Polyoxometalates (POMs) are discrete nuclearities of transition metals (Mo, V, W and Nb) at high oxidation states (+6, +5, +4) which bridge the gap between mononuclear oxo/hydroxometalates and polymeric metallic oxides with appropriate charge to ionic radius ratio and prohibit infinite polymerization by forming n-bonds with oxo groups [1,2]. In this context, Perchloromolybdate POM's has been synthesized and fully characterized both in solid state and aqueous solution structurally and compositionally. Hierarchical self-assembly ensues in emergence of such clusters through a sequence of complex interdependent pathways of reactions; whose principles and practical limits are still much left to be understood. Here, we present in-situ Cl- oxidation mediated ClMo12O40- formation. Such an 8 e- redox process with fast, reversible multi-electron redox transformation under rather mild conditions still remain unexplored with POMs and can serve a great deal in understanding systems like Photosystem II [3]. Such a strategy of in-situ chloride oxidation and contributions of perchlorate in the self-assembly of higher nuclearity cluster will be presented.


**Keywords:** Polyoxometalate single crystal, Chloride oxidation, Self-assembly