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PAPER

Surface assembly of porphyrin nanorods with one-dimensional zinc–oxygen spinal cords†

Marta Trelka,[a] Christian Urban,[a] Celia Rogero,[bc] Paula de Mendoza,[d] Eva Mateo-Marti,[b] Yang Wang,[e] Iñaki Silanes,[fg] David Écija,[a] Manuel Alcamí,[e] Felix Yndurain,[a] Andrés Arnau,[cfh] Fernando Martín,[ei] Antonio M. Echavarren,[d] José Ángel Martín-Gago,[bj] José María Gallego,[ij] Roberto Otero*[ai] and Rodolfo Miranda[ai]

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We have built long-range ordered, one-dimensional (1D) nanorods by self-assembly of zinc porphyrin derivatives through axial coordination with oxygenated ligands on different noble-metal surfaces. The structures were studied by a combination of Variable-Temperature Scanning-Tunnelling Microscopy (VT-STM), X-Ray Photoelectron Spectroscopy (XPS) and Density Functional Theory (DFT) calculations. The combined morphological, chemical and theoretical results demonstrate that the zinc atoms at neighbouring porphyrin molecules are coordinatively linked through oxygen-containing species, most probably water, leading to an adsorption geometry in which the porphyrin planes are perpendicular to the substrate plane, and the polymers are lying parallel to the surface.

Introduction

One-dimensional (1D) coordination polymers have attracted much attention due to its potential impact on the development of organic-based conductors.[1,2] In particular, metalated macrocycles such as porphyrins and phthalocyanines have been shown to polymerize into well-ordered, conductive 1D structures *via* axial coordination of polytopic ligands to the metal centres in neighbouring macrocycles (the so-called shish-kebab approach).[1,3–9] Such materials have shown conductivities up to 10^{-1} S cm^{-1}, which are attributed to conduction channels through the metal atoms along their spinal cords. This is a rather high value for organic-based materials even though most of the experimental measurements were carried out in powder form, where inter-grain barriers might significantly lower the conductivity of the material with respect to their intrinsic value.[1,3,4]

1D and 2D coordination polymers and networks have also been obtained on solid surfaces by codeposition of organic linkers and metal atoms,[10,11] where the organic linkers are planar molecules that adsorb parallel to the surface binding to neighbouring metal centres. Thus, in this case, all the coordination bonds in the network are coplanar and parallel to the surface, a geometry not compatible with the coordination geometry of the polymers described above.[1,3–5,7,9] For such compounds, all the bonds of the metal centre with the macrocycle are coplanar, but the axial coordination bond is oriented perpendicular to the macrocycle plane. Assembling shish-kebab coordination polymers made of phthalocyanines or porphyrins on solid surfaces implies, thus, one of the two following approaches: (a) if the macrocycle ring is adsorbed parallel to the surface, axial coordination must occur out of the plane, so that the polymers will grow perpendicular to the surface, or (b) if the macrocycle ring is perpendicular to the surface, axial coordination can occur parallel to the surface, and the polymers will grow parallel to the substrate.

In this paper we show Variable-Temperature Scanning Tunnelling Microscopy (VT-STM) experiments demonstrating that zinc *meso*-tetramesitylporphyrin (ZnTMP, see Fig. 1) molecules self-assemble on Cu(100) and Au(111) by forming long nanorods that are only one-molecule wide, in which the porphyrin core is not lying flat on the surface, but it is perpendicular to it. X-Ray Photoelectron Spectroscopy (XPS) reveals

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[a] *Dep. De Física de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Madrid, Spain. E-mail: roberto.otero@uam.es*
[b] *Centro de Astrobiología, CSIC-INTA, 28850 Madrid, Spain*
[c] *Centro de Fisica de Materiales CSIC-UPV/EHU, Materials Physics Center MPC, San Sebastian, Spain*
[d] *Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain*
[e] *Dep. de Química, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain*
[f] *Donostia International Physics Center (DIPC), 20018 San Sebastian, Spain*
[g] *Instituto de Hidráulica Industrial de Cantabria (IH), 39005 Santander, Spain*
[h] *Depto. Fisica de Materiales UPV/EHU, Facultad de Quimica, San Sebastian, Spain*
[i] *Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-NANO), Campus de Cantoblanco, 28049 Madrid, Spain*
[j] *Instituto de Ciencia de Materiales de Madrid—CSIC, Cantoblanco, 28049 Madrid, Spain*

