Funded by the European Union
cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY
4TH GENERAL MEETING OF COST ACTION CA21101 "COSY"
COSY C★ST ACTION
MINISTERIO DE CIENCIA, INNOVACIÓN Y UNIVERSIDADES
CSIC

# Molecules in Confinement: How Environmental Shapes Reactivity and Photochemistry

Leticia González[1]

[1]*Insitute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Währingerstrasse 17, 1090 Vienna, Austria*
*leticia.gonzalez@univie.ac.at*

Chemical function does not emerge from molecules alone, but from molecules embedded in complex environments. For this reason, understanding how microsolvation influences reactivity and stability of molecules remains a central challenge in catalysis and beyond. In this talk, I will present a theoretical perspective on how local surroundings modulate reactivity, photochemistry, and energy flow in several systems. One example is a manganese-vanadium cubane water oxidation catalyst, $[Mn_4V_4O_{17}(OAc)_3]^{3-}$, which we have characterized in different environments, comparing its properties in dry acetonitrile, acetonitrile-water mixtures and when embedded in a block copolymer membrane based on poly[2(dimethylamino)ethyl methacrylate] (pDMAEMA), here modelled as a polymer brush. Second, we explore a photosensitizer–bridge-catalyst dyad, where the bridge is protected by a mechanically interlocked ring reminiscent of a rotaxane architecture. Confining within this heterodinuclear rotaxane photocatalyst preserves both, structural integrity and activity of its components, leading to enhanced long-term photocatalytic performance, under enzyme-like H-bond-driven substrate preorganization. Finally, we examine the ultrafast photodynamics of a ruthenium complex in water, following excited-state relaxation and the associated energy flow from the solute into the solvent. These results highlight the active role of the environment in mediating dissipation pathways and determining excited-state lifetimes.