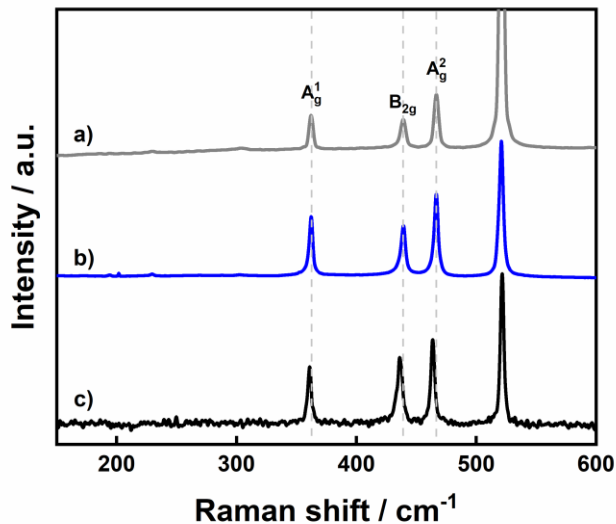


Fig. S1: Mean Raman spectra of a) BP + D3, b) BP + D1, c) pristine BP recorded at an excitation wavelength of 532 nm. BP + diazo salts in NMP reacted at room temperature for 24 h. In Comparison to the Raman spectrum of pristine BP, no difference can be observed and the peak list remains unchanged for the corresponding reaction products obtained *via* neutral route.

SI 2: TGA-MS analysis of covalently functionalized BP *via* neutral route

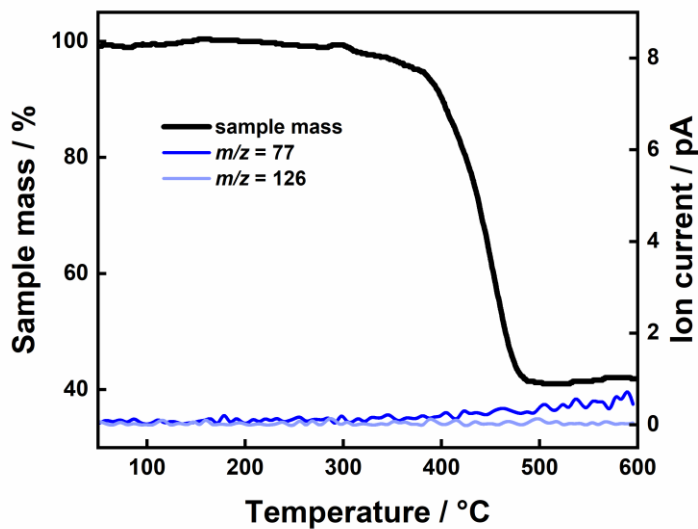


Fig. S2: TGA-MS analysis of BP + D1 reacted in NMP, at room temperature: No evident mass loss at around 160 °C can be seen and also no characteristic mass fragments of the aryl addend are detected by the MS indicating that the BP lattice is not covalently modified *via* neutral route.

SI 3: ^{31}P -MAS NMR Spectroscopy

We measured quantitative ^{31}P -MAS NMR of neutral BP with **D1** in NMP. The functionalization degree is determined to be less than 1% (no obvious shoulder at 22 ppm)

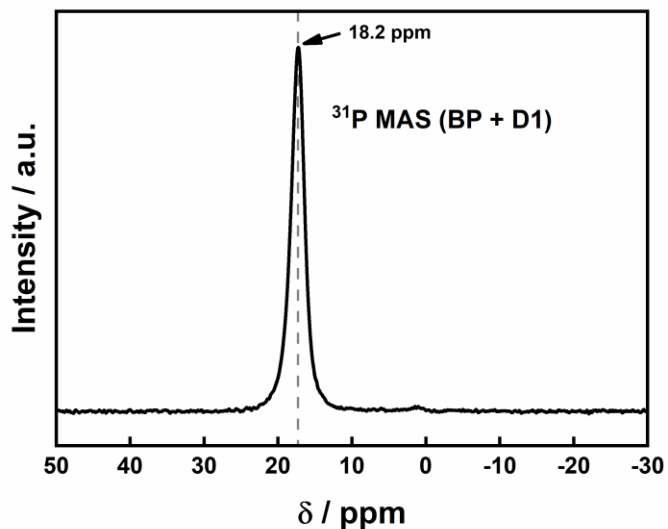


Fig. S3: ^{31}P -MAS NMR spectrum of neutral BP with **D1** in THF displaying the complete range and all associated spinning sidebands. No additional signals are observed in the area relevant to the functionalization of BP.

