

# Can Molecular Networks Preserve the Surface of Black Phosphorus?

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Black phosphorus (BP), one of several allotropic forms of phosphorus, has a layered structure and is a narrow gap semiconductor with a bulk band gap of  $\sim 0.3$  eV. Like other layered materials it can be exfoliated with scotch tape to form a single layer of black phosphorus known as phosphorene. Unlike gapless graphene, phosphorene has a bandgap which was predicted and later confirmed to be  $\sim 2$  eV. The band gap is thickness dependent and thus can be easily tuned. Since the first reports of exfoliation of BP, and some 100 years after the first high-pressure synthesis of black phosphorus crystals by Bridgman in 1914, phosphorene or few layered BP has been widely used to construct transistors, including flexible devices.

One of the biggest challenges in BP and phosphorene research remains its stability under atmospheric conditions.

In this work we explore a new route to the solution of this problem through an investigation of the compatibility of BP with the formation of supramolecular networks which have monolayer thickness and are stabilised by non-covalent in-plane interactions, specifically hydrogen bonding. We find that supramolecular networks can be formed on BP and demonstrate this for a mono-component nanoporous array of trimesic acid (TMA) and the bimolecular network formed by cyanuric acid (CA) and melamine (M). While the more open TMA array does not passivate the BP surface, the hexagonal melamine cyanurate (CA.M) array is highly effective and provides protection under ambient conditions over a period of more than three months. In addition, we identify the orientation of the CA.M relative to the rows of phosphorus atoms at the surface and, normal to the rows, observe moiré effects which are characteristic of a well-ordered interfacial structure. We have further demonstrated that CA.M monolayers on BP provide a stable platform for the sequential growth of additional molecular layers, for example, 1,2,4,5-tetrakis(4-carboxyphenyl)benzene (TCPB), leading to the formation of a supramolecular heterostructure and demonstrating the facility for further functionalisation of the BP substrate.

Our work demonstrates that a single layer of CA.M can successfully passivate the surface of BP and preserve it intact for at least 3 months. We believe that this facile approach of depositing a passivating organic monolayer stabilised by in-plane non-covalent bonding could be extended to the protection of other two-dimensional materials with air sensitive atomically flat surfaces and is likely compatible with other solvents and molecules.

The work also presents outstanding examples of high-resolution AFM imaging achieved under ambient conditions