

On-surface synthesis of polymeric chains through C-S activation

Fatima Hussein^{*[a]}, Rémy Pawlak^[b], Ernst Meyer^[b], Oliver Maclean^[c], Federico Rosei^[c], Kawtar Mouhat^[d], Corentin Pigot^[d], Frederic Dumur^[d], Didier Gigmes^[d], Wentao Song^[a], Younal Ksari^[a], Sylvain Clair^[a], Luca Giovanelli^[a]

- Aix-Marseille Univ, CNRS, IM2NP, Marseille, France.
- University of Basel, Department of Physics, Basel CH4056, Switzerland.
- Institut National de la Recherche Scientifique, Varennes, Québec J3X 1S2, Canada.
- Aix-Marseille Univ, CNRS, ICR, Marseille, France.

*Email: fatima.hussein@im2np.fr

On-surface synthesis is a newly developing field of research that aims at making use of well-defined solid surfaces as confinement templates to initiate chemical reactions[1]. It represents an efficient route to the formation of robust organic networks and one- or two-dimensional polymers. In this work we propose an original reaction mechanism to create C-C bonds taking advantage of C-S activation from thiophene-based precursors on the reactive Cu(111) surface. The formation of polymeric chains was investigated using Scanning tunneling microscopy (STM), non-contact Atomic Force Microscopy (nc-AFM) and X-ray photoemission spectroscopy (XPS).

Upon annealing at 130°C STM images at room temperature show the formation of a polymeric network consisting of straight chains up to 20 nm long and mostly aligned with the substrate high symmetry directions. High-resolution nc-AFM images with CO-functionalized tip show the breaking of the thiophene cycles and the formation of a mixture of cis- and trans- aliphatic chains connecting the intact benzene rings of the original precursor. The sulfur byproducts are observed in atomic form in the vicinity of the polymer chains.

We performed a temperature-dependent XPS study and followed the evolution of the S 2p and C 1s spectra during annealing. At room temperature we observe clear signature of 2D gas-phase accompanied by step-edge adsorbed molecules. Upon annealing, S atoms initially settle around the polymers in different binding energies and eventually show a unique component at higher annealing temperature. The C 1s displays core level shifts from C sites within the pristine molecule and upon polymerization. Namely, C-S components present at RT are first replaced by radical sites and, at higher temperatures, evolve towards a graphene-like line shape together with a sizable C-Cu (adatoms) component.

Our results confirm the possibility to initiate C-C coupling reactions at relatively low annealing temperature through an original C-S activation mechanism.

[1] Clair, S., De Oteyza, D.G., Chemical Reviews 119 :4717-4776 (2019)

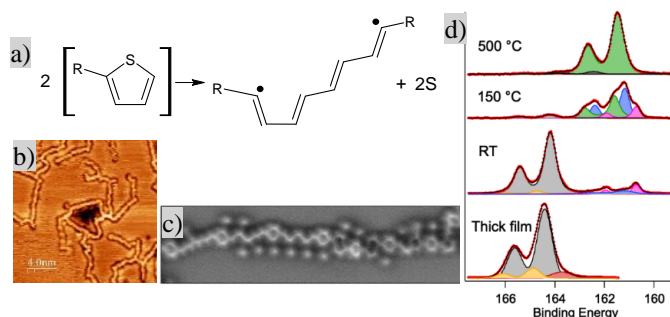


Figure 1: (a) reaction scheme of the carbon chain formation reaction from thiophene units, (b) STM image (20x20 nm²) of the polymer chains obtained on Cu(111) after annealing at 130°C, (c) High resolution nc-AFM image (7x2 nm²) revealing the chemical structure of the chains alongside the released sulfur. (d) XPS S2p core level spectra obtained after different annealing temperatures showing the polymerization and the release of various S byproducts at 150°C and the convergence to a unique component at high temperature.