DIRECT EVIDENCE OF NANOWIRES FORMATION FROM A Cu(II) COORDINATION POLYMER

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Coordination polymers, also named metal-organic frameworks (MOF), are formed by self-assembly of selected metal or metal complex and bridging ligands. They have been studied in recent years since they show relevant structural features and potential applications in many fields[1,2]. Our current research is focused on the isolation and morphological characterization of well-ordered individual 1D-MOF chains on surfaces aiming the investigation of their potential application as molecular wires. In first state, this has required the development of new adsorption methods to organized individual chains of MOF on surfaces[3]. Once the polymer is adsorbed on a surface, Atomic Force Microscopy (AFM) allows its morphological and physical characterization among others, conductivity and magnetism. However, just from AFM data it is not possible to elucidate the structure of the MOF and its interaction with the surface. For that reason, we have selected a particularly interesting 1D-MOF Cu(II) polymer with isonicotinic acid as terminal ligand, to study the composition of the coordination polymer on a surface (Figure 1a). Its selection has been done based on its structure (suitable for a supramolecular interaction via H-bonds of the carboxylic groups) and physical properties (semiconductor behaviour).

To adsorb $[CuBr(IN)]_n$ on different surfaces two methods has been used: (i) casting deposition of sonicated suspensions and (ii) solubilization of the compound by deprotonation of the carboxylic groups. The deposition methods employed so far to adsorb $[CuBr(IN)]_n$ lead to 1D-fibres formation on different surfaces (HOPG, mica and gold) (Figure 1b-d). Novel spectroscopic characterization, Polarization Modulated Reflection Adsorption Infrared Spectroscopy (PM-RAIRS) and X-ray Photoelectron Spectroscopy (XPS), of these fibers let us to establish their structure once adsorbed on gold. In situ PM-RAIRS characterization of the polymer immobilized on gold surfaces confirms the already known structure of the compound as determined by X-ray crystallography (Figure 2a). In addition, the vibrations found in the PM-RAIRS indicate that the COO^- groups are acting as linkers with the gold surface. On the other hand, XPS studies provides information about the metallic part of the compound, identifying the chemical state and composition of the polymer once is adsorbed on the gold surface (Figure 2b).

In summary, we present direct evidence of the subnanometer structure of the $[CuBr(IN)]_n$ on surface.

References:

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[3] D. Olea, S.S Alexandre, P. Amo-Ochoa, A. Guijarro, F. de Jesus , J. M. Soler, P. J. de Pablo, F. Zamora, J. Gomez-Herrero, Adv. Mat, 2005, **17**, 1761

Figures:
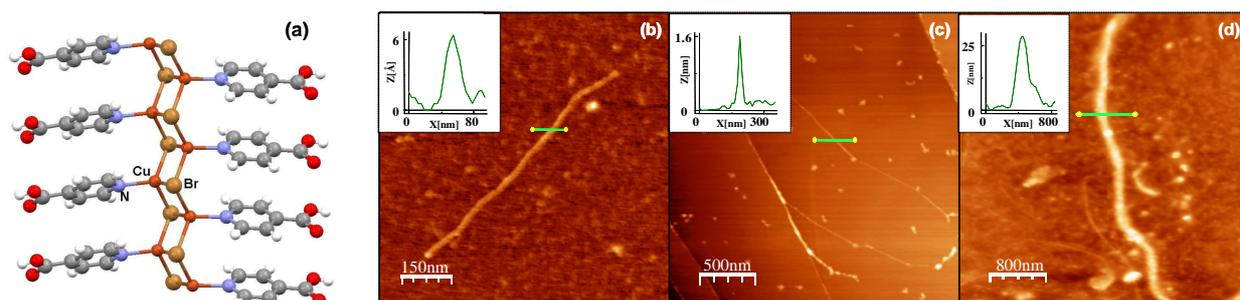
Figure 1. (a) Schematic representation of a $[CuBr(IN)]_n$ polymer chain. (b) AFM topography image of $[CuBr(IN)]_n$ deposited on mica treated with polylisine (b) HOPG (c) and gold (d) surfaces.
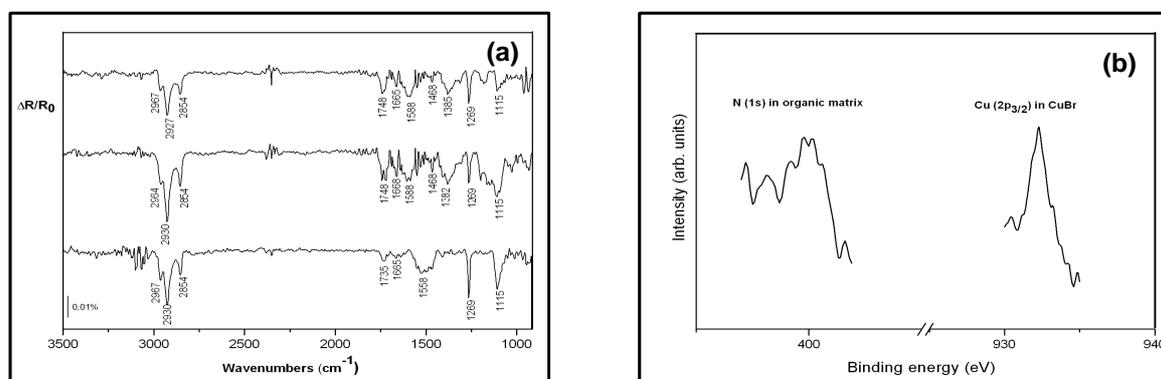
Figure 2. (a) PM-RAIR spectra after adsorption of $[CuBr(IN)]_n$ on gold from different adsorption methods. (b) XPS spectra after adsorption of $[CuBr(IN)_n]$ on gold surface.