Surface functionalization of black phosphorus nanosheets with nitrenes: Identification of P=N bonds using isotopic labeling

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Surface functionalization of two-dimensional nanosheets provides a facile path to tune their fundamental physical, chemical, and electronic properties. However, methods to directly probe new bond formation at modified surfaces are scarce. Materials characterization techniques often cannot distinguish between intentional surface functionalization and adventitious side reactions (e.g., oxidation) with sufficient resolution, making the assignment of surface binding motifs circumstantial and challenging to distinguish.

To circumvent these limitations, we applied techniques from molecular phosphorus chemistry to directly observe deliberate surface functionalization on black phosphorus. Black phosphorus (*b*P), a 2D van der Waals material composed entirely of tricoordinate phosphorus atoms, is particularly suited to mild and highly specific surface modification protocols due to the availability of lone pairs in its basal plane. While previous efforts to covalently functionalize *b*P rely primarily on harsh conditions traditionally used for less reactive nanosheets, a mild, surface-specific protocol is used to functionalize few-layer *b*P with a family of nitrenes (RN) photolytically generated from the corresponding azides. Functional groups with embedded spectroscopic tags installed on the *b*P surface allowed the chemical structure to be examined in detail with a multitude of characterization techniques including vibrational, X-ray (photoelectron, emission), NMR, and UV-vis spectroscopies. Bonds between functional groups and the *b*P surface were directly probed using infrared spectroscopy and ^{15}N labeling experiments in conjunction with DFT methods. Diagnostic P=N vibrational stretches were observed, allowing for conclusive identification of iminophosphorane units on the nanosheet surface.

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