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In this work we present both spectroscopic and morphological evidence showing one-dimensional organization of [CuBr(HIN)]$_n$ (HIN = isonicotinic acid) on surfaces.

Supramolecular organization is one of the most promising bottom-up approaches towards new nanomaterials.[1,2] In particular, the selective use of coordination bonds to self-assemble molecular tectons in order to generate well-organized nanostructures is a promisingly powerful tool.[3] Coordination polymers, also named metal–organic frameworks (MOF), are formed by the self-assembly of selected tectons, metal to metal complexes and bridging ligands. They have been widely studied in recent years, since they show relevant structural features and potential applications in many fields.[4–6] However, their potential as nanomaterials[7] is still poorly developed, and requires the isolation of well-organized supramolecules on surfaces with arrangements at the nanometer scale.[1,8] One- and two-dimensional MOFs are especially suitable on the search of nanoarchitectures. In particular, the first studies of MOF on surfaces have been mainly centered on two-dimensional arrangements.[7,9–12] Single chains of 1D-MOFs are adequate candidates for molecular wires.[13] In addition, they present advantages over the classic metal oxide or carbon based materials, such as easier synthetic procedures, higher reactivities and the fact that their magnetic, electronic and optical properties can be modified by carefully selecting the building blocks.[14] Our current research is mainly focused on the isolation and morphological characterization of well-ordered individual 1D-MOF chains on surfaces, aiming at investigating their potential as molecular wires. This has required the development of new adsorption methods to organize individual chains of MOF on surfaces.[13,15,16] Herein, we have selected a particular 1D-MOF Cu(I) polymer with bromide and isonicotinic acid as bridging and terminal ligands, respectively. This selection has been based on its

physical properties (as a semiconductor) and its molecular structure (single [CuBr(HIN)]$_n$ chains could interact with other molecules like DNA, via H-bonding). The adsorption of this MOF on selected surfaces and its morphological characterization by means of atomic force microscopy (AFM)[17] confirms 1D-organizations. Novel spectroscopic characterization, polarization modulated reflection absorption infrared spectroscopy (PM-RAIRS) and X-ray photoelectron spectroscopy (XPS), of these fibers let us to establish their structure once adsorbed onto the surface.

The hydrothermal reaction between CuBr$_2$, KBr, NaOH and isonicotinic acid (HIN) affords crystals of [CuBr(HIN)]$_n$ (1).[18] The crystals have been analysed by X-ray diffraction, CNH elemental analysis and IR spectroscopy. The structure of compound 1 consists of 1D-chains (Fig. 1) that are interconnected by hydrogen bonds involving the carboxylic groups to form two-dimensional sheets from the one-dimensional chains.[18] In these chains (i) the short Cu–Cu distance (2.8567(11) Å) and (ii) the existence of free carboxylic groups that can orientate the polymer on the surface and, therefore, its organization are both noteworthy.

Based on the structure of 1, two different adsorption methods on different surfaces have been used: (i) casting deposition of sonicated suspensions and (ii) solubilization of 1 by deprotonation of the carboxylic groups. As previously observed, the selective use of ultrasounds may induce breakage of weak bonds.[19] Therefore, it should be possible to find out conditions
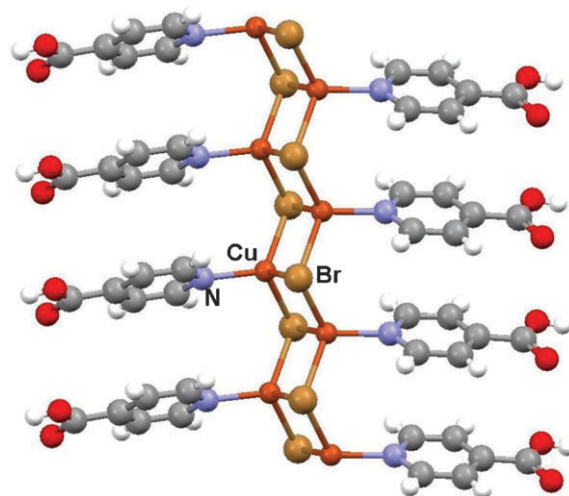
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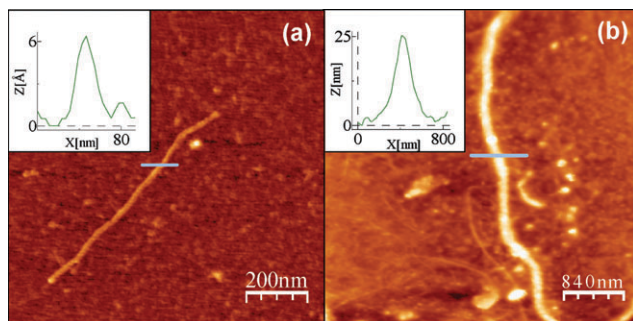† Electronic supplementary information (ESI) available: Experimental. See DOI: 10.1039/b711416h

Fig. 1 Schematic representation of a [CuBr(HIN)]$_n$ polymer chain.

