POM-BASICS Summer School

"Polyoxometalate Chemistry for Fundamentals and Applications"

La Rochelle-France, June 13-15th 2022

Session 2- Redox properties of POMs

Fundamentals aspects of POMs reduction and properties of reduced POMs

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Abstract of the course:

Type-I polyoxometalates are reducible through successive and reversible electron transfers. We will illustrate how high tuning of the redox potentials is achieved by combined effects of the molecular structure type (Keggin, Dawson..), the nature of the metal addenda (W/Mo/V) or of the heteroatom, the whole POM charge, the nature of the counter cations (in particular H^+), the solvent…. The redox behavior of POMs has been thoroughly investigated by electrochemistry and general trends have been drawn.

Theoretical calculations have allowed to rationalize the experimental data, to comment on the minor structural reorganization generally observed upon reduction and to give further insights about the mechanism of delocalization of the injected electrons. The course will also address the properties of reduced POMs and the extent of electron delocalization in these mixed valence species as inferred from spectroscopic studies (ESR, UV-vis-NIR and NMR).

We will finally present examples of highly reduced POMs and to finish with some perspectives, we will very briefly introduce fields of application relying on the redox activity of POMs (catalysis, electronic devices and energy storage or conversion).