SI 4: SRM of the reaction product of BPICs with different amounts of the alkali metal with D2

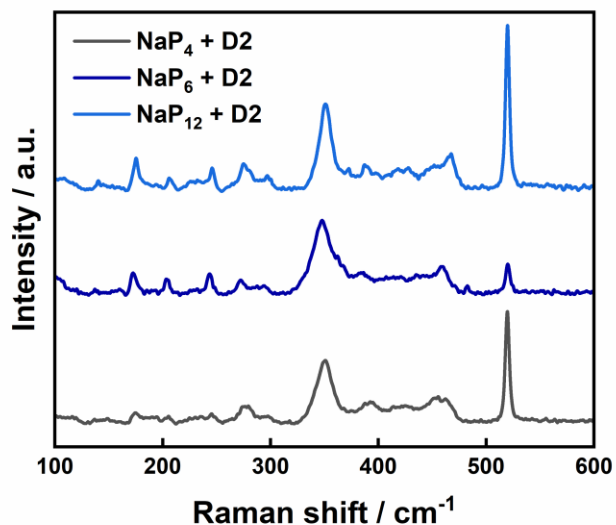


Fig. S4: Mean Raman spectra of NaP_4 , NaP_6 , and NaP_{12} + **D2**. Independent of the amount of the intercalated alkali metal – in this case, sodium – the structural evolution of crystalline BP to amorphous RP takes place.

SI 5: TG-MS analysis of the reaction product of KP₆ with D2

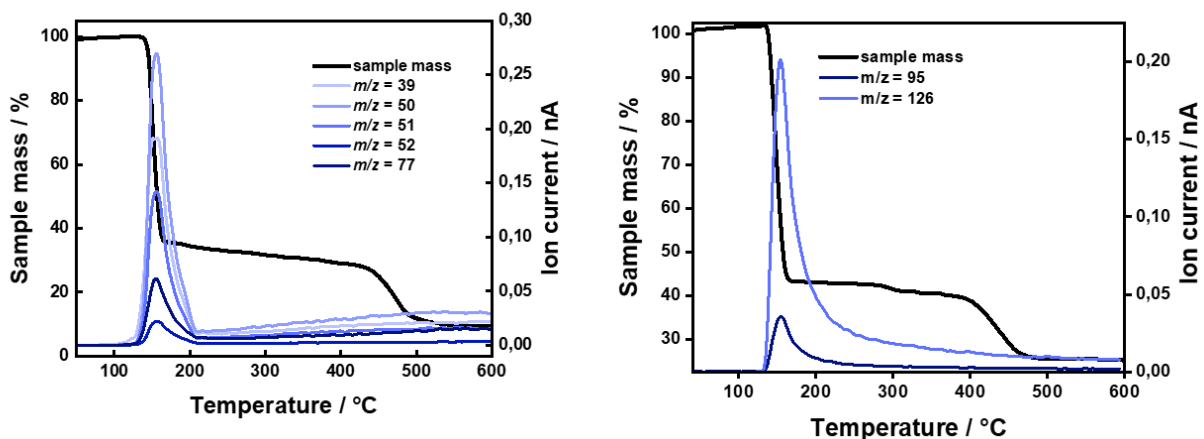


Fig. S5. TG analysis displays a significant mass loss at around 160 °C which can be correlated to mass fragments characteristic for the phenyl-cation/radical ($m/z = 39, 50, 51, 52, 77$) (left). Even the masses $m/z = 95$ for fluoro-benzene and $m/z = 126$ for the 1-fluoro-4-methoxybenzene can be detected in the MS analysis (right). Note that the slight increase observed below 160 °C is an inaccuracy of the instrumentation during the tare process.

