

Supplementary information

Voltammetric behavior of 1- and 4-[S₂VW₁₇O₆₂]⁵⁻ in acidified acetonitrile

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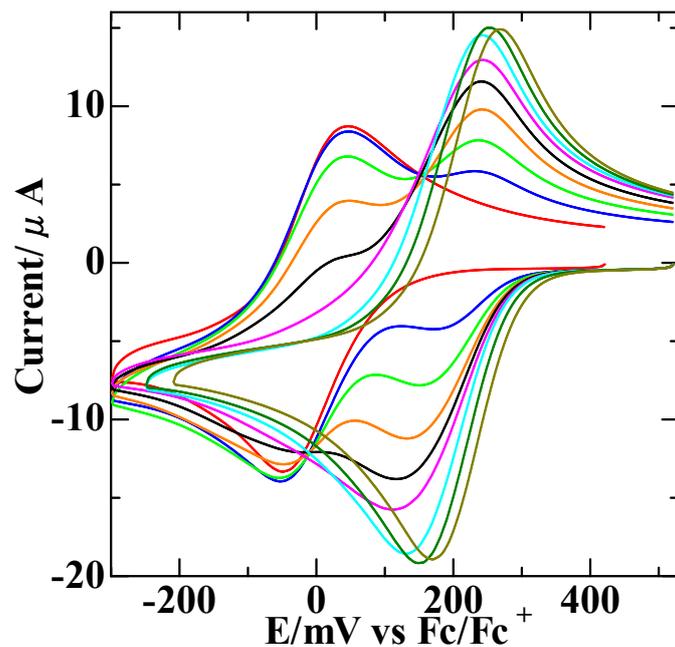


Figure S1 Cyclic voltammograms of 1mM 4-S₂V^VW₁₇ in CH₃CN (0.1 M [n-Bu₄N][PF₆]) after addition of the following concentrations of CF₃SO₃H. [CF₃SO₃H]/mM = (—) 0; (—) 0.2; (—) 0.4; (—) 0.6; (—) 0.8; (—) 1.0; (—) 2.0; (—) 4.0; (—) 10.0. Scan rate: 100 mV s⁻¹.

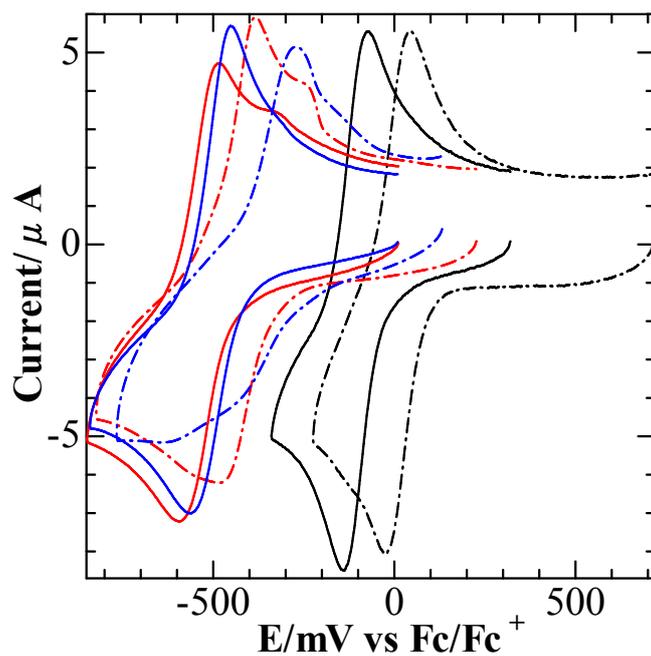


Figure S2 Cyclic voltammograms of (—) 1-S₂V^VW₁₇, (-•-•-) 4-S₂V^VW₁₇, (—) 1-P₂V^VW₁₇, (-•-•-) 4-P₂V^VW₁₇, (—) 1-As₂V^VW₁₇ and (-•-•-) 4-As₂V^VW₁₇ in CH₃CN (0.1 M [n-Bu₄N][PF₆]). Those for 1- and 4-X₂V^VW₁₇ (X=P, As) were obtained after neutralization of the proton in the cation.

