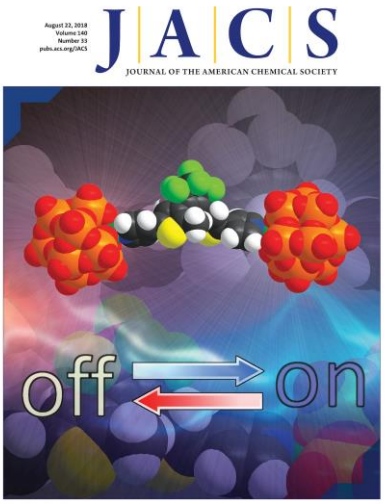
PPSM Seminar – Dr. Chris Ritchie

Tuesday afternoon, 12th of December 2023, 1:30pm – 2:30pm

ENS Paris-Saclay – 1st Floor – Room 1Z56 (North)

Dr. Chris Ritchie School of Chemistry, Monash University, Melbourne, Australia

"Polyoxometalate Containing Materials: Self-Assembly of Stimuli Responsive Systems"



This seminar presents the development and characterization of innovative polyoxometalate (POM) systems. An introduction to POMs will be provided alongside a recently developed strategy to target heterometallic systems composed of Vanadium and Molybdenum.[1] Our attention will then shift to compounds and materials that exhibit responsive behavior to pH and light stimuli. Capitalizing on the rich chemistry and structural diversity of POMs, we engineered multifunctional materials that can change their properties and behavior based on environmental cues. The pH-responsiveness of these systems is achieved through the integration of pH-sensitive organic moieties into polymeric nanoparticles encapsulating the POM structure, enabling switchable behavior in response to changes in pH.[2] The light-responsive behavior, on the other hand, is achieved through the incorporation of photoactive components, allowing for photoinduced structural transformations on illumination. In this seminar I will discuss both topics with recent examples including the preparation and chemistry of the first examples of photochromic polyoxometalate (POM)-based diarylethene (DAE) coordination complexes, prepared by ligation of the cobalt(III)-incorporated borotungstate $[B^{III}W^{VI}_{11}O_{39}Co^{III}]^{6-}$ and the trilacunary polyoxomolybdate $[PMo_9O_{31}]^{3-}$ with the ditopic pyridyl-containing diarylethene ($C_{25}H_{16}N_2F_6S_2$).[3-4] The solution-state composition, structure, and stability of the assemblies were probed using ^{1}H and ^{19}F nuclear magnetic resonance spectroscopy (NMR), electrospray ionization quadrupolar time-of-flight mass spectrometry (ESI-QTOF-MS), ultraviolet–visible spectroscopy (UV–vis), and small-angle X-ray scattering (SAXS), revealing that the complex self-organizes to adopt molecular dumbbell structures due to electrostatic and steric considerations. This conformation is a prerequisite for the photocyclization reaction. The assembly was found to be switchable between two states using visible light due to the perturbation of the DAE electronic structure on coordination to the POM. Photophysical data, including the reaction quantum efficiency of the molecular switch in both directions was measured using a custom-built quantum yield determination setup, while transient absorption spectroscopy and spectroelectrochemistry reveal a charge separated state in one example following electrocyclization.

[1] S. Spillane, R. Sharma, A. Zavras, R. Mulder, A. Ohlin, L. Goerigk, R. A. J. O'Hair, C. Ritchie, Non-Aqueous Microwave-Assisted Synthesis of Deca- and Hexa- Molybdovanadates, *Angew.Chem.Int.Ed.,* **2017**, 56, 8568-8572

[2] J. Xu, H. Volfova, R. J. Mulder, L. Goerigk, G. Bryant, E. Riedle, C. Ritchie, Visible-Light Driven "On"/"Off" Photochromism of a Polyoxometalate Diarylethene Coordiantion Complex, *J. Am. Chem. Soc,* **2018**, 140, 33, 10482-10487

[3] Y. Gao, J. Xu, C. Zhang, H. Venugopal, S. S. Kermaniyan, G. Such, C. Ritchie, Rationale Design of pH-Responsive Core–Shell Nanoparticles: Polyoxometalate-Mediated Structural Reorganization, *ACS Appl. Nano. Mater.* **2020**, 3, 11, 11247-11253

[4] M. Choudhari, J. Xu, A. I. McKay, C. Guerrin, C. Forsyth, H. Z. Ma, L. G. Richard A. J. O'Hair, A. Bonnefont, L. Ruhlmann, S. Aloise, C. Ritchie, A Photo-Switchable Molecular Capsule: Sequential Photoinduced Processes, *Chem. Sci.*, **2022**, 13, 13732-13740