SI 6: TG-MS analysis of the reaction product of KP₆ with D1

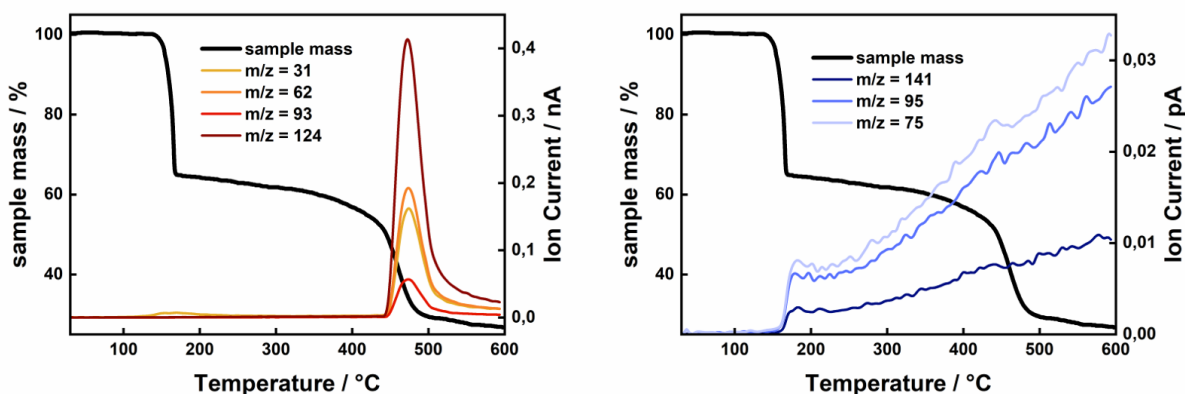


Fig. S6: (Left) TG analysis displays a significant mass loss at 160 °C which can be correlated to the decomposition of 1-fluoro-4-nitrobenzene before the BP lattice decomposes to P₄ above 400 °C. (Right) Signals of the ion current for the detection of the fluoro derivative ($m/z = 75, 95, 141$) are shown separately, for clarity reasons.

SI 7: TG-MS analysis of the reaction product of KP₆ with D3

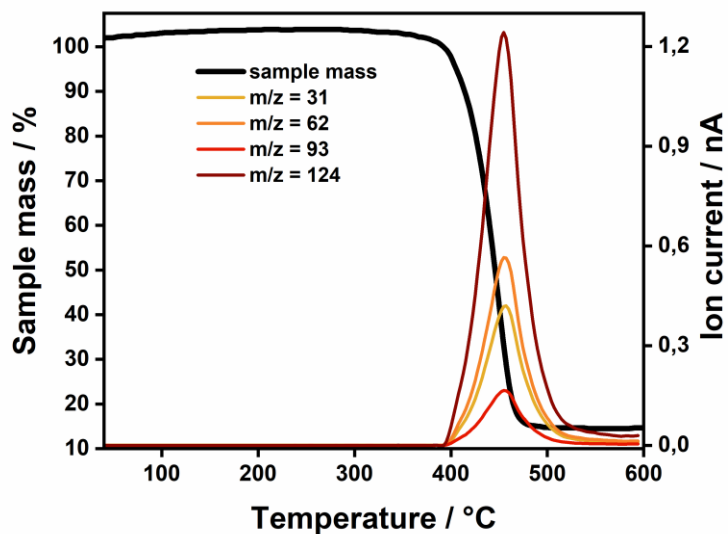


Fig. S7: TGA-MS analysis featuring complete decomposition of BP to P₄, P₃, and P₂ clusters ($m/z = 124, 93, 62, 31$). It was only possible to measure TG of unreacted remaining BP, the rest of the solution completely polymerized in the flask and therefore could not be characterized like the reaction products of KP₆ + D1/D2. Though, it is remarkable that the BP lattice is not modified covalently while the solution completely polymerizes.

SI 8: Mass spectrometry analysis of the reaction product of KP₆ and D2

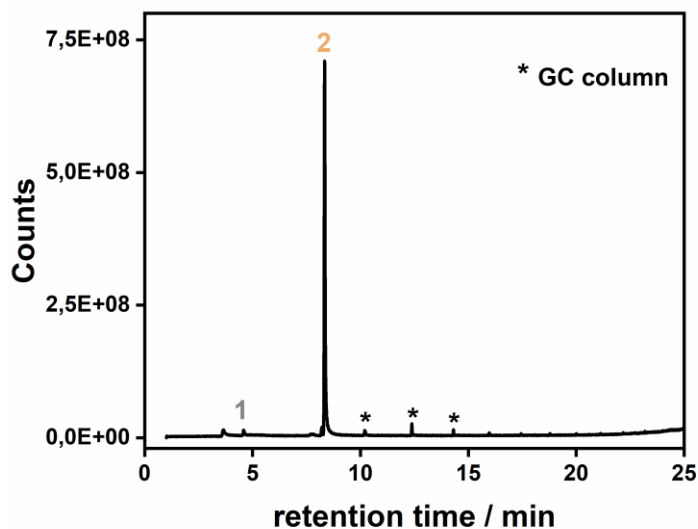


Fig S8a: GC-MS chromatogram/spectrum of the sample KP₆ + D2 at a TG injection temperature of 160 °C. The resulting elugram reveals two peaks: 1 (4.6 min): THF; 2 (8.3 min): 1-fluoro-4-methoxybenzene. The peaks at retention times >10.0 min (marked with *) belong to fragments of the GC column.