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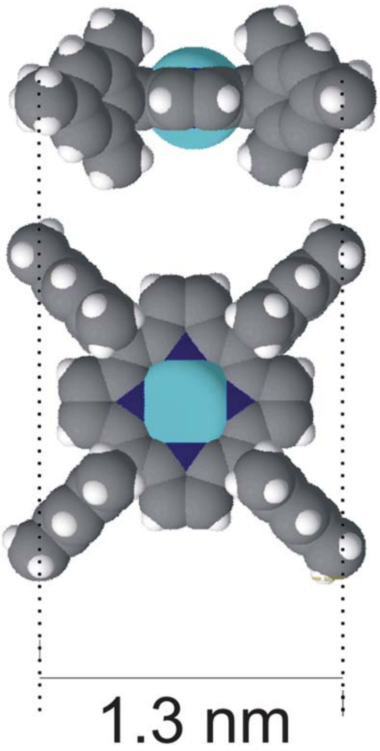

Fig. 1 Space-fill model of the ZnTMP molecule with a water molecule coordinated to the Zn atom.

the presence of oxygenated species that turn out to be necessary for nanorod formation, *i.e.* for all these situations in which the oxygen signal is not present, a planar adsorption geometry is found for the TMP molecules. The origin of such oxygenated species might be water or other small molecules present during the synthetic process or during the transportation to the UHV chamber where deposition is made. Actually, Density Functional Theory (DFT) calculations confirm the stability and geometry of ZnTMP linked axially by means of a variety of oxygen containing ligands, most prominently water or carbon monoxide, both for cluster models and extended periodic systems. The picture that emerges from the combination of these studies is that axial coordination is the driving force for nanorod assembly, providing a strong enough bond so as to keep porphyrin cores perpendicular to the surface in spite of the considerable decrease in adsorption energy.

Experimental and theoretical methods

ZnTMP molecules were synthesized from free-base tetramesitylporphyrin (TMP) following standard metalation methodology with $Zn(OAc)_2$.[12] The resulting metaloporphyin was characterized by ^1H NMR, mass spectrometry, IR and UV/vis spectroscopy (see ESI†).

Au(111) and Cu(100) surfaces were prepared under Ultra-High Vacuum (UHV) conditions by standard cleaning cycles of sputtering (Ar^+, 1 kV) and annealing (800 K). This preparation resulted in atomically flat terraces about 150 nm wide separated by monoatomic steps. ZnTMP molecules were deposited by sublimation from a glass crucible at 450 K onto the metals surfaces kept at room temperature. The STM images were obtained with an Aarhus-SPECS STM both at low and room temperature. XPS experiments were carried out at room temperature in a separate chamber (base pressure 5×10^{-10} Torr). This system is equipped with a hemispherical electron energy analyser and spectra were measured using Al Kα X-rays as excitation source. The overall energy resolution was estimated to be around 0.9 eV. RT STM images recorded at the XPS chamber were used to check the reproducibility of the results in both independent experimental chambers.

DFT calculations of the ZnTMP–molecule–ZnTMP complex in gas phase have been performed with the Gaussian 03 package.[13] The Perdew–Burke–Ernzerhof (PBE)[14] formula has been applied for correlation and exchange functional. The lanl2dz basis set[15–17] with an effective core potential (ECP) for inner shell electrons has been employed for Zn atoms. The 6-31G (d) basis set has been used for N atoms and the central molecule to get a good description of the interaction between the ZnTMP and the small central molecule. The 3-21G basis set has been employed for the rest of the atoms.

Calculations on the periodic system were carried out within the Density Functional Theory (DFT) framework using the SIESTA code.[18] The Perdew–Burke–Ernzerhof (PBE) functional was used, with a double-ζ plus polarization basis set, a 50 meV energy shift, and a 300 Ry cutoff for the spatial grid. Total energy minimization was performed, relaxing all internal degrees of freedom of the unit cell geometry subject to the only constrain that the metalomacrocycle be planar.

