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A scanning tunneling microscopy study of a two dimensional organometallic network on the Ag(111) surface

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Self-assembly is one of the most important bottom-up fabrication strategies to produce two-dimensional (2-d) networks at solid surfaces. Driven by an intricate equilibrium between molecule–molecule and molecule–substrate interactions, these interactions can be used to generate stable extended 2-d geometric structures. For example, halogen-terminated molecules can be activated on surfaces to form 2-d π-conjugated polymers [1].

In this work we focus on a particular class of 2-d nanomaterials in which metal atoms are incorporated into the molecular layer. The structures are characterized by organometallic coordination, i.e. C-metal-C linkage, between adjacent molecules. These materials are predicted to exhibit novel properties, i.e. topological insulators, superconductivity, and other exotic quantum phases [2].

We study the adsorption of a tribromo-substituted heterotriangulene molecule (TBTANGO [1]) on the Ag(111) surface using room temperature scanning tunneling microscopy (STM) in ultrahigh vacuum. We find that deposition of TBTANGO molecules onto a substrate held at elevated substate temperatures (~ 240℃) yields a high quality extended porous two-dimensional molecular network of TANGO molecules with organometallic C-Ag-C linkage. Each pore consists of six dehalogenated molecules and the honeycomb network can be characterized by a hexagonal unit cell with a lattice constant of 19.8 ± 0.5 Å. Within error, the overlayer is commensurate with the silver substrate (~ 7a₀). In addition, the molecular overlayer exhibits a single orientation, indicating it is aligned with the high symmetry directions of the underlying substrate.

At monolayer coverage, most of the surface is covered by the honeycomb network (80%), however adjacent to silver atomic steps we observe a novel compact molecular phase. This phase is characterized by a hexagonal unit cell with a lattice parameter of ~ 9.1 Å. STM images are consistent with C-metal-C linkage, however in the compact phase the Ag atom/cluster is linked to 3 TANGO molecules. To our knowledge this bonding motif has not been observed previously in similar 2-d organometallic networks.

[1] *Galeotti et al.*; Nature Materials **19**, 874–880 (2020).
[2] *Dong et al.*; Prog. in Surf. Sci. **91**, 101-135 (2016).

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