First name: Frédéric LAST NAME: CHERIOUX
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☐ Poster

ON-SURFACE SYNTHESIS: THE ROLE OF HALOGEN BONDING

Frédéric CHERIOUX,[1] Frank PALMINO,[1] Vincent LUZET,[1] Judicaël JEANNOUTOT,[1] Alain ROCHEFORT[2]

[1] Université Marie et Louis PASTEUR, CNRS, FEMTO-ST - Besançon (frederic.cherioux@femto-st.fr)
[2] Département de génie physique, Polytechnique Montréal, Montréal (Québec) – H3C 3A7, Canada.

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Summary: Over the past two decades, on-surface synthesis of organic nanostructures has been extensively investigated with the aim of fabricating molecular electronic components and functional nanomaterials. This growing interest is largely driven by the capabilities of scanning probe microscopy, which enable direct monitoring of reaction pathways with atomic-scale precision.[1] Here, we present two examples of on-surface chemistry directed by halogen bonding.[2,3] Using scanning tunneling microscopy, we observe the formation of novel supramolecular phases and demonstrate that this supramolecular organization promotes the subsequent formation of well-defined one-dimensional covalent networks upon thermal annealing. These 1D covalent networks exhibit a high degree of order and are nearly defect-free, owing to the geometry of the initial supramolecular network, which facilitates controlled polymerization at relatively low temperatures and limits excessive precursor diffusion. These results highlight the potential of supramolecular templating to control surface-confined polymerization and to achieve defect-free conjugated nanostructures. Ongoing work focuses on optimizing the polymerization conditions to obtain longer polymer chains.

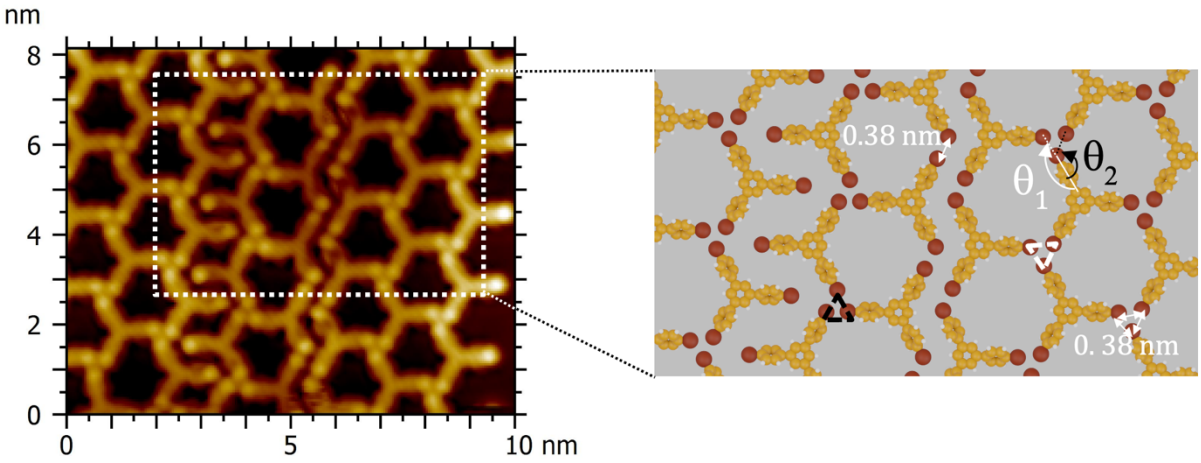

Fig. 1: STM image (10×8 nm², V_s = -0.01 V, I_t = 440 pA, 10K) of the TBB/Au(111) interface. The porous network is formed by three TBB molecules that interact through three halogen bonds in a X_3-synthon geometry, as highlighted by the dashed white triangle. The grain boundaries are stabilized by two halogen bonds between two TBB molecules (white arrows). The distance between bromine atoms involved in all Halogen bonds is 0.38 ± 0.04 nm. The two enantiomeric X_3-synthons are depicted, respectively with white and black dashed triangle.

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