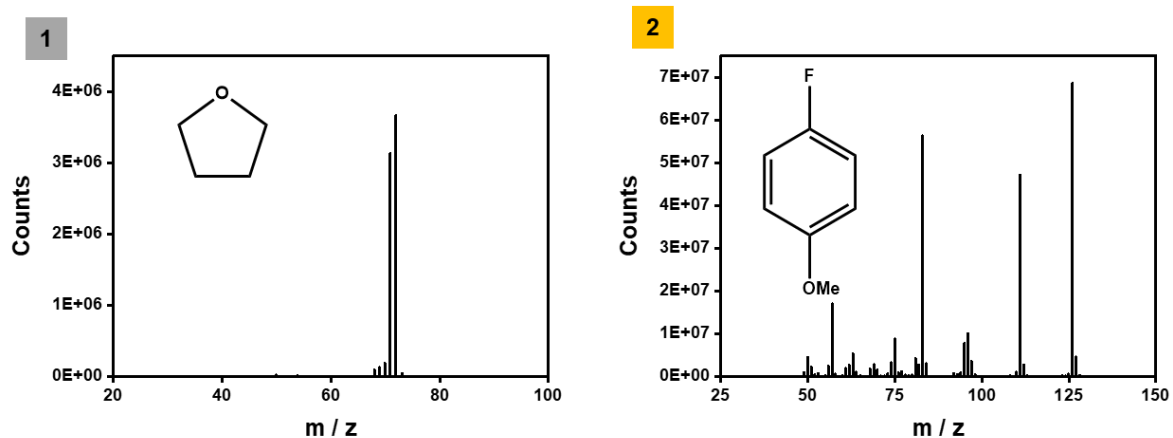


Fig S8b: Mass spectroscopic characterization of the separated GC fractions at 4.6 min identified as THF and at 8.3 min showing the typical fragmentation pattern of 1-fluoro-4-methoxybenzene.

