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## COMMUNICATION

## On-surface self-organization of a robust metal-organic cluster based on copper(I) with chloride and organosulphur ligands

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**Direct sublimation of a Cu<sub>4</sub>Cl<sub>4</sub> metal-organic cluster on Cu(110) in ultra-high vacuum allows the formation of ultra-large well-organized metal-organic supramolecular wires. Our results show that the large monomers assemble to each other by  $\pi$ - $\pi$  interactions connecting dipyrimidine units and are stabilized by the surface.**

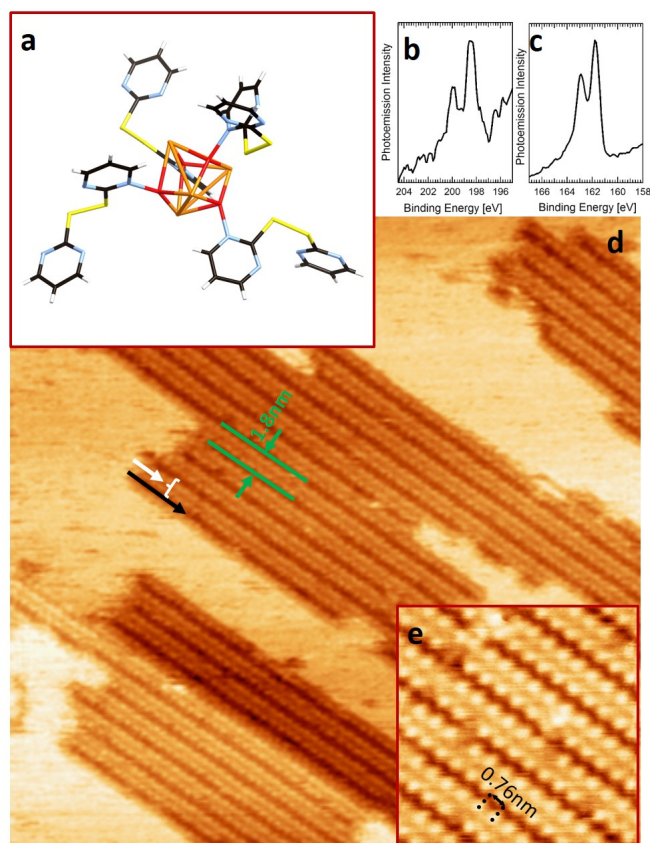
The design and fabrication of new nanostructures with controlled functionality, size, shape, and position is a major goal in nanoscience.<sup>1</sup> The concept of self-assembly of molecular building-blocks to generate well-defined architectures based on non-covalent interactions with the supporting substrate is technologically appealing.<sup>2</sup> Such intriguing supramolecular assemblies often possess polymeric characteristics and are referred to as "supramolecular polymers".<sup>3</sup> The generation of such organized structures, obtained by controlling supramolecular interactions, makes possible to tune their physicochemical properties of these molecular based materials. In this context, to combine organic molecules with metal entities is particularly useful.<sup>4,5</sup> On the other hand, the bottom-up approach for forming on-surface nanostructures by direct sublimation of their building blocks under ultra-high vacuum conditions has been shown as an excellent approach to this goal.<sup>6</sup> However, this experimental approach present a limitation coming from the stability that it is required for the molecule to allow sublimation without structural damage. This is the reason why there are a relatively high number of nanostructures based on organization of ideal organic molecules but few of them for those based on the combination of organic molecules with metal fragments.<sup>7</sup> The metal-organic structures formed up to now by sublimation are almost limited to those simple cases obtained by sequential sublimation of both building blocks, organic molecule and metal precursor, or just by sublimation of the organic molecule and its subsequent *in situ* reaction with the metal atoms coming from the metallic surface.<sup>8,9</sup> In both cases the selection of the building blocks has allowed to form a large variety of 1D- or 2D-coordination polymer architectures.<sup>10-12</sup>

In most of the previous studies of large complex molecules on surfaces the molecules were transferred from a solution<sup>13-19</sup> or by a dry imprint technique<sup>20</sup> to the substrate in order to preserve the fragile core. In this communication we focus on the search of a new metal-organic complex with a robust structure able to be sublimated keeping its molecular integrity and to self-assemble without being disrupted by the surface. We have been able to directly sublimate under Ultra High Vacuum (UHV) conditions a large metal-organic cluster that is, as far as we know, the largest molecular complex ever sublimated and *in situ* characterized by STM. This allows to form well-controlled nanoarchitectures readily on a surface and to use advanced surface *in-situ* techniques. To this goal, we combine *in situ* Scanning Tunnelling Microscopy (STM), X-ray Photoemission spectroscopy (XPS), Low Energy electron diffraction (LEED) experiments with *ab initio* calculations.

