Dehalogenative homocoupling: formation of cumulene units and benefits of H-dosing

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The interest in studying organic nanostructures on surfaces emerges from their prospective usage as nanoscale functional materials in applications ranging from electronics to spintronics and catalysis. By making use of molecular recognition processes based on non-covalent interactions, well-ordered 1D and 2D molecular structures can be formed on surfaces. Understanding the interplay of the underlying intermolecular and molecule-substrate interactions, and processes on the atomic and molecular scale is the key for being able to deliberately tune the functional properties of organic nanostructures. However, since the intermolecular interactions for such structures can be rather weak, on-surface covalent coupling has emerged as a viable alternative for obtaining structures with improved stability and conductivity.

Herein, two examples will be shown where we made use of Ullmann-type coupling for the formation of covalently coupled molecular structures. For a biphenyl derivative functionalized with an alkenyl gem-dibromide we observed the formation of cumulene units [1]. The reaction products and pathways were unambiguously characterized by the combination of high-resolution scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM) measurements together with state-of-the-art density functional theory (DFT) calculations. Moreover, for a pyrene derivative a hydrogen dosing treatment employed during the on-surface reaction was proven successful for the removal of the halogen atoms which are split off during the reaction and which often stay chemisorbed on the surface, thereby hindering the formation of well-ordered structures [2].

References:
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