Fig. 2 AFM topography images of [CuBr(HIN)]$_n$ deposited on polylisine treated mica (a) and gold (b) surfaces.

Fig. 3 PM-RAIR spectra after adsorption of [CuBr(HIN)]$_n$ on gold surface from different adsorption methods: from H$_2$O (a), H$_2$O–sodium dodecyl sulfate (b) and NaOH (c). Schematic model showing the orientation adopted by [CuBr(HIN)]$_n$ on a gold surface (down).

(solvent, sonication power and time) for a selective breakage of the H-bond interchain interactions in **1** by means of ultrasound. This has been achieved in water as solvent (see ESI†). Subsequent casting deposition of these solutions on mica allows isolation of individual chains. Fig. 2a shows an AFM topography image of a homogeneous fibre with a height of *ca.* 0.6 nm. This value is in good agreement with the one obtained by X-ray diffraction for individual polymer chains.[18] Large scale AFM topography images (25 μm^2) of **1** deposited on mica (20 μL of a 3.75 10^{-6} M solution) shows a total chain length close to 15 μm from the total expected length value of *ca.* 3 × 10^3 μm. The homogeneous fibre distribution on mica allows estimating a value of chain density of 0.6 μm μm^{-2} and indicates that only one over 1000 monomers in solution are adsorbed on mica. Bundles of **1** with variable height (from 1 to 25 nm) are observed on gold (Fig. 2b) and on highly oriented pyrolitic graphite (HOPG) surfaces (see ESI†). The typical length of the isolated wires ranges from 250 nm to several microns. Contrary to the homogeneous adsorption of **1** on mica, an inhomogeneous distribution and bundle formation of **1** on both HOPG and gold substrates is observed by AFM. This behaviour can be explained by taking into account the existence of carboxylic groups in the structure of **1** that will present a preferred interaction to a hydrophilic (mica) surface than to hydrophobic (HOPG) surface. Therefore, in the former case the chains interact with each other *via* H-bond formation between the carboxylic groups. The interaction of **1** with the gold surface consists of a chemisorption process *via* partial deprotonation of the carboxylic groups (see RAIRS below) which is different to the adsorption of **1** on both mica and HOPG, physisorption processes. Besides the large scale gold surface topography is completely different to the mica surface.

Finally, treatment with NaOH of the coordination polymer suspensions may lead to deprotonation and solubilization of those by forming the corresponding polyanion, which may allow isolation of individual chains.[19] Compound **1** presents carboxylic groups along the chain which are potentially susceptible of deprotonation. Thus, formation of the polyanion derived from **1** was induced by treating the neutral polymer with NaOH. Casting deposition of the polyanionic solution also leads to the isolation of individual chains and bundles of **1** on mica, gold and HOPG surfaces with heights and lengths varying from 0.6 to 12 nm and from few nanometres to several microns, respectively (see ESI†).

The deposition methods employed so far to adsorb 1D coordination polymers lead to fibres formation on surfaces, ensuring their morphological characteriza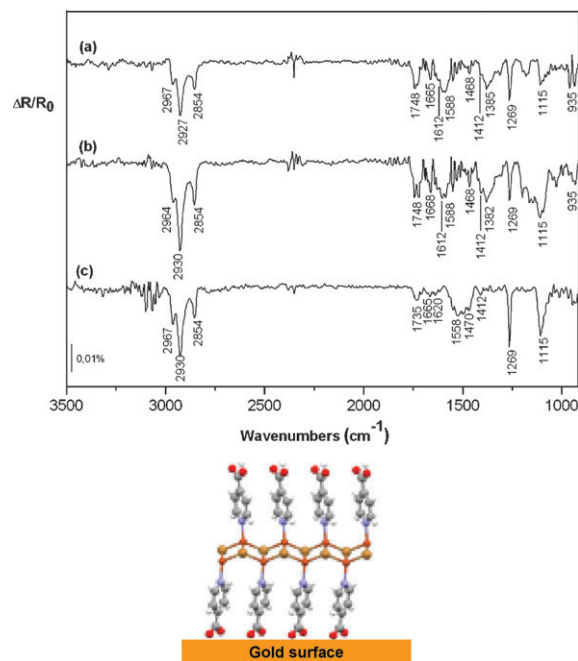tion at the nanometer scale. How-ever, just from the AFM images it is not possible to elucidate their structures and interactions with the surface. In order to gain more information on these issues, spectroscopic characterization of the structures adsorbed on gold surface has to be performed.

