Self-assembly of intrinsically saddle-shaped molecules on noble metals

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Self-assembly processes are of utmost importance for tailored molecular nanoarchitectures. The versatility of chemical functionalizations of molecular units allows access to a plethora of supramolecular systems. The underlying intermolecular interactions in these systems and, resulting properties can be affected by the shape of the molecules [1]. Recently, systematic efforts focus on the influence of molecular curvature on the self-assembled structures, via shape-assisted self-assembly. Under ambient conditions on surface and when dropcasted, saddle-shaped carpyridine molecules assemble in columnar structures on the micrometer scale, resulting from the intrinsic, non-planar shape of the molecule [2, 3]. Hence, shape-assisted self-assembly offers a promising opportunity for the design of extended materials.

Here we present a surface science study where carpyridine molecules are probed on noble metal supports, namely Ag(111) and Au(111). Specifically, the 2H-Car-C2 species is characterized in ultra-high vacuum with low-temperature scanning tunneling microscopy and spectroscopy, X-ray photoelectron spectroscopy as well as near-edge x-ray absorption fine structure. The molecules adsorb parallel to the surface and assemble in ordered rectangular structures, as revealed by imaging with sub-molecular resolution(see Fig. 1). Moreover, the saddle shape of the molecules is characterized via NEXAFS. In contrast to the behavior in solution, the interaction of the molecules with the metal substrate has a crucial influence on the resulting self-assembled structures. Even in the second molecular layer, we did not observe evidence for commensurate columnar growth. Accordingly, this study provides unprecedented insight into intrinsically saddle-shaped molecules on noble metal supports.

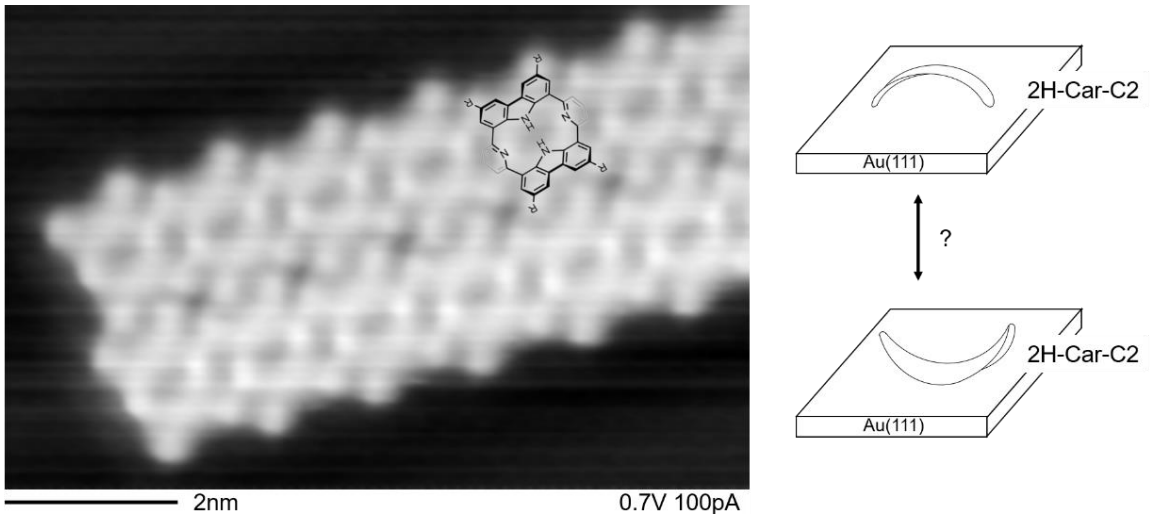

Fig. 1. STM image of 2H-Car-C2/Au(111) and schematic representation of two distinct adsorption configurations

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[2] Woods, Joseph *et al.*, Nature Communications, **13**, 3681 (2022)
[3] Woods, Joseph *et al.*, 10.26434/chemrxiv-2023-whjkw