Towards alternative 2D polymers based on coordination polymers

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Coordination polymers are a class of compounds formed by two building-blocks, the metal units (metal ions or complexes) and the ligands (molecules or ions), connected by means of coordination bonds. A wide variety of architectures with a broad panel of properties can be achieved by suitable selection of the building-blocks. Large amount of work has been done towards potential applications of materials based on coordination polymers. Probably, the most studied being gas storage and gas separation [1]. However, little is known about their potential use as alternative materials of nanometric dimensions. We have recently pointed out that a particular type of 1D coordination polymers seems particularly suitable as molecular wires [2]. In addition, the development of the unique properties of graphene has originated a scientific "revolution" around this material. This scenario has motivated us to consider new alternatives for the isolation of 2D polymers, in other words, new 2D materials with one atom or molecule of thickness [3]. As for the preparation of graphene, one feasible route to achieve this end consists of delamination of a layered compound [4].

Herein, we present the synthesis and structure of a laminar Cu(I) coordination polymer $[Cu(\mu\text{-}pymS_2)(\mu\text{-}Cl)]_n \cdot nMeOH$ (Fig. 1). It was synthesized by diffusing a dipyrimidindisulfide ($PymS_2$) MeOH:MeCN solution into a $CuCl_2 \cdot 2H_2O$ methanolic solution. Isolated red crystals of $[Cu(\mu\text{-}pymS_2)(\mu\text{-}Cl)]_n \cdot nMeOH$ exhibit semiconducting and luminescent properties. X-ray diffraction analyses evidenced that the sheets are weakly face-to-face stacked through pyrimidine ligand moieties (Fig 1a). The packing of these sheets allocate channels along the *c* axis which are occupied with disordered guest methanol molecules (Fig1b). The solvent molecules can be selectively exchanged by *ie.* water or ethanol molecules, resulting in a slight shift in the relative position of the layers. As evidenced by crystallographic data and interchange host-guest properties let us to envision a feasible compound exfoliation.

In fact, crystalline $[Cu(\mu\text{-}pymS_2)(\mu\text{-}Cl)]_n$ can be exfoliated into colloidal sheets by micromechanical cleaving. Both hydrophilic and hydrophobic sites can be found in the layer structure, hence mica (hydrophilic) and HOPG (hydrophobic) surfaces were explored in order to adsorb the compound by casting deposition of previously sonicated and diluted sample suspensions. Atomic force microscopy techniques were employed to characterise deposited sheets of $[Cu(\mu\text{-}pymS_2)(\mu\text{-}Cl)]_n$ on HOPG (Fig.2) and mica (Fig.3). Its is noticeable the morphological features of the sheets adsorbed on HOPG which angles resemble to those observed in the monocrystals of this material.

References

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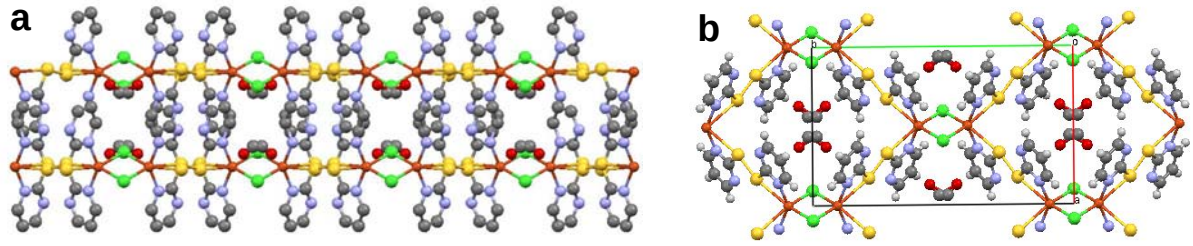

Figure 1. (a) *bc* plane view showing the interlayer interactions and (b) *ab* plane view of $[Cu(\mu\text{-}pymS_2)(\mu\text{-}Cl)]_n \cdot nMeOH$ showing the structure of a layer with the cavity filled by molecules of methanol.

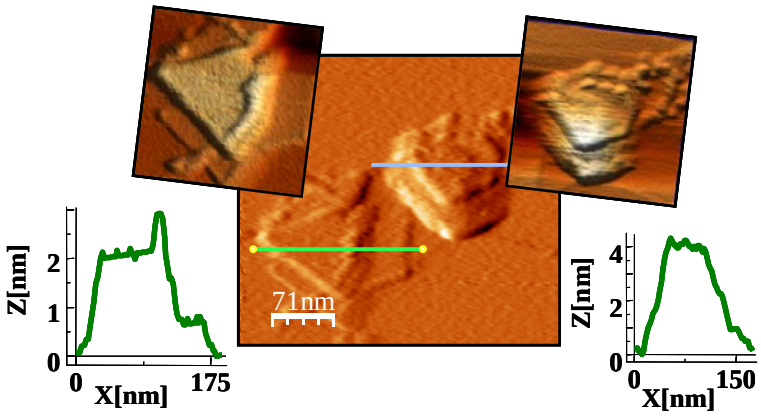

Figure 2. AFM image and two zoomed areas with their height profiles showing two sheets of $[Cu(\mu\text{-}pymS_2)(\mu\text{-}Cl)]_n$ deposited on HOPG.

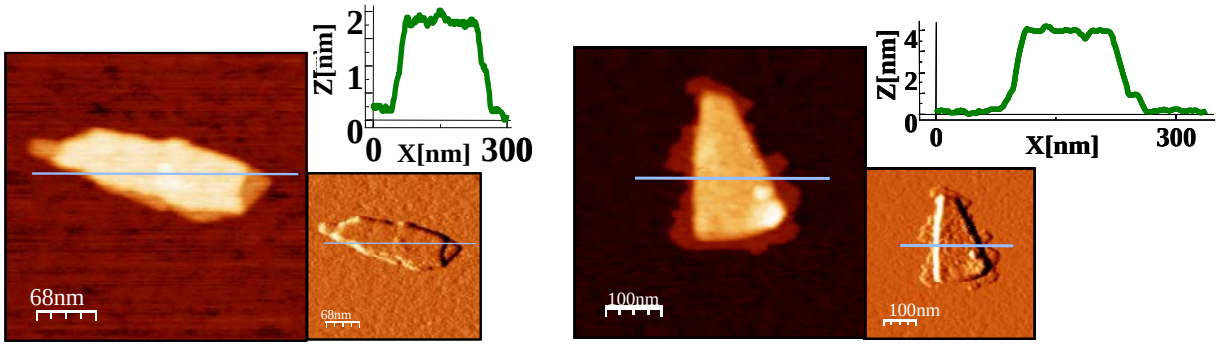

Figure 3. Two AFM images and their height profiles sheets of $[Cu(\mu\text{-}pymS_2)(\mu\text{-}Cl)]_n$ deposited on mica.