

Direct evidence of nanowires formation from a Cu(I) coordination polymer

Eva Mateo, Lorena Welte, Pilar Amo-Ochoa, Pablo J. Sanz Miguel, Julio Gómez-Herrero, José A. Martín-Gago, Félix Zamora

Supporting Information

Experimental Procedure

Preparation of the Substrates. In order to obtain reproducible results, very flat substrates of a size of 1 cm x 1 cm with precisely controlled chemical functionalities, freshly prepared just before the chemical deposition, were used. Two different commercially available supports were used: Muscovite Mica and Highly Oriented Pyrolytic Graphite (HOPG). Both of them were cleaved with adhesive tape. Gold surfaces were commercially purchased by Arrandee company. In order to obtain reproducible results, gold substrates were treated just before the chemical deposition. They were immersed on a solution of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ (3:1) for 10 min., then washed with 5 mL of water, sonicated 5 min. (680 W, 40 kHz, 20 °C) on water. Residual organic contaminants were removed by flaming annealing (for 1 min.) of the gold surface (Fig. S1).

Sample Preparation

Solutions were prepared under argon and used freshly prepared before deposition. Milli-Q water was deoxygenated by bubbling nitrogen through it for at least 10 min.

Method (a).- 1 mg of $[\text{CuBr}(\text{HIN})]_n$ were suspended in 1 mL of H_2O : sodium dodecyl sulfate 0.01 % and sonicated (680 W, 40 kHz) for 3h at 30 °C, to form a yellow mother solution. From the former solution a 20 μL and 40 μL of a diluted solution (10^{-3} mg/mL) were deposited on a Muscovite mica substrate previously treated with polylysine and on a Gold surface, respectively. Upon standing 2 min. on mica and 30 min. on gold surfaces at 20 °C, the substrates were washed with water and then dried under a flow of argon (Fig. 2 and Fig. S2). Similarly, 40 μL of 10^{-10} mg/mL diluted mother solution were deposited for 15 min. on HOPG and then dried with a flow of argon (Fig. S3).

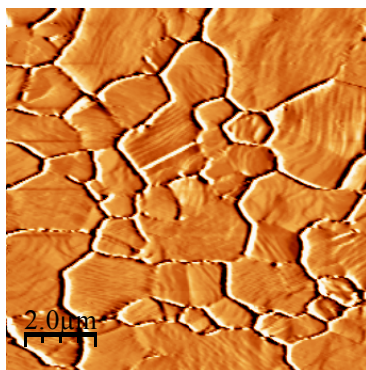


Figure S1. AFM topography image of a well-cleaned gold surface showing its characteristic terraces.

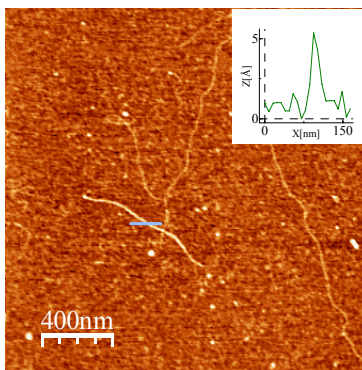


Figure S2. AFM topography image of $[\text{CuBr}(\text{HIN})]_n$ on mica.

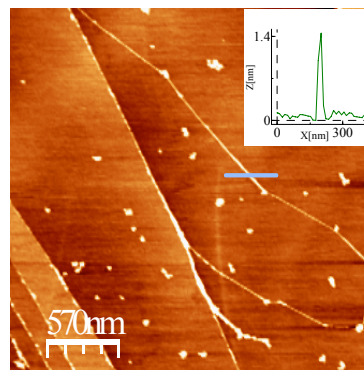


Figure S3. AFM topography image of $[\text{CuBr}(\text{HIN})]_n$ on HOPG.