Results and discussion

Fig. 2a and b show STM images recorded at 150 K of the molecular structures formed upon deposition of ZnTMP

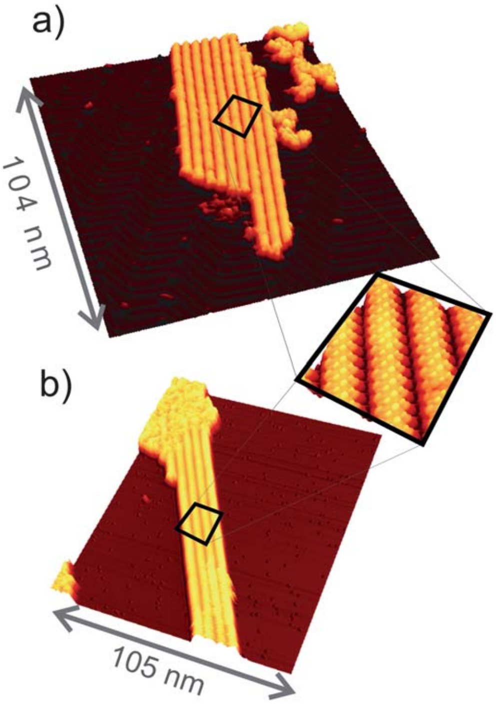

Fig. 2 (a) 104 × 96.5 nm^2 STM image (It = 0.5 nA, $V_{bias} = -1.9$ V) of the nanorods formed on the Au(111) surface upon ZnTMP deposition. (b) 104.5 × 126 nm^2 STM image of the nanorods on Cu(100).

molecules on Au(111) and Cu(100) respectively. The formation of long (hundreds of nm) 1D rod-looking structures is clearly observed on both surfaces, independent of the substrate's chemical nature and structural symmetry, a clear indication that intermolecular interactions must be the main driving force for nanorod self-assembly. High-resolution images of the porphyrin nanorods reveal an ordered array of protrusions with a typical diameter of about 0.6 nm (significantly smaller than the size of a single molecule) distributed helicoidally over the extension of the tube with a periodicity of four units per turn, and a typical height of about 0.9 nm. A planar adsorption geometry, in which the porphyrin ring is placed parallel to the surface, seems to be inconsistent with these observations. On the contrary, as it will become clear later, such observation can be explained by assuming that each protrusion corresponds to a single mesityl group, each porphyrin showing two mesityl groups (see Fig. 4). STM images recorded at higher temperatures do not reveal any structure that can be attributed to molecular adsorption, so the nanorod structures are not stable at higher temperatures. High-resolution STM images reveal a periodic corrugation along the tube direction which is identical for both metal surfaces, showing that the substrate's influence on nanorod formation is negligible.

A non-planar adsorption geometry for macrocyclic molecules on metal surfaces is not expected at all on the basis of previous studies.[19–24] Standing-up geometries have been reported for the adsorption of porphyrins functionalized with polar groups on insulating surfaces, due to the reduced dispersive interactions (π–π, vdW) between surface and macrocycle, and the strong electrostatic interactions between the polar groups and ions at the surface.[25] In our case, however, neither the substrate is insulating, so the interactions between the porphyrin core and the substrate are not expected to be weak, nor the peripheral functional groups are polar to mediate new molecule substrate interaction. Such argument directly points towards strong

