## On-Surface Synthesis of Extended and Heteroatom-Doped Polycyclic Molecules

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On-surface chemistry protocols on metal supports provide elegant routes to individual molecular complexes, oligomers, and advanced architectures with distinct structural, physical, and chemical properties [1,2]. In this context, porphyrins represent versatile precursors for introduction of nitrogen and other heteroatoms, as well as metal centers, into structures achieved via ring-closing or ring-opening reactions [3].

In this presentation, I will introduce our efforts towards the fabrication of atomically precise, surfacesupported molecular nanostructures and two-dimensional materials in ultrahigh vacuum. The main part of the talk will focus on temperature-induced ring-closing reactions of porphyrins on coinage metal supports, aiming for extended polycyclic heteroatomic molecules. Comprehensive characterization by low-temperature scanning tunneling microscopy, spectroscopy, bond-resolved atomic force microscopy and complementary theoretical modelling provides insight into the structural and physical properties of the resulting interfacial molecular structures.

Specifically, an on-surface chemistry route to unsubstituted square-type porphyrin tetramers with a central planar cyclooctatetraene moiety will be presented [4]. Such tetramers, as well as other oligomers, were achieved on Ag(100) by dehydrogenative homocoupling employing Zn- and free-base porphines as precursors (see Fig. 1). The resulting fully-fused structure represents the simplest model of two-dimensional porphyrin sheets and exhibits closed-shell character, as well as distinct (anti)aromatic pathways. In addition, the introduction of oxygen in  $\pi$ -extended porphyrins will be addressed. O-annulation reactions on Au(111) provide high selectivity and yield for planar porphyrin products with distinct symmetries and oxygen content, which are not easily achieved by solution chemistry. The peripheral heteroatom doping promotes self-assembly and modifies the electronic structure compared to the oxygen-free analogue. Such studies give access to novel surface-supported polycyclic molecules with distinct chemical and physical properties and provide insights on the role of heteroatom doping.



Fig. 1. Scheme of dehydrogenative porphine (2H-P, Zn-P) homocoupling to square-type porphyrin tetramer and corresponding bond-resolved AFM image.

[1] Grill, Hecht, Nat. Chem., 12, 115 (2020)

[2] Houtsma, de la Rie, Stöhr, Chem. Soc. Rev., 50, 6541 (2021)

<sup>[3]</sup> Bischoff et al., J. Am. Chem. Soc., **143**, 15131 (2021)

<sup>[4]</sup> Corral Rascon et al., J. Am. Chem. Soc., 145, 967 (2023)