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## ABSTRACT:

### On-Surface Synthesis Without a Metal Surface

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In the realm of on-surface synthesis, establishing C-C covalent bonds between organic molecules on surfaces are a pivotal strategy, being Ullmann coupling [1] and (cyclo)dehydrogenation reactions [2] the most successfully used in the field. They benefit from the catalytic properties of metallic surfaces that favor the rupture of the corresponding C-halogen or C-H bonds, usually assisted by the presence of native metallic adatoms even at RT. However, in the pursuit of advanced carbon-based nanostructures to be applied into functional devices that operate in the “real world”, the use of metallic surfaces (and particularly single crystals) is a handicap. Consequently, novel synthetic routes that do not require of the catalytic properties of these surfaces are mandatory.

In the last years, we have introduced novel on-surface synthetic strategies that transcend the conventional Ullmann coupling by inducing reactivity between non-functionalized precursors. High-resolution scanning probe microscopy (SPM) combined with complementary synchrotron-based X-Ray photoemission techniques and first principles calculations (DFT) has allowed us to visualize and characterize the resulting nanostructures, shedding light on reaction intermediates and fundamental structure–property relationships.

This presentation will delve into two novel approaches. Hydrogen-Induced Activation: controlled dosing of hydrogen atoms leads to a hydrogenation of the adsorbed molecule, changing from sp<sup>2</sup> to sp<sup>3</sup> hybridization and inducing a local rupture of the aromaticity that confers it a radical-like character. As these activated molecules diffuse on the surface, they readily couple with neighboring species, enabling the formation of covalent networks at considerably lower temperatures than those required by traditional Ullmann coupling [3]. Light-Induced Activation: We exploit photochemical processes to trigger reactivity. By irradiating the adsorbed precursor molecules with carefully tuned light, specific molecular orbitals are excited, effectively lowering the activation barriers for bond rearrangement or cleavage. This light-induced activation not only circumvents the need for thermal energy and metallic catalysts but also could allow for a precise control over the reaction pathways. Both processes take place at lower temperatures and they do not require the presence of a metallic substrate, pushing the boundaries of surface-assisted synthesis, and paving the way toward fabrication of the next-generation organic electronic components directly on a surface.

- [1] F. Villalobos et al. *J. Am. Chem. Soc.* 147, 7245 (2025)
- [2] N. Ruiz del Arbol et al. *Angew. Chem. Int. Ed.* 130, 8718 (2018)
- [3] C. Sánchez-Sánchez et al. *J. Am. Chem. Soc.* 141, (2019) 3550