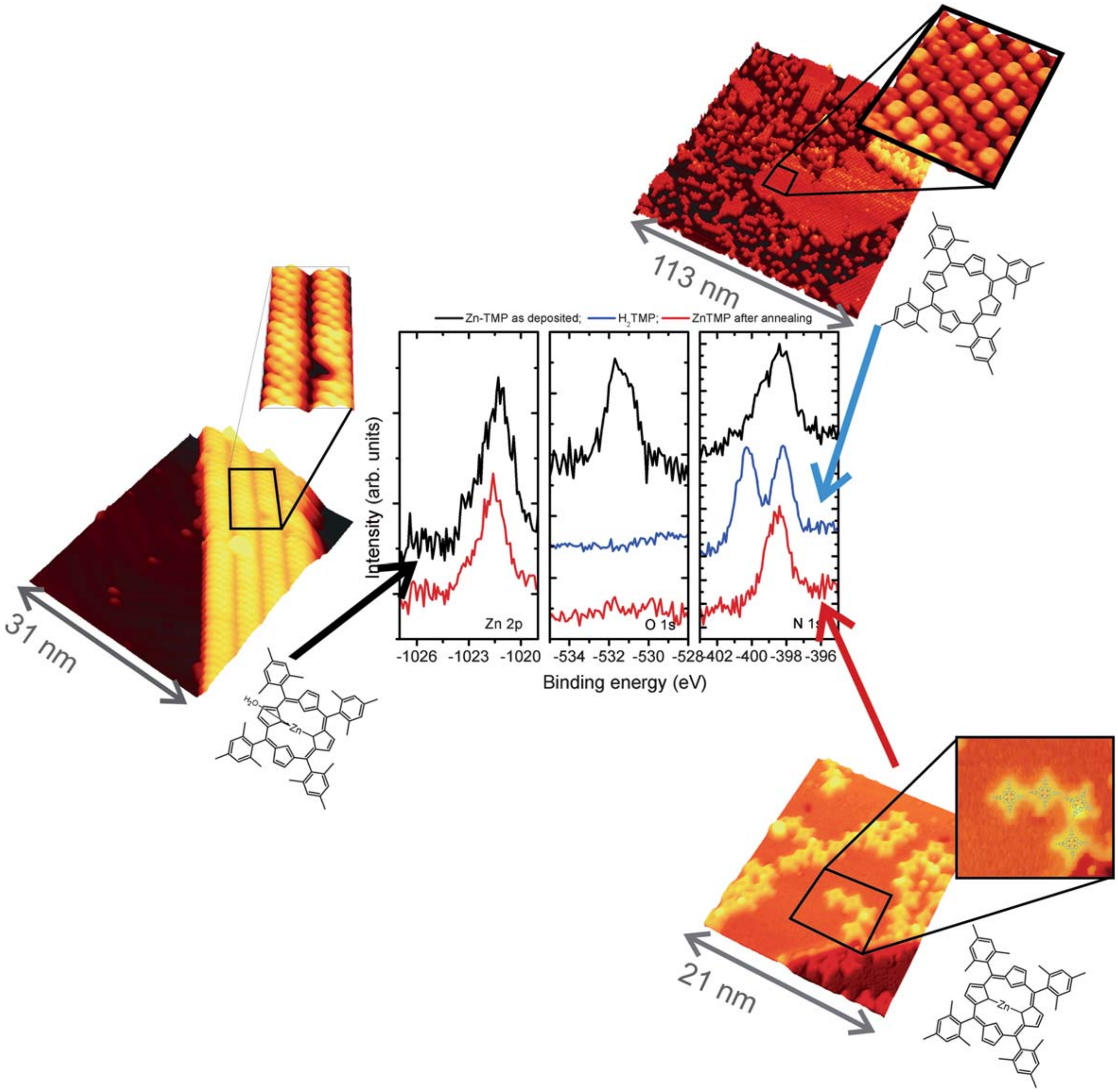

Fig. 3 Correlation between XPS spectra on self-assembled tetramesitylporphyrin (TMP) derivatives on Cu(100) and characteristic STM images. Upon deposition of ZnTMP a clear oxygen peak can be found in the XPS spectra (black curve), a situation in which STM images reveal nanorod formation (left inset). Deposition of base-free H_2TMP, however, does not show either oxygen in the XPS spectra (blue curve) or nanorod formation (top inset). Similarly, water detachment achieved by annealing to 525 K (see red curve in the XPS spectra) also lead to nanorod dissociation (bottom inset).

