

Designing Electronically Active Metal Oxide Host-Guest Clusters

Leroy (Lee) Cronin*

School of Chemistry, WestCHEM, The University of Glasgow, Glasgow, G12 8QQ
web: www.croninlab.com email: Lee.Cronin@Glasgow.ac.uk

Polyoxometalate cluster capsules comprise a metal-oxide cage with internal 'dopants' or templates which not only determine the physical properties of the cluster, but increasingly has been found to control the range and connectivity of the building blocks.[1] Amongst the structural diversity of HPOMs architectures, $[M_{12}O_{36}(XO_4)]^{n-}$ and Wells-Dawson (WD) [2] anions $[M_{18}O_{54}(XO_4)_2]^{m-}$ form a basic set of extensively reviewed geometries which encapsulate tetrahedral heteroanions such as $[SO_4]^{2-}$, $[PO_4]^{3-}$, etc. In general, POMs exhibit significant stability for both the oxidized and one-electron reduced form and the electrochemistry of HPOMs has been extensively studied. In this respect, in an effort to tune the redox properties of POMs, we have been able to engineer clusters that incorporate redox-active anions and expand the classic WD family.[3-5] Building on this fundamental understanding we have been using theory, synthesis, modelling, and spectroscopy to both understand, control, and develop a range of new devices, see Scheme. In this talk I will describe our approach as well as highlighting some fundamental new aspects of these molecules[6-8].

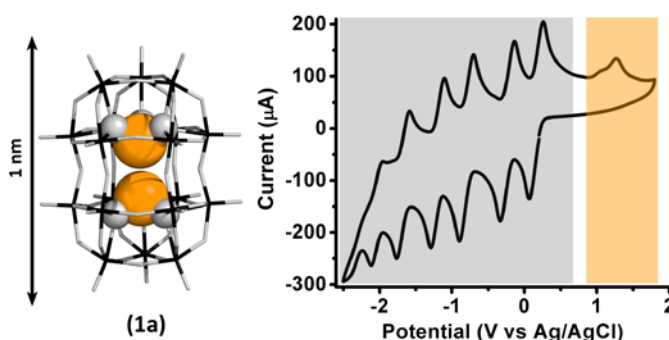


Figure 1 Structure of a $\{W_{18}O_{54}\}$ capsule with two embedded $[SeO_3]^{2-}$ anions on the left and the picture of the CV on the right.

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