

## Nanofunctionalised materials based on polyoxometalate-polymer interaction

Leire Ruiz-Rubio<sup>1,3</sup>, Beñat Artetxe<sup>2</sup>, Leyre Pérez-Álvarez<sup>1,3</sup>, Juan Manuel Gutierrez-Zorrilla<sup>2,3</sup>, José Luis Vilas-Vilela<sup>1,3</sup>

<sup>1</sup>Macromolecular Chemistry Group (LABQUIMAC), Department of Physical Chemistry, University of the Basque Country (UPV/EHU)

<sup>2</sup> Department of Inorganic Chemistry, University of the Basque Country (UPV/EHU)

<sup>3</sup> BCMaterials, Basque Center for Materials, Applications and Nanostructures Organization, Address, City, Country  
Leire.ruiz@ehu.es

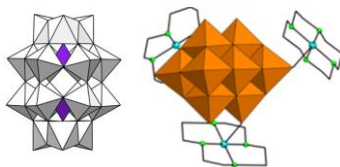
The versatility and diversity of application areas of organic-inorganic hybrids have improved the interest of the researchers, as exemplified by polymeric systems that incorporate polyoxometalate (POM) anions. POMs are anionic clusters formed by the combination of oxygen and early transition metals V, Mo or W in their highest oxidation states that can exhibit a wide variety of properties, sizes and structures as well as potential applications in fields like catalysis, materials science and biomedicine.

**Methods:** In this work, we have developed two different POM-based polymeric hybrid material (Figure 1). On the one hand, considering the anticancer properties of some POMs, chitosan-based nanocarries have been synthesized by microemulsion and loaded with bioactive  $[P_2Mo_{18}O_{62}]^{6-}$  anions. The physicochemical properties of this system have been thoroughly characterized, in addition to their application as drug delivery system. On other hand, another interesting property of POMs is their capability to catalyse several organic reactions. Thus, surfaces with micrometric patterns have been developed to immobilize functional POM anions. Polymeric substrates have been prepared by breath figure methods with PS/PS-b-PAA blends in order to allow the interaction between acrylic acid groups and different functional POM anions.

**Results and discussion:** The obtained POM-chitosan nanogels are good candidates for specific drug delivery in breast cancer therapies, since chitosan networks swell at acidic pH, while they remain collapsed at physiological pH. The suitability of these nanocarriers to successfully load and release the POMs in a biological medium have also been evaluated.

The anchoring of the POMs onto the patterned polymeric surfaces have been analysed by ToF-SIM technique. The polyoxovanadates present a good immobilization capability whereas the other POM-based systems studied present difficulties to be suitably incorporated into the functional device.

The authors thank EG/GV (IT718-13; bG18) and MINECO (MAT2017-89553-P) for financial support. Technical and human support provided by SGIKER (UPV/EHU) is gratefully acknowledged



**Figure 1:** Structures of the polyoxometalates used in these studies.