On-surface synthesis and electronic structure of surface-supported molecular networks

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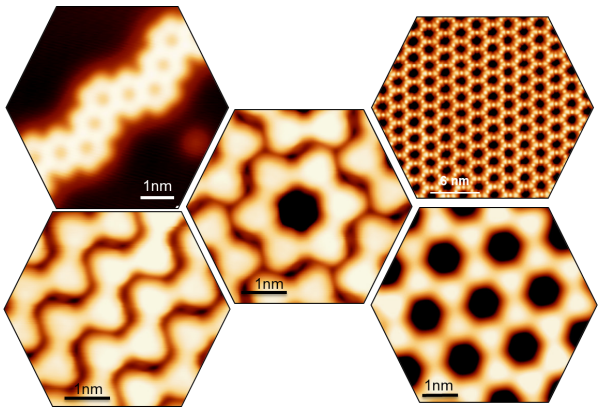
The interest in molecular nanostructures on surfaces emerges from their prospective applications in nanoscale electronics, solar cells, energy storage devices, and other fields. Non-covalent intermolecular interactions in self-assemblies facilitate the formation of long-range ordered patterns. In contrast, the stability and intermolecular charge transport are improved in covalent molecular networks fabricated by on-surface synthesis, however, at the expense of structural control owing to the irreversible nature of the newly formed covalent bonds.
In my presentation, I will discuss recent high-resolution scanning probe microscopy experiments about the on-surface synthesis of one- and two-dimensional molecular nanostructures on metal surfaces and their electronic properties.[1-3] First, I will outline how porous nanoribbons can be fabricated from conformationally flexible threefold-symmetric molecules.[3] Second, I will show two examples of nanoporous 2D networks, where we made use of coupling reactions via debromination.[1-2] Besides the structure formation, the local electronic structure of the 2D networks will be discussed. In particular, we could observe a narrowing of the band gap from the single molecule to the 2D network in triphenylamine-based nanostructures because of the increased π-system. Moreover, we found delocalized states in surface-supported organometallic networks with Ag-*bis*-acetylide bonds corroborating their covalent character.
A major challenge in realizing single molecular electronic devices is to mechanically stabilize and electrically decouple molecules at and from a surface. Hence, I will conclude with a comparison on the structure formation of molecular self-assemblies on bulk insulators and metals. I will show how the interplay between intermolecular and molecule-substrate interactions can be tuned by functional groups to achieve one-, two- or three-dimensional assemblies in a controlled way on insulators.



On-surface synthesis of molecular nanostructures. Left: porous nanoribbons on Ag(111) [3] and chains on Au(111)[1]; middle: macrocycles from triphenylamine derivatives on Au(111) [1]; right: organometallic Ag-bis-acetylide networks featuring delocalized unoccupied states along the entire network on Ag(111) [2], 2D network from triphenylamines on Au(111) [1].

References:
[1] C. Steiner et al. Nature Communications, 8, 14765 (2017).
[2] Z. Yang et al. Nanoscale, 10, 3769-3776 (2018).
[3] M. Ammon, T. Sander, S. Maier, J. Am. Chem. Soc., 139 (37), 12976–12984 (2017).