RAIRS spectra of **1** immobilized on gold surface following different adsorption methods are shown in Fig. 3. The infrared spectra contain absorptive features indicative that **1** has been successfully adsorbed on the gold surface. We consider different chemical functional groups present in the MOF structure for the infrared analysis. The main infrared features corresponds to: (i) the pyridine-ring vibrations modes ν(CC/CN) at 1588–1552 cm^{-1}, 1468 cm^{-1} and 1269 cm^{-1}; (ii) in-plane and out-of-plane CH deformations, δ(CH) at 1115 cm^{-1}, γ(CH) at 1022 cm^{-1}; and (iii) ring breathing at 935 cm^{-1}.[20,21] The presence of all these ring vibration modes suggests that, orientation of the ring should be tilted respect to the gold surface, allowing these vibrations to be infrared active. It is known that in the presence of the metal surface, only the modes with a non-zero dynamic dipole moment perpendicular to the surface can be detected by RAIRS. The COOH groups present an intense characteristic ν(C=O) vibration mode at 1748 cm^{-1}, which is related to the C=O bond, adopting a perpendicular orientation relative to the surface. Furthermore, two vibration frequencies ν_{asym}(COO$^-$) and ν_{sym}(COO$^-$) at 1612 and 1412 cm^{-1}, respectively, are identified in the spectra. The presence of the carboxylate features in the spectra indicates partial deprotonation of the carboxylic group present in **1**. Therefore, the new COO$^-$ groups generated in **1** are acting as linkers with the gold surface. The similar intensity shown by both carboxylate stretching modes, suggests a tilted orientation of the COO$^-$ groups, where the two oxygen atoms are non-equidistant to the surface.[22] Moreover, the infrared spectra

(Fig. 3a) show intense bands at 2930 and 2854 cm^{-1} related to the CH groups attached to the aromatic ring, lower shift in these infrared frequencies could be due to the so-called improper hydrogen bonds[23] between carboxylic groups, as observed in the infrared spectrum recorded for crystals of **1** in KBr pellets (see ESI†). Their strong intensity suggests a dipole moment almost perpendicular to the surface, which reinforce the idea of an upright ring orientation. The presence of the molecular vibrations suggests that **1** does not decompose on the surface and that it is adsorbed as an entire entity. As expected, the absence of broad-medium bands in the region of 2500–2100 cm^{-1} (hydrogen bond of the type O–H···N) indicate that all nitrogen atoms are coordinated to the metal centre.[21] In summary, we propose a molecule–surface interaction model where the COO$^-$ is the anchoring point, upright ring orientation and N-metal coordination (see Fig. 3).

The analyses of the infrared spectra of the polyanion derived from the deprotonation in solution of **1** (see ESI†), confirm the almost full deprotonation of the carboxylic groups (high decreased of ν(C=O) vibration mode intensity). Moreover, the absence of the two vibration modes expected for the COO$^-$ groups in the spectra [ν_{asym}(COO$^-$) and ν_{sym}(COO$^-$)] suggests a flatter orientation of these groups on the gold surface, whereas the ring slightly modify its orientation with respect to the gold surface.

While infrared spectroscopy provides information about the organic part of **1**, a XPS analysis is required to gather further information related to the metallic part of the compound.‡ In a XPS spectra overview the following atomic species can be identified: O, C, N, Cu and Au. In order to obtain the chemical state and composition of each element, selected energy regions of these elements were individually scanned. Fig. 4 shows the core-level spectra of the N (1s) and the Cu (2p$_{3/2}$). The binding energies of those peaks are 400.0 and 932.1 eV which can be assigned to nitrogen, of the isonicotinic ligand, and copper bound to bromide, respectively.[24] It is also remarkable the presence of an oxygen peak at 532 eV which is compatible with the presence of COO$^-$ species, also corroborated by RAIRS.

Therefore, both spectroscopic techniques (RAIRS and XPS) confirm, on surfaces, the already known structure of **1** as determined by single-crystal X-ray crystallography.

As already mentioned, **1** was selected for two intrinsic added values: (i) preliminary electrical conductivity measurements at roo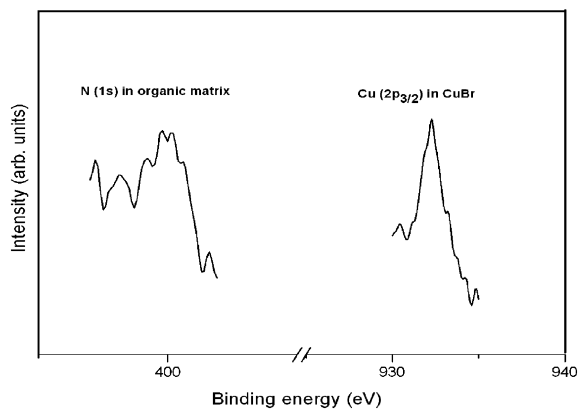m temperature show semiconductor behaviour (4.35 × 10^{-7} Scm^{-1}) of **1** in crystal state, as expected by the short metal–metal distances (Fig. S9†). This is one of the few examples of MOFs showing conductivity in solid state.[4,5] (ii) Its structure shows "free" carboxylic acids groups orthogonal to the chains which are potentially useful for subsequent supramolecular interactions to attach to other polymeric molecules *i.e.* DNA.[25]

In summary, we present direct evidence of the subnanometer structure on surface of a 1D-MOF. Besides, based on its *in situ* spectroscopic characterization, an interaction model with the gold surface is proposed. Electrical characterization of the single polymer chains on surfaces is currently in progress.

Notes and references

‡ CCDC 667677. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711416h

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Fig. 4 XPS spectra after adsorption of [CuBr(HIN)]$_n$ on gold surface.