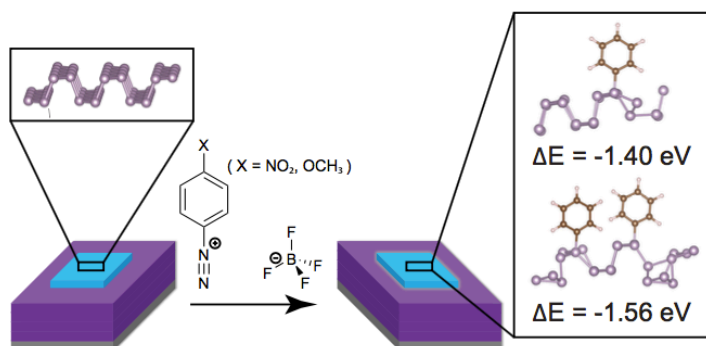


## Covalent Functionalization and Passivation of Exfoliated Black Phosphorus Via Aryl Diazonium Chemistry

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**Caption:** Depiction of the reaction scheme of benzene-diazonium tetrafluoroborate derivatives with 2D black phosphorus (blue) on a SiO<sub>2</sub> (purple) on Si (gray) substrate. The calculated lattice distortions resulting from adsorption of the aryl groups, and their respective adsorption energies, are shown on the right.

### Scientific Achievement

In an inter-use-case group collaboration with Marks, Hersam has utilized the chemical reactivity of few-layer black phosphorus (BP) to covalently functionalize the surface of mechanically exfoliated few-layer BP with 4-nitrobenzene diazonium and 4-methoxybenzene diazonium tetrafluoroborate salts. This chemical modification results in a controllable p-type doping of the BP that significantly improves BP field-effect transistor (FET) device metrics. In addition to higher hole carrier mobility, FETs fabricated from the diazonium-doped few-layer BP exhibits an increase in current on/off ratio by more than 100-fold. Furthermore, the diazonium functionalization passivates the few-layer BP surface, preventing degradation for over 10 days of ambient exposure.

### Significance

Few-layer black phosphorus (BP) is a two-dimensional semiconducting material with high carrier mobilities (up to 1000 cm<sup>2</sup>/V-s) and highly anisotropic properties that are promising for high performance nanoelectronics. However, the chemical reactivity of few-layer BP has limited its applicability due to rapid degradation over a few hours in ambient conditions. This work overcomes this limitation by suppressing the ambient degradation of BP through covalent organic passivation. Moreover, the extent of p-type doping of BP can be controlled through the concentration and duration of the diazonium covalent modification chemistry.

Overall, this work realizes an approach that simultaneously controls doping and imparts chemical passivation to BP, thereby enhancing its applicability to nanoelectronic technologies.

**Citation**

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