

*Supramolecular chemistry of polyoxometalates: from small clusters to giant keplerates*

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In "Inorganic Supramolecular Chemistry", the self-assembly through metal coordination has shown remarkable potential for the construction of well-defined architectures. The use of supramolecular interactions in the creation of new types of functional materials with desired physical properties is a challenging task in contemporary crystal engineering research. In the course of our supramolecular research, we have been working towards the construction of supramolecular functional systems of potential applications. This talk includes diverse supramolecular aspects of polyoxometalate (POM) chemistry under following headings: the co-existence of crown ethers and POM cluster anions, in which it will be demonstrated that POM cluster anions play an important role in stabilizing unusual supramolecular structures; [1] bringing other metal-macrocyclic systems into POM matrices to demonstrate the influence of POM cluster anion on the properties of metal-macrocyclic coordination complexes; how a POM cluster influences chiral separation through spontaneous resolution (chiral crystallization); [2] metallomacrocyclic formation in a POM matrix. Subsequently, the linking propensity of some well-defined POM clusters to obtain metal-oxide based new materials will be discussed including the role of Keggin-type heteropolyanion in the self assembly of metal phosphonate architectures. Finally, a giant Keplerate type POM system will be described in a crystal engineering story of how an amorphous nano-material goes to its crystalline state in a mechanochemical solid to solid transformation. [3]

[1] Shivaiah, V & Das, S. K. (2006), *Angew. Chem. Int. Ed.* 45, 245-248.

[2] Sarma, M. et al. (2012), *Dalton Trans.* 41, 1862-1866.

[3] Mekala, R. et al. (2016), *Inorg. Chem.* 55, 12504–12507.

**Keywords:** [Polyoxometalates](#), [Supramolecular chemistry](#), [Solid to solid transformation](#)