# Mastering the chaotropic effect from the templated synthesis to the design of hierarchical supramolecular core-shell

Emmanuel Cadot and Coll.
Institut Lavoisier de Versailles, CNRS, UVSQ, Université Paris-Saclay, Versailles, France
Contact : emmanuel.cadot@uvsq.fr

Controlling the assembly processes at the sub-nanometer scale offers opportunities for tailoring multi-component systems with emergent and collective properties. As polyoxometalate molecular systems exhibit promising perspectives for electrochemical or photochemical applications due to their remarkable capacities of electrons storage, their integration within devices remains still problematic. In context, the use of the supramolecular concepts appears highly appealing for the simplicity of implementation through non-covalent interactions which govern strength, dynamic and specificity of the resulting assembly. However, better understanding of the molecular interactions is critical, especially those arising from the hydration shell of the POM solute in aqueous solution.

Using γ-cyclodextrin as non-ionic substrate, we show in selected examples that the molecular recognition process is directly governed by the hydration properties of the ions. For instances, along the Keggin-type series, the stability constant of the POM-CD complex varies from 0 to $10^5$ as the charge of the ion decreases from -6 to -3 (see Figure). Such a behavior, driven from the chaotropic nature of the POM opens new avenues for mastering supramolecular POM assemblies. In this presentation, we highlight how the chaotropic effect may:

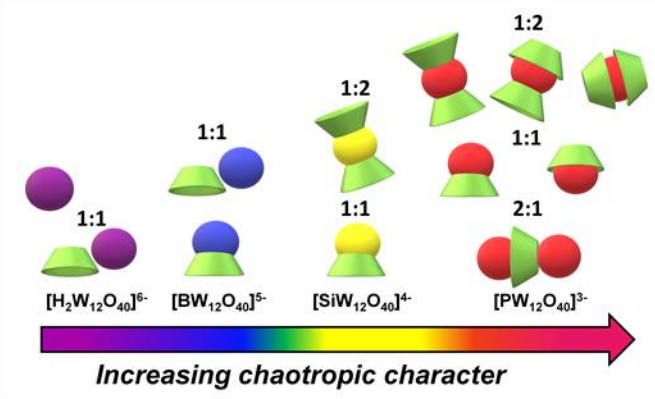


Illustration of the most representative binding modes involved in the supramolecular assemblies built from γ-CD (green tore) and Keggin anions (colored sphere).

1- Alter the redox properties of the POM species;
2- Modify the speciation diagram of molybdates or tungstates in aqueous solution;
3- Control the self-assembly process of the Mo-blue ring-shaped anion;
4- Be involved to design multicomponent chemical systems.

In conclusion, we will discuss about the location of POM species within the Hofmeister series, thus revealing their extreme chaotropic nature compared to the classical thiocyanate ion.