

## On-Surface Hydrogen-Induced Covalent Coupling of Polycyclic Aromatic Hydrocarbons via a Superhydrogenated Intermediate

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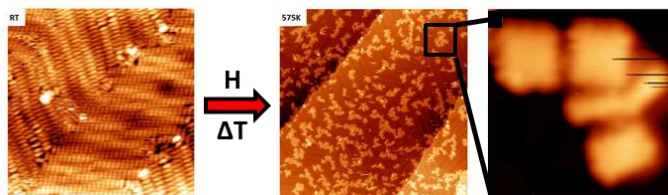
The covalent coupling of aromatic molecules via dehydrogenation reactions is of pivotal importance in organic chemistry, energy, biology, and astrochemistry, to name a few. It is involved in a plethora of processes, ranging from drug synthesis to the formation of polycyclic aromatic hydrocarbons (PAHs) in space. So far, dehydrogenation reactions are based on the utilization of metal catalysts and/or in the previous functionalization of the molecules, both being aspects which can complicate the aimed process. For these reasons, it is highly interesting to find a new strategy to covalently bind unfunctionalized PAHs without the presence of a metal catalyst.

Here, we present a novel approach for the activation and subsequent covalent coupling of unfunctionalized polycyclic aromatic hydrocarbons (PAHs) which does not significantly depend on the nature of the surface.[1] This strategy is based on the rupture of the local aromaticity of the molecule induced by the  $sp^2$  to  $sp^3$  hybridization transition taking place upon superhydrogenation of the molecules when exposed to atomic hydrogen. This process results in the formation of a new covalent C-C bond and the release of two hydrogen molecules. This mechanism, which has been characterized by high-resolution STM and rationalized by DFT calculations, opens a door toward the activation and covalent coupling of unfunctionalized PAHs on low reactive surfaces and could explain the formation of larger PAHs in space.

### References

- [1] Carlos Sánchez-Sánchez, José Ignacio Martínez, Nerea Ruiz del Arbol, Pascal Ruffieux, Roman Fasel, María Francisca López, Pedro L. de Andrés, and José Ángel Martín-Gago, *J. Am. Chem. Soc.*, 141 (2019) 3550-3557

### Figures



**Figure 1:** STM images of the Au(111) surface covered by a pentacene layer before (left) and after (middle) annealing the system at 575 K in the presence of atomic hydrogen. Right: nanographenes formed upon exposure to H.