STM Study of Magnetic Polyoxometalates on HOPG Surfaces

E. Pinilla-Cienfuegos[(1)], *A. Forment-Aliaga* [(1)], *E. Coronado*[(1)], *G. Sáenz-Arce*[(2)] *and C. Untiedt* [(2)]

[(1)] Instituto de Ciencia Molecular, Universidad de Valencia, PO Box 22085, E-46071 Valencia, Spain
[(2)] LT-NanoLab Departamento de Física Aplicada, Facultad de Ciencias (Fase II), Universidad de Alicante, San Vicente del Raspeig, E-03790 Alicante, Spain.

elena.pinilla@uv.es

Polyoxometalates (POMs) are a large class of discrete oxides composed of early transition elements (especially vanadium, molybdenum, and tungsten) exhibiting extensive applications in diverse fields such as catalysis, electronics, magnetism and medicine [(1)]. From a magnetic point of view the heteropolynuclear complexes of W and Mo form diamagnetic frameworks that can coordinate paramagnetic metal ions while keeping them well isolated from the neighbouring magnetic clusters. In fact, mononuclear lanthanide-based POMs have recently demonstrated the occurrence of Single Molecule Magnet (SMM)-like relaxation in this sort of compounds [(2)].

In these metal-oxide molecular clusters, a variety of physical techniques including the spectroscopic technique of inelastic neutron scattering (INS), can be used to determine the energies and wave functions of the different spin state of the cluster[(3,4)]. However, all these measurements are performed on bulk samples. In order to obtain information about the low energy levels from a single polyoxometalate, scanning tunneling spectroscopy (STS) at low temperatures can be used when the molecules are deposited on a conducting substrate. Therefore the interaction of the metal-oxide cluster with the surface has to be taken in consideration.

Herein we will describe the controlled deposition of magnetic POMs onto High Oriented Pyrolitic Graphite (HOPG) with two different examples: the Preyssler-type $K_{12}[DyP_5W_{30}O_{110}]$ (SMM) and the Kegging-type K_{10} $[Co_4$ $(H_2O)_2(PW_9O_{34})_2]$. Scanning Tunneling Microscopy (STM) was used to image the shapes, packing, and orientation of the two molecules at room temperature.

STM images show the formation of highly regular 1D and 2D molecular arrangements. Therefore it is possible to find single molecules to perform spectroscopy experiments as a preliminary step for the development of the study of the lowest electronic levels of magnetic molecules by STM and to determine the molecule-substrate interaction complementing the INS studies.

References:

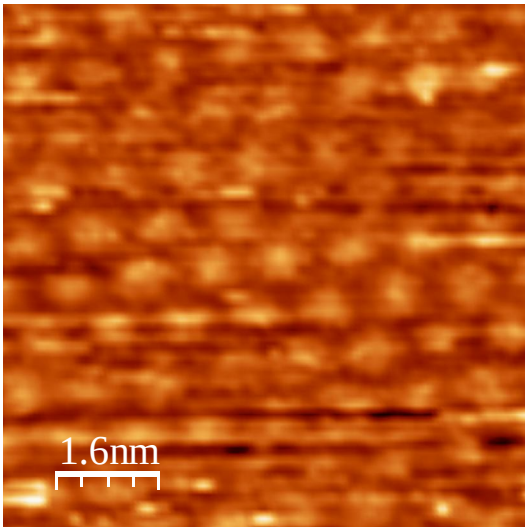
[1] Special thematic issue of Chem.Rev. , **98** (1998), 1-390.

[2] Murad A. AlDamen, Juan M. Clemente-Juan, Eugenio Coronado, Carlos Martí-Gastaldo, and Alejandro Gaita-Ariño, J. AM. CHEM. SOC.,**130**, (2008), 8874–8875.

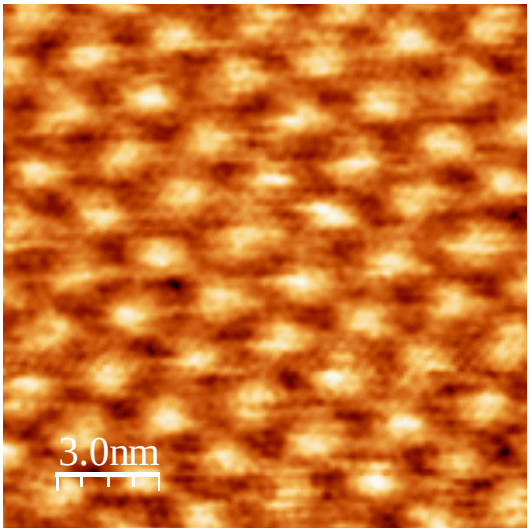
[3] Juan M. Clemente-Juan, Hanspeter Andres, Juan J. Borrás-Almenar,Eugenio Coronado, Hans U. Gu1del, Michael Aebersold, Gordon Kearly, Herma Bu1ttner, and Markus Zolliker, J. Am. Chem. Soc., **121** (1999), 10021-10027.

[4] Hanspeter Andres Juan, M. Clemente-Juan, Michael Aebersold, Hans U. Gu1del, Eugenio Coronado, Herma Bu1ttner, Gordon Kearly, Julio Melero and Ramón Burriel, J. Am. Chem. Soc., **121** (1999), 10028-10034.

Figures:



STM Image of $K_{12}DyP_5W_{30}O_{110}$.
8 nm x 8 nm



STM image of K_{10} $[Co_4$ $(H_2O)_2(PW_9O_{34})_2]$.
15 nm x 15 nm