TETRAPYRROLE MOLECULES ON, AT, AND BELOW EPITAXIAL SP^2-SHEETS

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Atomically thin sp^2-hybridized sheets of hexagonal boron nitride (*h*-BN) can be grown on various single-crystal metal surfaces via chemical vapour deposition, complementing the library of two-dimensional materials including graphene and opening perspectives for van der Waals hetero-structures. *h*-BN monolayers are widely used as templates with the potential to electronically decouple and spatially order atoms, functional molecules and nanostructures.

Here, I will focus on the interaction of tetrapyrrole molecules with sp^2-sheets (*h*-BN, graphene) on Ag and Cu(111) supports. Tetrapyrroles as porphyrins possess an impressive variety of functional properties - including axial ligation, light harvesting and catalytic transformations - that have been exploited in natural and artificial systems. From a surface science perspective, tetrapyrroles are thus ideally suited as building blocks for surface-anchored functional nanostructures [1]. We apply low-temperature scanning tunnelling microscopy (STM), spectroscopy (STS) and non-contact atomic force microscopy (nc-AFM) in an ultra-high-vacuum setting to comprehensively characterize the tetrapyrrole/sp^2 systems with sub-molecular resolution. Specifically, I will address the spatial organization, energy-level alignment, on-surface metallation and coordination reaction of porphyrins on an electronically super-structured h-BN/Cu(111) template [2,3]. Furthermore, an intercalation protocol will be discussed, yielding porphine assemblies buried below a *h*-BN sheet. Given the insulating character of *h*-BN, the covered tetrapyrroles can be addressed by STM. Additionally, we present a dehydrogenative coupling reaction employed to fuse porphines to graphene edges, where distinct bonding motifs are identified by nc-AFM. These approaches provide access to new tetrapyrrole-based systems, metallo-supramolecular arrays and hybrid architectures with prospects for novel, tunable functionalities, e.g., in sensing, heterogeneous catalysis or molecular electronics.

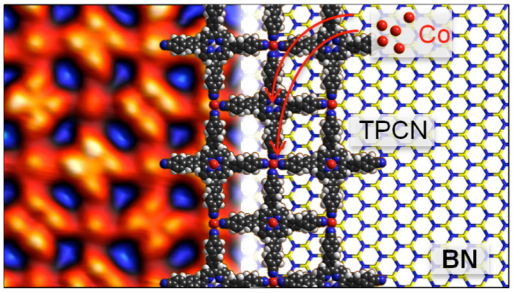

Fig. 1. STM image of a metal-organic coordination network on *h*-BN/Cu(111) formed from functionalized porphyrins (TPCN) combined with Co (left) and schematic model (right).

Keywords: Boron Nitride; Graphene; Porphyrin; Self-assembly, Scanning probe microscopy

References

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