

Atomically Precise Molecular Design: Insights from Sub-molecular Resolution Scanning Probe Microscopy

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The set of tools known generally as scanning probe microscopes (SPMs) have allowed us to view the world with unprecedented detail. The non-contact atomic force microscope (nc-AFM) in particular enables us to directly measure the forces acting between individual atoms and image molecules with incredible submolecular detail.

Whilst submolecular resolution imaging with nc-AFM has provided unparalleled insight into many interesting molecular systems [1,2], non-planar molecular structures and imaging outside of vacuum conditions have proved far more challenging. Here I will discuss studies on tetra(4-bromophenyl)porphyrin (Br₄TPP) molecules deposited onto a Cu(111) surface, using nc-AFM to unambiguously determine the adsorption configuration of the adsorbed conformers with submolecular detail. We show through direct measurement that the lateral forces required to manipulate each conformer significantly differ [3], suggesting unusually strong binding arising from vdW interactions that consequently dramatically affect the molecular density of states [4].

Following this, I will discuss the perceived limits of imaging molecules with non-planar structure and the potential to achieve single bond resolution outside of UHV conditions as a general analytical tool.

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[2] N Pavlicek and L. Gross. *Nature Reviews Chemistry*, **2017**, 1, 0005.

[3] Jarvis, S. P. *et al*, *Nature Commun.* **2015**, 6, 8338.

[4] Jarvis, S. P. *et al*, *J. Phys. Chem. C* **2015**, 119, 27982.