Recent Advances in Terminal Alkyne On-Surface Chemistry: Novel reactions and unprecedented mechanism

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On-surface synthesis provides a promising route toward the atom-precise bottom-up construction of nanostructures through controlled coupling processes of rationally designed precursors often with pathways not accessible in solution. Homo-coupling of terminal alkynes represents an interesting approach towards novel carbon-based nanomaterials related to graphdiyne via on-surface synthesis under ultra-high vacuum conditions [1] as well as in solution [2]. On the Ag(111) surface, the coupling reaction allowed for the selective synthesis of novel molecular species and irregular, conjugated 2D polymers at mild conditions.[3] The reaction proceeds via a pathway fundamentally different from the classical Glaser coupling schemes under solution conditions.[4] Recent reports already demonstrated that alkyne surface chemistry is rich and extends far beyond butadiyne formation. Here, we focus on two systems where novel reactions with unprecedented mechanisms occur. First, the convergent multi-step chemical transformation of a simple dissymmetric precursor is reported allowing the self-assembly of a rare 3.4.6.4 Archimedean tiling in high yield.[5] Second, a hydroalkoxylation reaction preceding at low temperatures (onset ~150 K) is investigated.[6] In both cases, a multi-technique approach combined with density functional theory calculations is employed to unravel the underlying mechanisms.

References:

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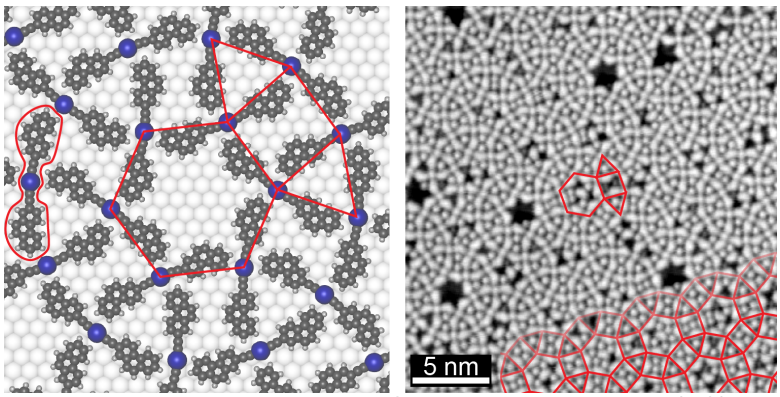

Figure 1: DFT-optimized model of the 3.4.6.4 tesselation (left) and STM topograph of the self-assembled tiling.