Recently, we have reported on the synthesis and characterization of a robust metal-organic cluster [Cu<sub>4</sub>( $\mu_3$ -Cl)<sub>4</sub>( $\mu$ -pym<sub>2</sub>S<sub>2</sub>)<sub>4</sub>] (pym<sub>2</sub>S<sub>2</sub>= dipyrimidinedisulfide) (**1**) showing interesting physical and chemical properties. Previous studies indicate a remarkable stability of this molecule and their capability to change its structure to produce a 2D-coordination polymer, [Cu( $\mu$ -pym<sub>2</sub>S<sub>2</sub>)( $\mu$ -Cl)]<sub>n</sub>·nS (S= H<sub>2</sub>O or EtOH), when is exposed to water or ethanol.<sup>21</sup> We deposited **1** (Fig. 1a) by sublimation in UHV from a home-made Ta crucible at 370K on a atomically clean Cu(110) surface. More details related with the sample preparation are presented in the ESI.

STM images (Fig. 1d) show that **1** spontaneously self-organize on the Cu(110) surface forming a complex molecular array. The complex structure of **1** (Fig. 1a) together with the large level of interconnection between metal-organic clusters (Fig. 1d and 1e) impeach directly relating an individual molecule with any particular motive observed in the STM images. However, the observed molecular network can be described as a double-bumped rows (white arrow) surrounded by dark undulating stripes (black arrow) aligned along the [1-10] surface crystallographic direction. We notice that the observed morphology does not strongly depend on the bias

voltage in the range -2000 mV to +2000 mV. Importantly, both, surface coverage and chain length, can be modulated by adjusting the deposition time (ESI).



**Fig. 1** a) Model of compound **1** from DFT calculations. (b,c) Core level XPS peaks of Cl2p (b), and S2p (c). STM images showing the large supramolecular assembly d) Large scale (50×50) nm<sup>2</sup>, I=0.047nA, V=800mV and (e) high-resolution (10×10) nm<sup>2</sup>, 0.2nA, V=-320mV. In (a) Cu atoms are in red, Cl in brown, C in black, N in blue, S in yellow and H in white

The distance between two consecutive dark stripes is 1.8 nm in the [00-1] crystallographic direction while the distance between two consecutive bumps is 0.76 nm in the [1-10] direction. These values are in good agreement with the distance between five and three copper atoms of the substrate in the respective crystallographic directions. Furthermore, the high level of the molecular organization detected by STM is reflected in the (5×3) diffraction patterns obtained by LEED (ESI). These observations indicate that the supramolecular structure is not self-supported but the interaction with the metal surface underneath is playing an important role in the stabilization of these macromolecular wires. On the other hand, successive STM images reveals that for intermediate coverages (ESI) the molecules can diffuse on the copper surface and part of the rows change their position. These facts indicate that the interaction with the surface is low although cannot be completely neglected “opening the door” for the formation of different supramolecular structures on different substrates.

The chemical and structural integrity of the building-blocks in the structure visualized by STM is evident after exploring the XPS results, which report binding energy values in good agreement with the

expected oxidation states of the metal organic cluster (ESI). The S2p core level, Fig. 1(c), shows a single doublet, S2p<sub>3/2</sub> and S2p<sub>1/2</sub>, located at 161.8 and 163.0 eV, respectively. Their binding energies can be assigned to the C-S-S-C bond,<sup>22</sup> indicating that the amino-phenyl rings are preserved. The Cl2p region, Fig.1b, consists of one doublet at 198.5 and 200.1 eV, attributable to the Cl-Cu bonding configuration in agreement with the metal-organic nature of the molecular core.

To directly obtain the detailed structure of the observed arrays when a complex molecules are involved by a simple inspection of the STM images is an impossible task. Although, considering all the experimental information together, we have carried out *ab-initio* atomistic and molecular dynamics simulations STM-DFT on different possible organizations of **1** on the surface. We have combined the localized-basis-set and plane-wave schemes as implemented in the FIREBALL<sup>23</sup> and PWSCF<sup>24</sup> simulation packages, respectively. In the latter, a perturbative van der Waals (vdW) correction was implemented.<sup>24</sup> Additionally, tunnelling currents for the STM images were calculated using a Keldysh–Green function formalism, together with the first-principles tight-binding Hamiltonian obtained from the local-orbital DFT-FIREBALL method<sup>23, 25</sup> (a detailed explanation of the theoretical methods can be found in the ESI).

