THE UNIVERSITY OF TOLEDO
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Department of Chemistry and Biochemistry Colloquium Speaker

Prof. Cláudio Verani

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"Molecular Diodes, Corrosion Inhibitors, and Water-splitting Catalysts Inspired by the 5-coordinate Iron of Tyrosine Hydroxylase"

Abstract: A five-coordinate iron [N_2O_3] active center has been described for Tyrosine Hydroxylase, which catalyzes the hydroxylation of tyrosine to L-DOPA via a rich redox and radical-based sequence of mechanisms. Aiming at redox-responsive metallosurfactants for applications in molecular electronics, the Verani group developed asymmetric and phenolate-rich [$^{HS}Fe^{III}(N_2O_3)$] complexes to understand the electrochemical and spectroscopic behavior of such bioinspired environments. We will start this talk by focusing on the efforts to understand how five-coordinate molecular diodes for current rectification can be obtained by matching the energy of electrode Fermi levels with the SOMOS of $^{HS}3d^5$ iron(III) in [$Fe^{III}(N_2O_3)$] surfactants. We will then progress from this Fermi/SOMO argument to the use of similar environments for the mitigation of corrosion in metallic surfaces. Ligands will be adapted to accommodate $3d^{10}$ zinc(II) in [N_2O_2] environments, as a means to purposefully mismatch the Fermi/SOMO energies, thus preventing electronic communication between the surface and the corroding media. Then, we will discuss how these bioinspired [N_2O_3] environments can find further applications in catalytic water splitting when the $^{HS}3d^5$ iron(III) ion is replaced by a $^{LS}3d^6$ cobalt(III) capable of water oxidation in electroactivated monolayers. Finally, we will discuss how replacement of phenolates by pyridines generates Co(III)[N_2N_3] species capable of water reduction to H_2 with turnover numbers as high as 7,000.

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