

[2+2] cyclo-addition reactions for efficient polymerization on a HOPG surface at ambient conditions

Lihao GUAN¹, Frank PALMINO², Jean-Christophe LACROIX¹, Xiaonan SUN¹, and Frédéric CHERIOUX²

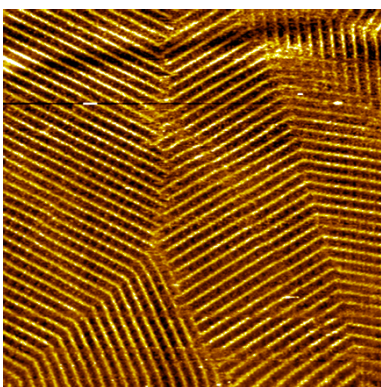
¹ *Université de Paris, ITODYS, CNRS, 15 rue Jean Antoine de Baïf, 75013 Paris, France.*

² *Université de Franche-Comté, FEMTO-ST, CNRS, 15B Avenue des Montboucons, F-25030 Besancon cedex, France.*

On-surface synthesis was developed as an efficient way to create covalent nanostructures. All on-surface polymerizations require an external stimulus to provoke the initial bond cleavage which will lead to the polymerization. Among all used approaches, photochemical reactions on surfaces emerge as an elegant solution because they can proceed at room temperatures which can limit the number of defects in synthesized nanostructures, a major weakness of on-surface thermal-induced reactions [1,2].

Here, we propose to investigate the role of the stimulus to achieve the synthesis of long 1D polymers by activation of C=C bonds on a highly oriented pyrolytic graphite (HOPG) surface at ambient conditions. We propose to answer to several questions: 1) Are the [2+2] cycloaddition always governed by Woodward-Hoffman rules on a surface? Does the surface impose constraints that favor new mechanism of polymerisation? What are the parameters to get the longest 1D-polymers on a surface? In order to fully answer these fundamental questions, we designed specific molecular building blocks and then, all adsorbates are fully characterized by scanning tunneling microscopy (STM). We investigate and compare the role of light and thermal annealing as external stimuli that initiates the [2+2] cycloaddition, to give long 1D-polymers on a HOPG surface.

a)



b)

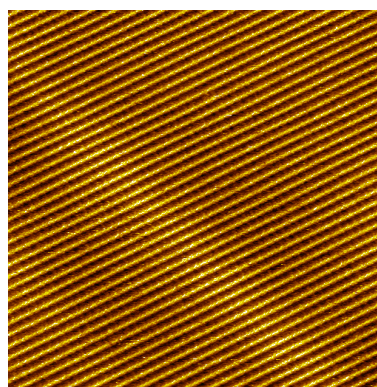


Figure: STM images of a) supramolecular network ($I_t = 10$ pA, $U_s = -0.5$ V, 100×100 nm²) and b) 1D-polymers after activation ($I_t = 20$ pA, $U_s = -0.5$ V, 100×100 nm²).

References

- [1] Grossmann, L.; King, B. T.; Reichlmaier, S.; Hartmann, N.; Rosen, J.; Heckl, W. M.; Bjork, J.; Lackinger, M. *Nature Chem.* **13**, 13, 730 (2021).
- [2] Palmino, F.; Loppacher, C.; Chérioux, F.; *ChemPhysChem* **20**, 2271 (2019).