Method (b).- 1 mg of $[\text{CuBr}(\text{HIN})]_n$ was treated with 1 ml of a NaOH solution (0.01 M) and then sonicated (680 W, 40 kHz) 30 min. at 27 °C. A yellow mother solution was obtained. 20 μL and 40 μL of a 10^{-8} mg/mL diluted mother solution were deposited on mica and HOPG, respectively. Upon standing these solutions at 20 °C for 2 min. on mica and 15 min. on HOPG, the substrates were gently washed with water and then dried under a flow of argon (Fig. S4 and S5). Similarly, 40 μL of 10^{-6} mg/mL diluted mother solution were deposited for 30 min. on gold surface and then washed with water and dried under a flow of argon (Fig. S6).

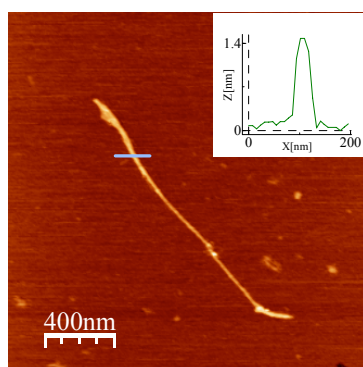


Figure S4. AFM topography image of $[\text{CuBr}(\text{HIN})]_n$ treated with NaOH on mica.

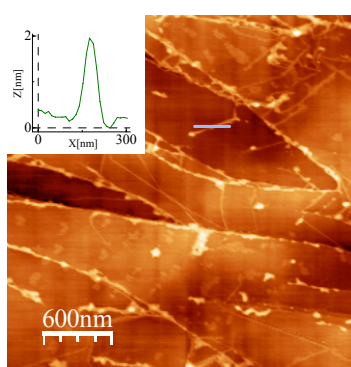


Figure S5. AFM topography image of $[\text{CuBr}(\text{HIN})]_n$ treated with NaOH on HOPG.

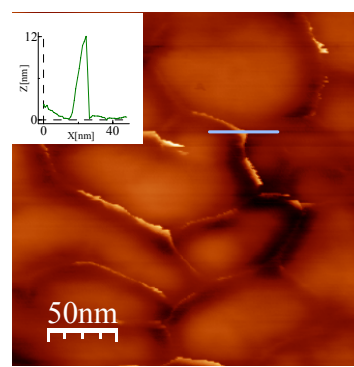


Figure S6. AFM topography image of $[\text{CuBr}(\text{HIN})]_n$ treated with NaOH on gold.

Atomic Force Microscopy

Atomic Force Microscopy images were acquired in dynamic mode using a Nanotec Electronica system (www.nanotec.es). Olympus cantilevers (RC800PSA (ORC8)) were used with a nominal force constant of 0.75 N/m with a pyramid shape and < 20 nm nominal radius tip. The images are processed using WSxM (freely downloadable SPM software from www.nanotec.es) operating at room temperature in ambient air conditions.

Spectroscopic Techniques on Surfaces

Polarization Modulated Reflection Absorption Infrared Spectroscopy (PM-RAIRS)

The PM-RAIRS spectra were recorded on a commercial NICOLET Nexus spectrometer. The external beam was focused on the sample, with a mirror, at an optimal incident angle. The incident beam was modulated between p and s polarisations using a ZnSe grid polarizer and a ZnSe photoelastic modulator (HINDS Instruments, PEM 90, modulation frequency = 37 kHz). The light reflected at the sample was then

focused on a nitrogen-cooled MCT detector. An important advantage of the PM-RAIRS technique, over the classical RAIRS mode of analysis, is that the signal is directly extracted from the $\Delta R/R$ data, avoiding a reference spectrum to be recorded on a bare sample. Also, this technique provides an enhanced sensitivity to the vibration modes normal to the surface, at a short distance from the surface ($< 1 \mu\text{m}$). All the spectra reported below were recorded at 8 cm^{-1} resolution by co-adding 64 scans.

