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On-Surface Synthesis of Conjugated Polymer Guided by Supramolecular Orientation on an Au(111) Surface

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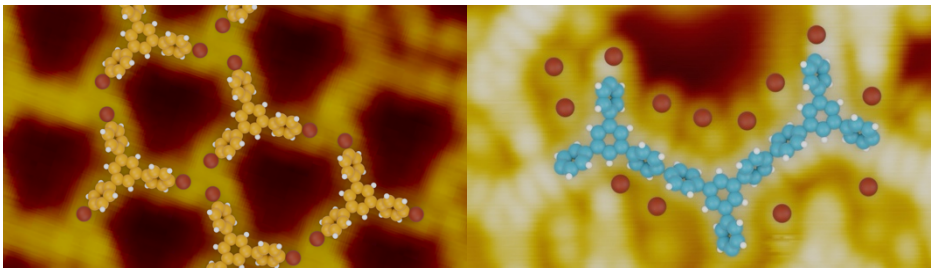
Among all the proposed precursors for creating 2D covalent networks, the molecule 1,3,5-tris(4'-bromophenyl)benzene (TBB) stands out as the most extensively examined molecule under ultra-high vacuum conditions using scanning tunneling microscopy (UHV-STM). This star-shaped molecule features three branches, each terminating with a bromine atom, and it serves as the prototype for generating a conjugated 2D network containing hexagonal pores.[1]

We have demonstrated the existence of a novel supramolecular self-assembly resulting from the deposition of TBB molecules on the Au(111) surface. This self-assembly is guided by a triple halogen bond, locally forming an X3-synthon. Halogen interactions are stronger compared to other no-covalent interactions, and the network remains stable up to temperatures of 373 K. By adjusting the annealing temperature to 383 K, we have demonstrated the formation of 1D sawtooth-like polymers through an Ullmann-like cross-coupling process.



The formation of ordered covalent network is guided by the propagation of polymerization

These 1D covalent networks are highly ordered and nearly defect-free, thanks to the initial supramolecular network geometry, which promotes the propagation of polymerization at low temperatures to limit excessive precursor diffusion. This result highlights the potential for controlling surface polymerization and achieving defect-free conjugated nanostructures guided by supramolecular orientation. Ongoing work is focused on optimizing polymerization conditions to produce longer polymer chains.[2]

Références

[1] Russell, J. C.; Blunt, M. O.; Garfitt, J. M.; Scurr, D. J.; Alexander, M.; Champness, N. R.; Beton, P. H. Dimerization of Tri(4-bromophenyl)benzene by Aryl−Aryl Coupling from Solution on a Gold Surface. *J. Am. Chem. Soc.* **2011**, *133*, 4220-4223.

[2] Palmino, F.; Jeannoutot, J.; Luzet, V.; Rochefort, A.; Chérioux, F. *J. Phys. Chem. C* **2024**, *128*, 12482-12487.