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Single-molecule study of the intermediate steps in a coupling reaction

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Breaking and formation of intermolecular bonds are the processes underlying the bottom-up growth of 2D materials and their covalent functionalization. A deeper knowledge of how a bond breaks or forms is of fundamental importance to control the synthesis of 2D architectures at the atomic or molecular level. Ullmann coupling on metal surfaces is a chemical reaction often employed for the synthesis of covalently bonded 2D networks [1]. Therefore, the study of this chemical reaction between single building block molecules adsorbed on crystalline metal surfaces is important to understand polymerization processes.
Bond breaking and formation, in single molecules on a surface, can be triggered by tunneling electrons in a scanning tunneling microscope (STM) [2, 3]. STM manipulation allows the geometrical arrangement and characterization of the precursor molecules [4]. Thus, the consecutive steps involved in the Ullmann coupling can be studied, from the activation of the precursors to their covalent linking, including the organometallic intermediates that can be involved [5, 6]. However, the function of catalytic active sites, like single metal atoms, needs to be further investigated. Moreover, in many cases, chemical reactions between small molecules have been studied with STM. Thus, there is very limited, or no, access to the geometrical arrangement of the building blocks during the coupling reaction.
Here, we use the STM tip at low temperature (7 K) to induce step-by-step the coupling reaction between two molecules adsorbed on a Ag(111) surface. The elongated shape of this molecule allows to arrange them in specific relative orientations prior to the reaction. Thus, an organometallic complex is synthesized, and the geometrical conformations of the complex are explored to study the coupling reaction. The results show the important role of the metal substrate in on-surface polymerization reactions. Moreover, this precise and controlled synthesis demonstrates new methods for studying the function of single metal atoms in coupling reactions. A deeper understanding of these reactions would allow better control over the structure of 2D materials and targeted engineering of their functions.

References

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