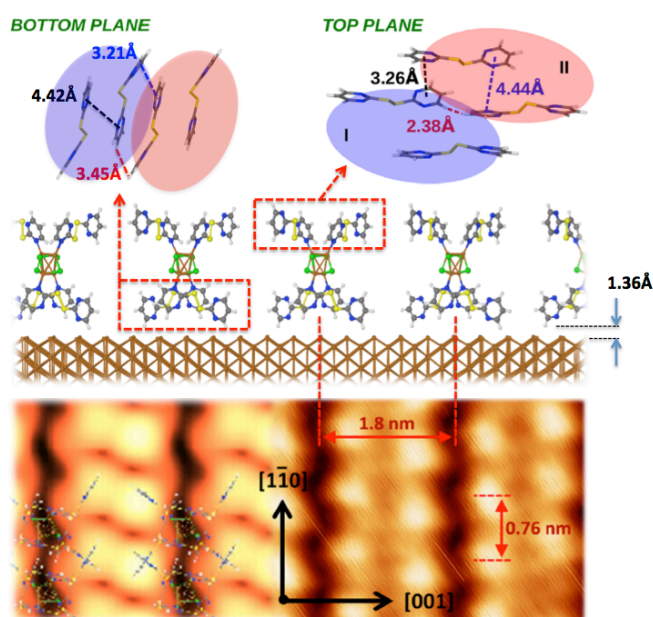
We notice that the geometrical structure obtained for the gas-phase molecule changes when it is adsorbed on the Cu(110) surface. The structural flexibility of the legs of **1** allows its accommodation with the surface. The most significant changes affect to the dipyrimidine rings of each dipyrimidinedisulfide ligand while the Cu<sub>4</sub>Cl<sub>4</sub> core undergoes a readjustment in both distances and angles (ESI). After some first geometrical discard, *ab initio* calculation shows that the most likely structures for the molecular chains observed in the STM images consist of molecules with the Cu<sub>4</sub>Cl<sub>4</sub> core localized either on the highlighted protrusions areas or between them (dark undulating stripes observed by STM). Calculations indicate that the case is the presented in Fig. 2. Bottom part of Fig. 2 shows a comparison between the simulated and experimental STM images. We show that the metallic-core of the molecule is displayed as a depression at the STM images, which mainly gives signal related to the  $\pi$  electrons. The agreement is fair good for this intricate system.

The structural and chemical integrity of the metal-organic core is preserved as it is interacting neither with the surface nor with other molecules. The nature of the intermolecular interactions can be gathered by calculations. The metal-organic clusters ensemble to each other forming an ultra-large supramolecular array mediated by  $\pi$ - $\pi$  interactions along the rows ([1-10] direction) at two different levels of height (upper panel of Fig. 2). This intermolecular bonding consists of a parallel-displaced  $\pi$ - $\pi$  stacking of all the four dipyrimidine rings. As can be seen in upper panel Fig. 2, both lower and higher rings pack at centroid-centroid distances of 0.33 and 0.44 nm, which are typical values for this kind of interactions.<sup>26</sup>

The interaction of the metal-organic molecular chains and the Cu surface, although important, is a weak bonding via the H atoms from the most prominent ring, which suggest that the molecular chains are weakly coupled and that they preserve their own molecular properties. The substrate is exclusively playing the role of a template, helping to stabilize the structure. This is in good agreement with the high molecular diffusion observed in the experiments.

It is curious that the STM images of the rows exhibit signal between them. This suggests the existence of an intermolecular interaction in the [001] direction that can be mediated by the weak overlap caused by the extended  $\pi$  electrons clouds of the dipyrimidine external groups. Recently, this kind of intermolecular contrast in STM and NC-AFM images has been discussed for several systems.<sup>27-29</sup>

Occasionally, we observe small defects along the molecular array in the form of missed bumps or extra STM signal either in the dark undulating stripes or in the double bumped wires (see Fig. 1e). The most probable defects we can expect are a lack of local-order between two neighbour molecules or a lost dipyrimidine group from the original cluster. Unfortunately, due to the complexity of the nature of the STM images it is not possible to unequivocally relate the observed features with a particular defect. However, a statistical analysis based on large area STM images over hundreds of molecules allow us to estimate the quantity of defects smaller than 5 %.



**Fig. 2** Lower panel: top view of the simulated (left) and experimental (right) STM images of the self-organized compound **1** in a (5x3) configuration. Tunnel parameters:  $I=0.25$  nA and  $V_s=-0.75$  V. Also, the structural model is over imposed to the STM image (left). Middle panel: Side view of the DFT derived model of the molecular array. Upper panel: schematic representation of the intermolecular interaction along the rows, both at the lower and upper part of the clusters.

Interestingly, it is important to notice that the same molecular arrangement experimentally detected on Cu(110) may form *a priori* on the Cu(111) surface, given the degree of decoupling between the structure and the surface (see ESI).

In summary, we have shown that direct sublimation of **1** in UHV forms supramolecular rows, in which the central Cu<sub>4</sub>Cl<sub>4</sub> metallic core maintains its molecular integrity. This 1D molecular macrostructure is stabilized laterally by  $\pi$ - $\pi$  intramolecular interactions and vertically via the interaction between the H atoms from the most prominent dipyrimidine ring with the Cu surface atoms. The self-assembled rows extend over the whole surface. The low interaction between the molecules and the copper substrate allows the molecular diffusion

and their self-organization in large arrays covering all the substrate suggesting that the assembled structure could structurally reversibly transform in [Cu( $\mu$ -pym<sub>2</sub>S<sub>2</sub>)( $\mu$ -Cl)]<sub>n</sub>·nH<sub>2</sub>O as it has been reported for the bulk compound.<sup>21</sup> The possibility of evaporating large metal-organic units for direct self-assembling on the surface suggests a new approach to form (multi-)functional nanostructures and bring the possibility to explore new chemical reactivity based on the knowledge of coordination chemistry.

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## Notes and references

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Electronic Supplementary Information (ESI) available: Synthesis, experimental and theoretical details, effect of the coverage and time, XPS results and Theoretical results. See DOI:10.1039/c000000x/

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