Micrometer-long covalent organic fibres by photo-initiated chain-growth radical polymerization on an alkali-halide surface.

Franck PARA[1], Franck BOCQUET[1], Laurent NONY[1] and Christian LOPPACHER[1]; Michel FERON[2] and **Frédéric CHERIOUX[2]**; David Z. GAO[3], Filippo Federici CANOVA[3] and Matthew B. WATKINS[4].

[1] Aix-Marseille Université, CNRS, IM2NP UMR 7334, 13397 Marseille, (France)
[2] Institut FEMTO-ST, Univ. Bourgogne Franche-Comté, CNRS, 15B avenue des Montboucons, F-25030 Besançon, (France)
[3] Nanolayers Research Computing LTD, 15 Southgrove Road, Sheffield, (UK)
[4] School of Mathematics and Physics, University of Lincoln, (UK)

We present a new way to fabricate polymer fibers obtained by surface radical polymerization from dimaleimide-type molecules (see fig.1-a) [1]. The molecular tectons are evaporated under ultra-high vacuum on mono-crystals of alkaline halides such as KCl (001), NaCl (001) and KBr (001). We discuss the results of the surface that led to the best results, KCl (001). The deposits were imaged by atomic force microscopy in non-contact mode at room temperature, as well as the operations of manipulation of the formed fibres by the tip. The results show that the deposition of the molecules leads to the formation of fibers whose length can reach more than 1 µm (cf. fig.1-b). The number of fibers increases when the sample is illuminated by a UV - LED at 266nm (cf. fig.1-c).

The approach is innovative in three ways: first, a radical chain-like polymerization is used rather than a step-like growth. Second, the polymerization is initiated from a two-dimensional gaseous molecular phase rather than from a fixed self-assembled structure. Third, the cations of the substrate promote the adsorption of molecules in a configuration that facilitates the radical polymerization and guides the propagation of the polymeric fiber without defects along the <100> directions of the substrate (cf. fig.1-d).

We discuss the different mechanisms that initiate the on-surface polymer reaction, which can be both spontaneous (see fig. 1-b) or assisted by UV illumination (see fig.1-c), at room temperature. Once initiated, the polymerization develops easily in the form of fibers and is stopped only by defects on the surface or by the exhaustion of the precursor molecules. The well-ordered and defect-free growth of the fibres is assisted by the electrostatic molecule-substrate interaction.

The interpretation of the experimental data is supported by density functional theory (DFT) calculations and by calculations of the transition barriers by means of nudged elastic band calculations (NEB).

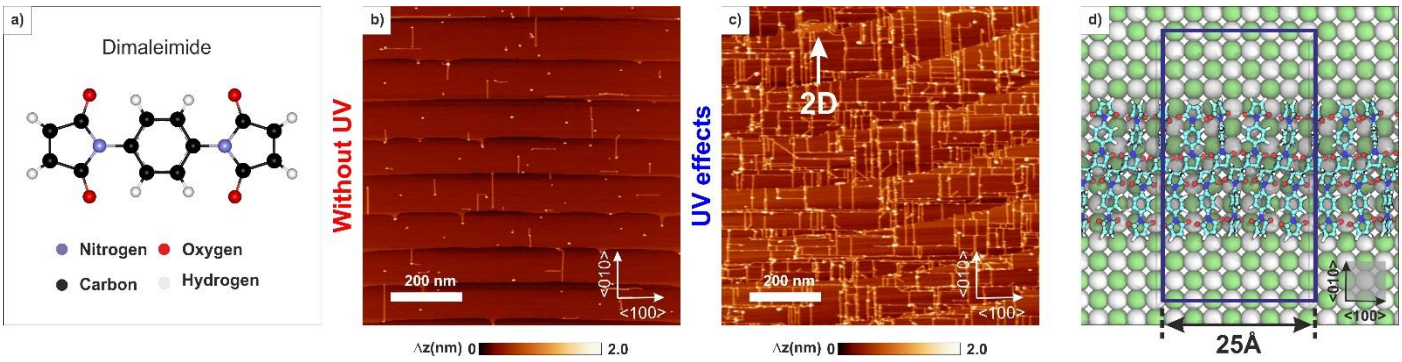

Figure 1: *a) Dimaleimide molecule ; b) nc-AFM Image : 0.7 ML of dimaleimide deposited without UV light; c) nc-AFM Image : 0.7 ML of dimaleimide deposited with UV light;. d) DFT relaxed structure of the polymer fibre on the KCl surface (white K and green Cl atoms).*

References

[1] Para, F. ; Bocquet, F. ; Nony, L. ; Loppacher, Ch. ; et al. ; *submitted*.