On-surface assembly and reaction of molecular nanostructures: from metals to insulating surfaces

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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 molecular self-assemblies facilitate the formation of long-range ordered patterns by usage of molecular recognition. In contrast, the stability and intermolecular charge transport are improved in covalent molecular networks fabricated by on-surface reactions, however, at the expense of structural control owing to the irreversible nature of the newly formed covalent bonds.

In my presentation, I will focus on recent high-resolution scanning probe microscopy experiments in combination with density-functional theory about the bottom-up fabrication and electronic properties of atomically precise one- and two-dimensional molecular nanostructures on metals.[1-4] Thereby, the effect of the flexibility, the symmetry, and chirality of the precursor molecules on the structure formation of covalently-linked 2D networks will be discussed.[1-3] I will present how the band gap with the extension of the π-system changes [1] and the observation of delocalized electronic states in surface-supported organometallic networks.[2]

A major challenge in realizing molecular electronic devices is to mechanically stabilize and electrically decouple molecules at and from a surface without losing the control on the structure formation. The electronic decoupling of molecules on insulating surfaces results in a weaker and unspecific molecule-surface interaction, such that molecular assemblies often suffer from diffusion and the assembly of disordered aggregates. Hence, I will conclude with a comparison on the structure formation of molecular self-assemblies on bulk insulator and metal surfaces.

[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).
[4] C. Steiner et al. , *Chem. Commun.* **54**, 11554-11557 (2018).