intermolecular interactions stabilizing the non-planar adsorption geometry. Since the electronic polarizability of a metal surface is necessarily larger than the polarizability of the π-clouds in the macrocycles, dispersive interactions alone cannot account for the preference of the molecular units to bind to each other instead of binding to the substrate. On the other hand, it is well known that columnar structures in metallic macrocycles are very often stabilized by coordination between neighbouring metal centres through an organic ligand.[1,3–6,8,9] It seems thus natural to attribute this strong intermolecular interaction to axial coordination to yield shish-kebab polymers such as those described in previous works.[1,3,4]

In order to check the presence of axial ligands in the observed nanorods, we have carried out X-ray Photoemission Spectroscopy (XPS) experiments on samples grown under the same conditions and the same dosing system as those investigated by STM. Apart from the expected C 1s, N 1s and Zn 2p core level peaks, at about 284.8 eV, 398.3 eV and 1021 eV binding energies, respectively, we clearly detect an oxygen signal (O 1s centred at 531.4 eV binding energy, see black curves in Fig. 3) which is not present before deposition, *i.e.* it cannot be attributed to surface contamination. Oxygen is not present in the chemical structure of ZnTMP, but X-Ray Diffraction studies carried out with crystals of ZnTMP showed a water molecule axially coordinated to the Zn atom.[26]

If the nanorods were hold together by intermolecular interactions such as π-stacking, they should also be observed for free-base tetramesitylporphyrin (H_2-TMP) molecules, something that can be ruled out if the interaction is mediated by coordination with axial linkers. Our experiments indeed show that H_2-TMP molecules do not form tubes (see top STM image in Fig. 3). On the contrary, they adsorb on Cu(100) with the porphyrin ring parallel to the surface, and the mesityl groups acting as "spacer legs" lifting the molecular board from the substrate.[20] For high enough coverage, close-packed 2D islands appear on the surface. The height of both individual molecules and self-assembled 2D islands is about 0.32 nm, *i.e.* about three times smaller than the height of the nanorods. Their XPS spectra show no measurable traces of oxygen, while two components in the N1s core level are observed, corresponding to the two chemically different nitrogen species, –NH (400.3 eV) and =N– (398.2 eV), on the non-metallated porphyrin ring (see blue spectra in Fig. 3). Similar results have been found for other porphyrins on a variety of metal surfaces.[20,21,27,28]

Moreover, ligand detachment from the adsorbed nanorods can be achieved by annealing the surface up to 575 K (higher than the ZnTMP sublimation temperature), as supported by the absence of the oxygen peak in XPS spectra (see red curves in Fig. 3). At the same time the N1s and Zn2p core levels slightly shift to the reported values for other Zn porphyrins (398.5 eV and 1021.7 eV, respectively).[21] STM images reveal that, upon annealing to 575 K the nanorods no longer exist on the surface. Instead, the molecules are imaged as rings with four little protrusions at 90° from each other. Superimposing a stick-and-ball model for the ZnTMP molecules on the experimental STM images, we can ascribe the central ring to the porphyrin ring and the four protrusions to the peripheral mesityl groups. The STM images in the bottom inset of Fig. 3 are very similar to the results for other metalated and free-base porphyrins on a surface after an annealing procedure.[24,29,30] The molecules can be imaged by STM even at room temperature, but they cannot be pushed away from their adsorption positions. The enhanced stability in the adsorbed porphyrins after a thermal treatment could possibly be explained by the formation of a covalent bond by dehydrogenation of the methyl groups at the mesityl legs, as previously suggested.[24]

The possible effect of oxygen-containing axial ligands in bridging two neighbouring ZnTMP molecules has also been investigated by Density Functional Theory calculations for water and other small molecules present in the atmosphere. A stable structure corresponding to a minimum in the ZnTMP–water–ZnTMP potential energy surface was found in which a water molecule is sandwiched between two ZnTMP molecules rotated 45° around their C_4 axis, in such a way that the lone pairs in the oxygen atom of the water molecule can interact with both Zn centres (see sketch in Fig. 4a, and ESI†). The calculated binding energy is about 0.6 eV, indicating that the formation of the ZnTMP–water–ZnTMP complex is significantly exothermic. This interaction leads to a deformation of the porphyrin ring to allow the Zn atoms to approach the encaged water molecule. This deformation might raise the question on whether it is possible or not to continue the structure beyond the dimer. However, periodic arrangements of stacked Zn porphyrin rings (without the mesityl groups) can also bind to each other through a water molecule in a similar fashion (see ESI†). The calculations yield binding energies in the range of 0.4–0.6 eV per dimer.

