Bridging the gap between solution and solid state studies in Polyoxometalate chemistry: Discovery of a family of $[V_1M_{17}]$ -based cages encapsulating two $\{V^VO_4\}$ moieties

Haralampos N. Miras,^a De-Liang Long,^a Paul Kögerler^b and Leroy Cronin^{*a}

^a University of Glasgow, Department of Chemistry, Joseph Black Building, University Avenue, Glasgow, G12 8QQ,, United Kingdom. E-mail:

L.Cronin@chem.gla.ac.uk

^b Institut für Anorganische Chemie RWTH Aachen D-52074 Aachen, Germany

Redox Titrations

(1) Compound 1 Na₄(NH₄)₂H₂W₁₇V₃O₆₂, mass used =200 mg Oxidant = 0.01 M Ce^{IV} in 0.5 M of sulphuric acid solution Theoretical amount of oxidant for one electron reduced species in mL: 4.33 Experimental amount required: 4.78



Figure S1. Redox titration of Compound 1

(2) Compound **3** TEAH₆H₂Mo₁₇V₃O₆₂, mass used =200 mg Oxidant = 0.01 M Ce^{IV} in 0.5 M of sulphuric acid solution Theoretical amount of oxidant for one electron reduced species in mL: 5.23 Experimental amount required: 5.90



Figure S2. Redox titration of Compound **2a** with TEAH cations (for solubility in water)