CENTER FOR SELF-ASSEMBLED CHEMICAL STRUCTURES – SEMINAR

WEDNESDAY SEPTEMBER 17, 12:30 – 1:30PM, ROOM 217

SUPRAMOLECULAR CHEMISTRY WITH POLYOXOMETALATES

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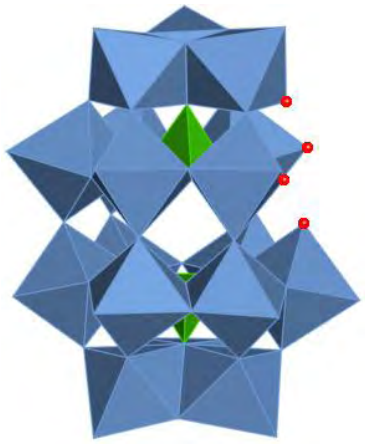
Polyoxometalates (POMs) are well established polymetallic molecules with applications in many areas of chemistry. This presentation will focus on classic polyoxotungstates (Dawson and Keggin structures) to illustrate new synthetic methodology and applications based on supramolecular interactions with these nanosized clusters.



$[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$

$[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ can be used as ligand for lanthanide ions. We have shown that such complexes are useful catalysts in organic transformations that require Lewis acids. New variations of the catalytically active metal ion allowed the tuning of the reactivity, maintaining the selectivity and recyclability of the catalyst. $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ and its derivatives are chiral compounds, that have never been optically resolved. We tackled this problem by the study of hydrogen bonds with enantiomerically pure organic ligands.

In a second approach, we have optimized the reactions of amines, alcohols or thiols with a carboxylic acid in the organic side chain of functionalized POMs by an unprecedented intramolecular activation. Click chemistry on functionalized POMs was also developped to couple them with a variety of organic molecules. The combination of this covalent strategy together with the study of hydrogen bonds to organic ligands allowed finally the optical resolution of the chiral POM.

These compounds together with other classic POMs are nanomolar non-competitive inhibitors of protein kinase CK2. A thorough study with this enzyme of medical importance (cancer treatment) reveals the potential POM binding site to be outside the substrate binding site, and indicates a particular stabilization of POMs towards hydrolysis in the presence of proteins. Thus, the supramolecular interactions of POMs with proteins open the way to more active and more selective CK2 inhibitors.

Key references:

[1] R. Prudent, V. Moucadel, B. Laudet, C. Barette, L. Lafanechere, B. Hasenknopf, J. Li, S. Bareyt, E. Lacote, S. Thorimbert, M. Malacria, P. Gouzerh, C. Cochet, *Chem Biol,* **2008**, *15*, 683-692.
Identification of polyoxometalates as nanomolar noncompetitive inhibitors of protein kinase CK2

[2] C. Boglio, K. Micoine, E. Derat, R. Thouvenot, B. Hasenknopf, S. Thorimbert, E. Lacote, M. Malacria, *J. Am. Chem. Soc.*, **2008**, *130*, 4553-4561.
Regioselective Activation of Oxo Ligands in Functionalized Dawson Polyoxotungstates

[3] C. Boglio, G. Lemiere, B. Hasenknopf, S. Thorimbert, E. Lacôte, M. Malacria, *Angew. Chem., Int. Ed.,* **2006**, *45*, 3324-3327.
Lanthanide complexes of the monovacant Dawson polyoxotungstate [alpha$_1$-P$_2$W$_{17}$O$_{61}$]$^{10-}$ as selective and recoverable Lewis acid catalysts