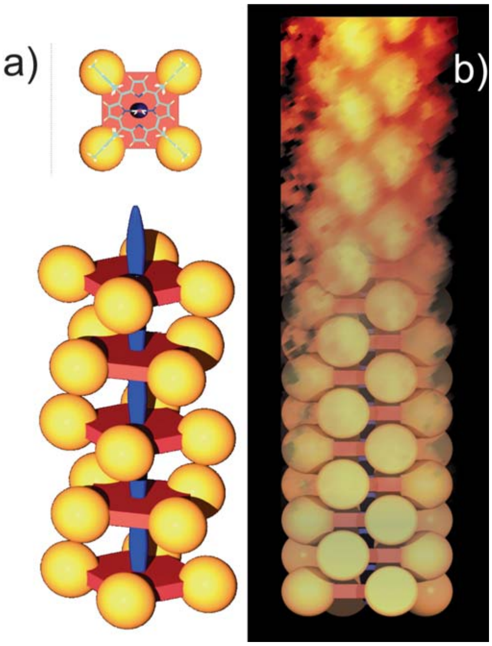

Fig. 4 Schematic diagram showing the proposed structure for the nanorods. Each ZnTMP molecule is rotated by 45° with respect to their common C_4 axis, in such a way that the mesityl groups (orange spheres) fit between the neighbouring mesityl groups of the adjacent ZnTMP molecule. The Zn atoms are bound to each other through a bridging water molecule (blue ellipsoid). (b) Comparison with STM images reveals that the brightest central protrusions in the nanorods can be ascribed to the uppermost methyl groups whereas the lighter bumps correspond to the methyl groups pointing sideways.

Similar results were obtained for CO, but not for O_2, which is not able to bridge neighbouring porphyrin molecules in a stable way, while CO_2 forces a non-linear geometry that is not compatible with our observations. Finally, although CO shows a similar behaviour as that shown by water, its scarcity in the atmosphere renders it an unlikely candidate to explain our observations. Moreover, the presence of CO can usually be recognized by a characteristic peak in the C1s spectra at about 286.7 eV, which is absent in our measurements.

Based upon the theoretical models described above we propose the structure depicted in Fig. 4a for the observed nanorods. Each porphyrin molecule is rotated by 45° around its C_4 axis with respect to its neighbours. The ZnTMP molecules are linked to each other through coordination with bridging water molecules. Similar structures are known to occur in solution for a variety of metaloporphyrins and phthalocyanines with different ligands acting as linkers. An STM image of such a tube can be expected to show bright protrusions at the position of the topmost mesityl groups, and lighter protrusions for the remaining mesityl groups pointing towards the top of the tube. This description fits well with the observed STM images (Fig. 4b).

Conclusions

In this paper we describe the synthesis of shish-kebab type coordination polymers of porphyrin derivatives on solid surfaces. The polymers have a straight conformation for over hundreds of nanometres. We suggest that the axial ligands that bridge the Zn atoms are water molecules that can bind to the upper and lower Zn atoms *via* the lone pairs at the oxygen atom, but other possibilities cannot be excluded. The synthesis of individual molecular wires on solid surfaces also opens up the possibility of probing their conductivity one by one, obtaining thereby information about the real internal conduction mechanisms along the rod spinal cord, not mixed up with grain boundary resistance. Moreover, a purely 1D sequence of zinc and oxygen atoms might show fascinating photovoltaic behaviour.

