**Covalent Functionalization of Black Phosphorus**

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**Abstract**

Black Phosphorus shows promising properties but its ambient stability remains a key issue that hinders its use in applications. We have investigated the degradation of black phosphorus in ambient conditions and demonstrate oxidation occurs through the formation of P-O-P species which react further to form volatile phosphoric acids. Covalent functionalization using aryl diazonium salts has previously been used to increase its ambient stability. We present a new functionalization strategy using arylidonium salts that does not induce oxidation and provides a higher degree of covalent functionalization by attachment to both O- and P- sites. The iodonium functionalization strategy results in increased oxidation resistance due to inhibition of P-O-P formation. Furthermore, the diazonium route leads to oxidation, multilayer formation and non-covalent solvent passivation. We provide a comparison between the two functionalization methods and show that functionalization using alkyl- and arylidonium salts is a more compatible stabilization strategy which also allows potential tuning of optical and electronic properties.

**References**