SI 9: Mass spectrometry analysis of the reaction product of KP₆ and D1

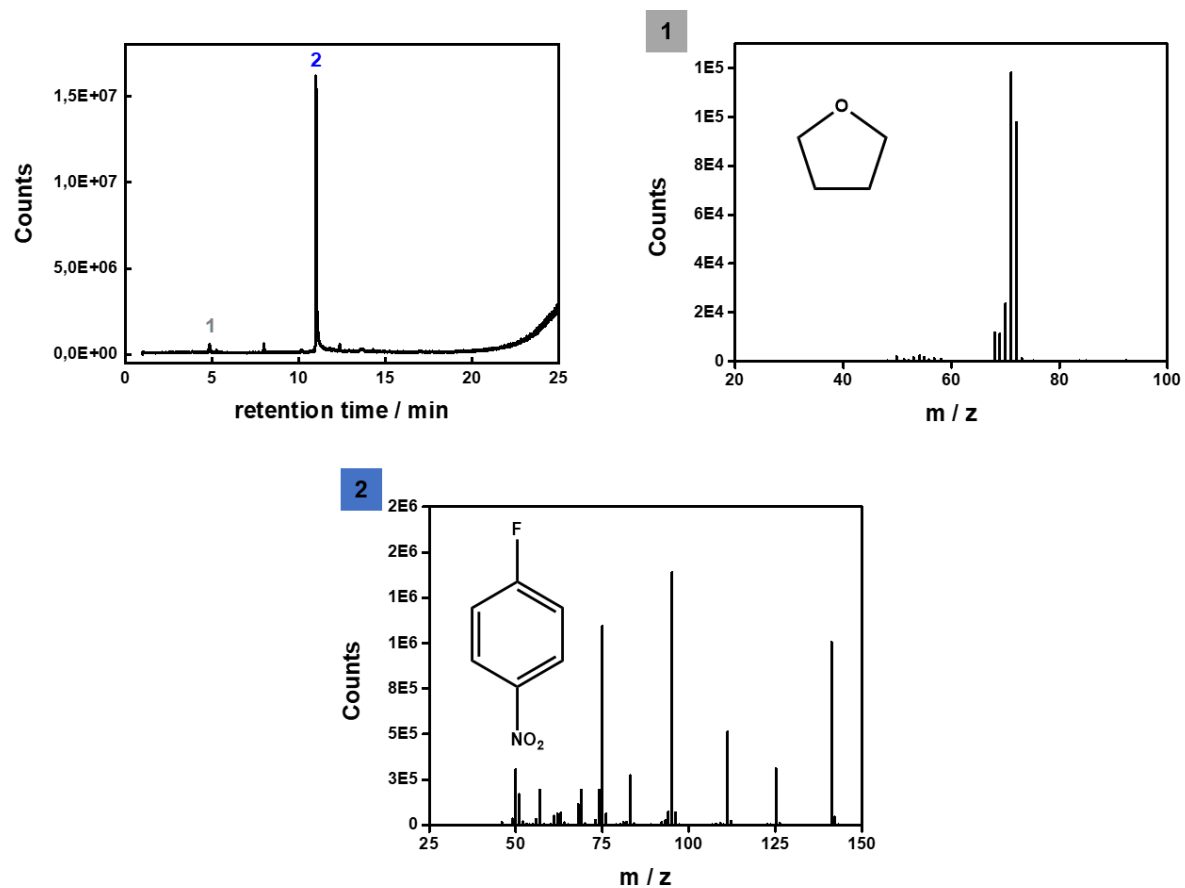


Fig S9: GC-MS chromatogram/spectrum of the sample KP₆ + D1 at a TG injection temperature of 160 °C. The elugram reveals three peaks: 1 (4.6 min): THF; 2 (10.8 min): 1-fluoro-4-methoxybenzene. Again, the fragmentation pattern undoubtedly confirms the structure of the fluoro derivative.

SI 10: EPR of NaP₆

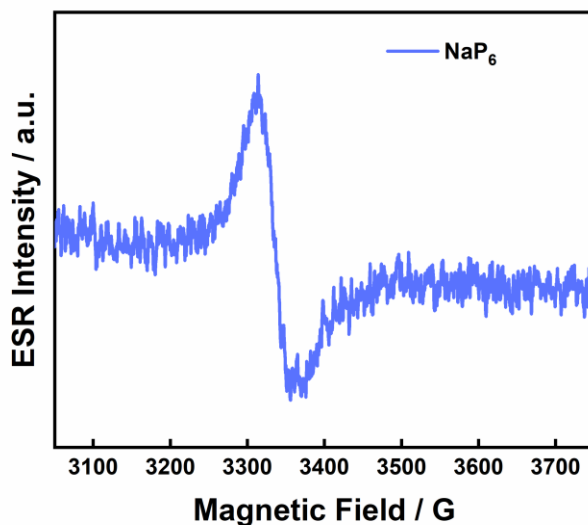


Fig S10: EPR spectra of NaP₆.

The EPR of the investigated NaP₆ sample is presented in Fig. SI 11. The pristine black phosphorus does not show any signal, as it is expected from a diamagnetic semi-metal, as discussed in a previous article.^[1] In the alkali intercalated BP, a broad resonance is observed with a slight asymmetry, thus identified as a Dysonian lineshape in the slowly diffusive limit (also referred to as the NMR limit).^[2] This kind of lineshape is observed when the signal is originating from mobile, conducting charge carriers and the microwave field cannot completely penetrate through the volume of the grain because of the skin effect. In this regime, the Dysonian can be approximated by a sum of absorption and a dispersion curve with a phase, which describes the asymmetry of the curve.^[3]

We identify that the signal is originating from the charge carriers present in the intercalated phosphorene sheets. The breadth of the line is 4.00(2) mT in NaP₆, which suggests a spin relaxation time of 1.49 nanoseconds. The peak is located at $g=2.02240$, which is higher than that of the g -factor of the free electron. The phase is 11.2(1), which also suggests weak metallicity and the presence of new charge carriers compared to the pristine material.

- [1] B. G. Márkus, F. Simon, K. Nagy, T. Fehér, S. Wild, G. Abellán, J. C. Chacón-Torres, A. Hirsch, F. Hauke, *physica status solidi (b)* **2017**, *254*, 1700232.
- [2] F. J. Dyson, *Physical Review* **1955**, *98*, 349-359.
- [3] L. Walmsley, *Journal of Magnetic Resonance, Series A* **1996**, *122*, 209-213.