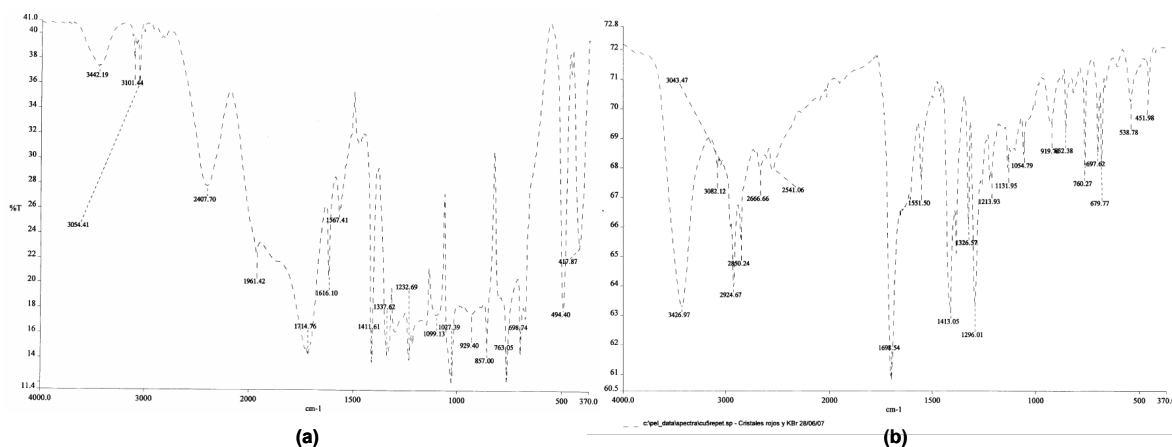


Figure S7. FTIR spectra in KBr pellets of HIN (a) and compound 1 (b).

X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) analysis of the sample was carried out in an ultra high vacuum chamber equipped with a hemispherical electron analyser, and using a Mg K α X-ray source (1253.6 eV) with an aperture of 4mm x 7mm. The base pressure in the chamber was 1×10^{-9} mbar, and the experiments were performed at room temperature. The following core level peaks were recorded under the same experimental conditions: O (1s), C(1s), N(1s), Cu(2p), Br (3d), and Au(4f). The pass energy applied for taking the overview sample was 30 eV, while 20 eV pass energy was applied for the fine analysis of the core level spectra. Their binding energies were calibrated against the binding energy of the Au(4f) peak set to 84.0 eV (attributed to metal surface, this reference give accurate BE values within $\pm 0.1 \text{ eV}$).

Conductivity Measurements

Preliminary studies of dc electrical conductivity were carried out at 300 K with two contacts. For the measurements prismatic crystals of $[\text{CuBr}(\text{HIN})]_n$ were employed (*ca.* $0.08 \times 0.08 \times 0.9 \text{ mm}^3$). The contacts between the crystals and the platinum wires (0.3 mm diameter) were made using silver paint (Fig. S8). The samples were measured applying an electrical current with voltages from +10 V to -10 V. Analysis of the data (Fig. S9) allows concluding qualitatively semiconductor behaviour, $4.35 \times 10^{-5} \text{ S m}^{-1}$, of the crystals of **1**.

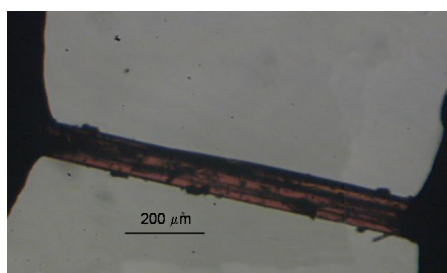


Figure S8. Picture of a crystal of **1** connected to the Pt wires.

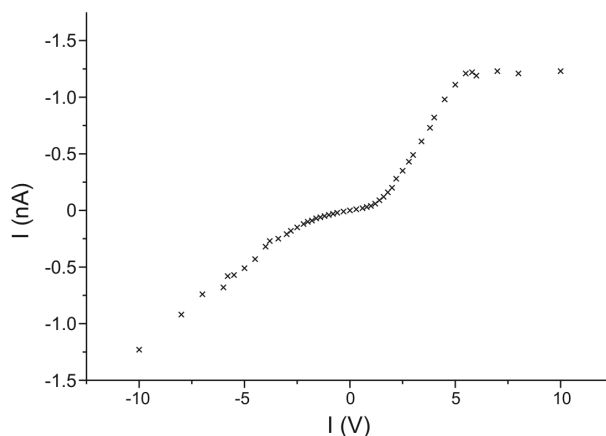


Figure S9. Variation of the intensity at different voltages for **1** at 300 K.