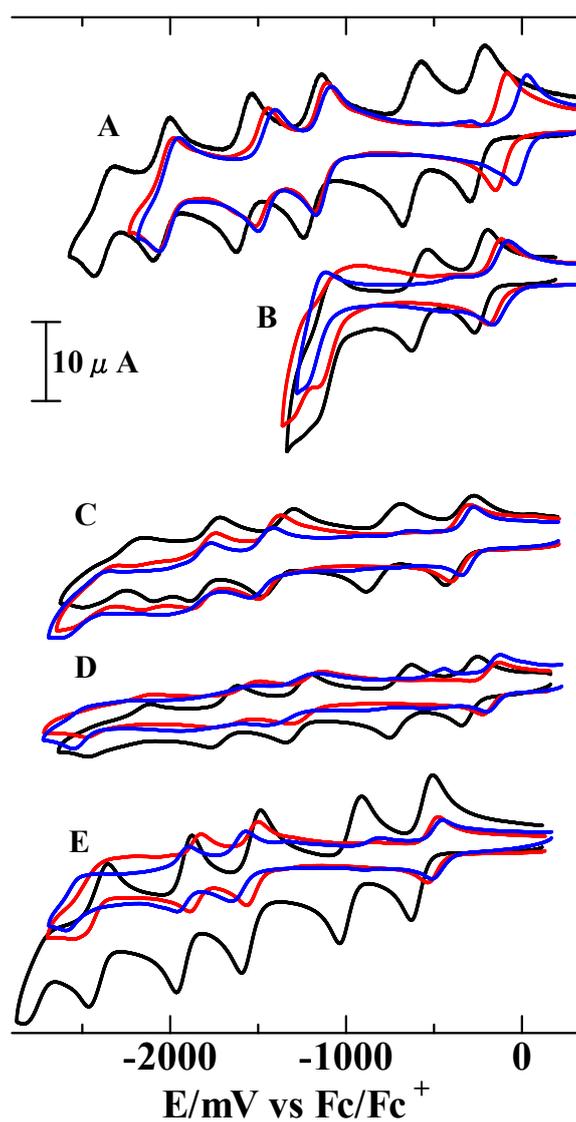


Figure S3 Cyclic voltammograms of (—) 1-S₂V^VW₁₇, (—) 4-S₂V^VW₁₇ and (—) S₂W₁₈ in (A) acetonitrile, (B) nitromethane, (C) DMF, (D) DMSO and (E) acetone containing 0.1 M [n-Bu₄N][PF₆] as the supporting electrolyte. Scan rate: 100mV s⁻¹.

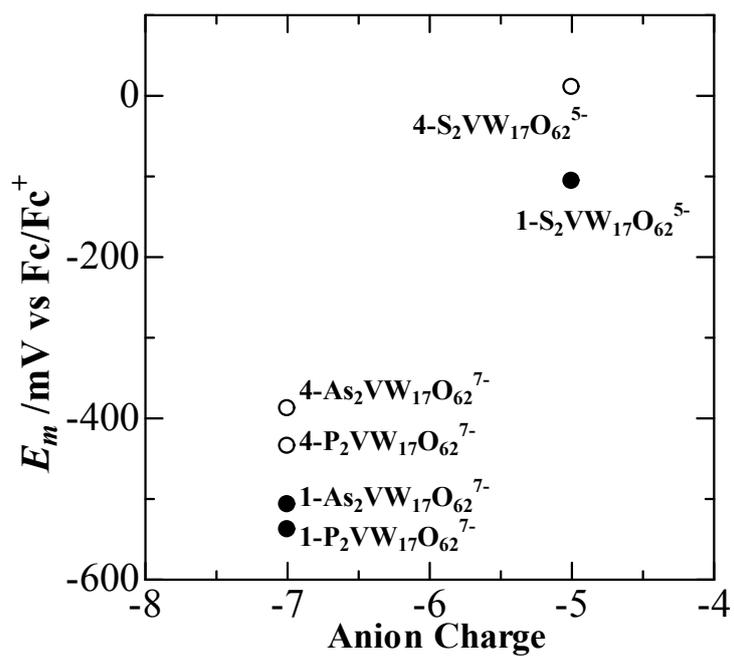


Figure S4 Plot of E_m values for the $V^{V/IV}$ redox process and anion charge of Wells-Dawson type vanadium-substituted polyoxometalates.