Acknowledgements

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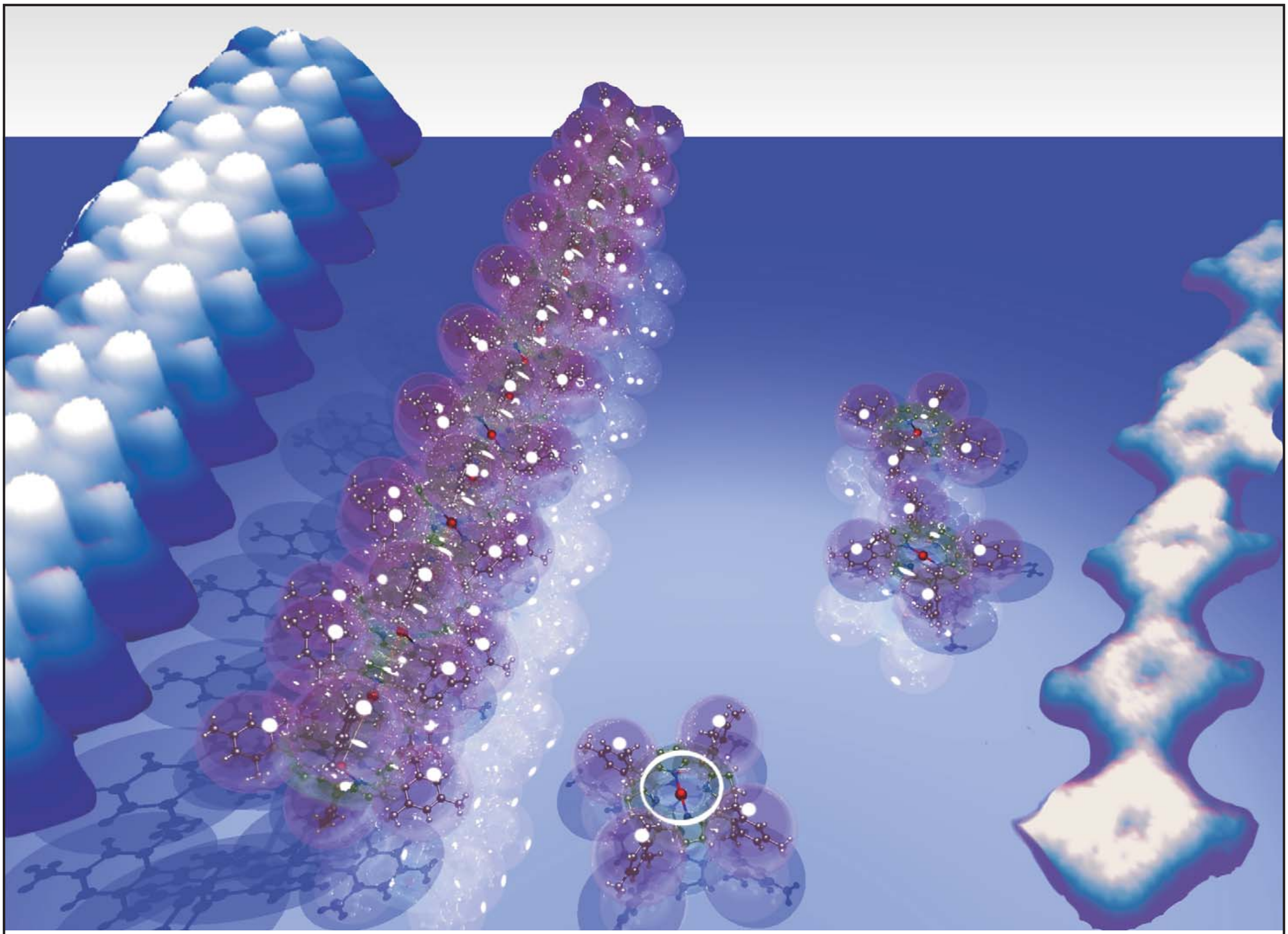

Showcasing research from LASUAM, The Surface Science Lab at Universidad Autónoma de Madrid (Prof. Roberto Otero).

Title: Surface assembly of porphyrin nanorods with one-dimensional zinc–oxygen spinal cords

1D metalloporphyrin nanorods have been grown on solid surfaces. A combination of Scanning Tunnelling Microscopy (STM), X-ray Photoelectron Spectroscopy (XPS) and Density Functional Theory calculations has been used to demonstrate that the nanorods are held together by axial coordination of the metal atoms with polytopic linkers.

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