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Constructing two-dimensional molecular networks on metal surfaces: a scanning tunneling microscopy study

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Molecular self-assembly is one of the most important bottom-up fabrication strategies to produce two-dimensional networks at solid surfaces. The formation of complex two-dimensional (2-d) surface structures at the molecular scale relies on the self-assembly of functional organic molecules on solid substrates. Driven by an intricate equilibrium between molecule–molecule and molecule–substrate interactions, a number of different non-covalent molecular interactions can be used to generate stable 2-d geometric structures. For example, in the case of halogen-terminated monomers halogen bonding.

In addition to being the building blocks of self-assembled networks, halogen-terminated molecules can be activated on surfaces to form 2-d π-conjugated polymers. Ideally the process follows a two-step procedure whereby the carbon halogen bonds break to form organometallic structures and subsequent covalent C-C coupling. These organic analogues of graphene, the only natural 2-d conjugated polymer, represent a promising new class of high-performance functional nanomaterials.

In this work we study the adsorption of a tribromo-substituted heterotriangulene molecule (TBTANGO) the Au(111) and Ag(111) surfaces using room temperature scanning tunneling microscopy in ultrahigh vacuum. The resultant two-dimensional molecular networks range from: self-assembled networks held together by non-covalent Br···Br halogen bonds on Au(111); organometallic networks with C-Ag-C linkage on Ag(111); and a π-conjugated polymer when the TBTANGO monomers are deposited directly onto a hot Au(111) surface.

Authors: Mr MARCHESE, Davide (Lakehead University); Prof. GALLAGHER, Mark (Lakehead University)

Presenter: Prof. GALLAGHER, Mark (Lakehead University)

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