Supporting information for

Electrochemical Probing of the Photoreduction of Molybdenum and Tungsten Dawson-type Polyoxometalates in Molecular and Ionic Liquid Media Using Water as an Electron Donor

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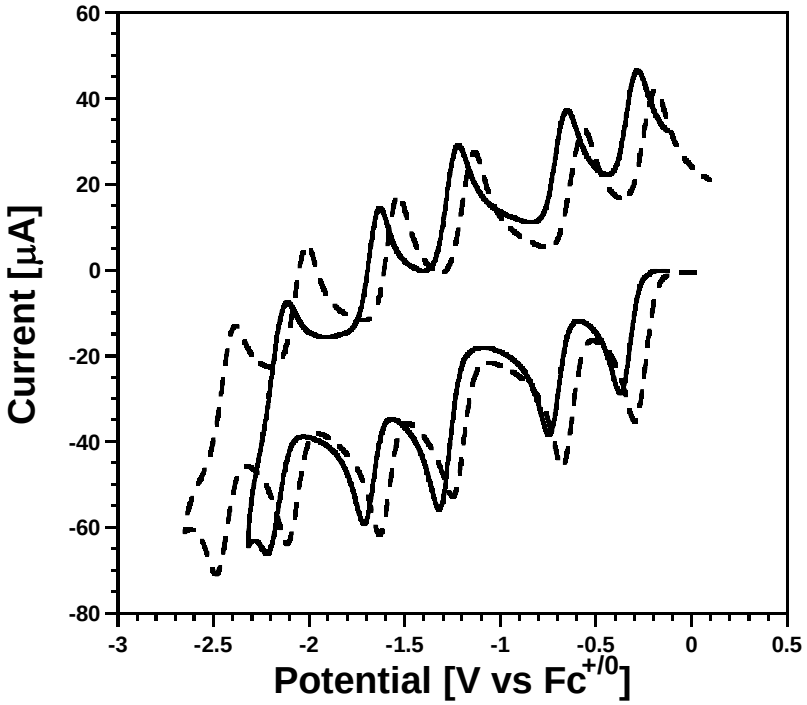


Figure S1 Cyclic voltammograms at a glassy carbon electrode (v = 0.1 V s^{-1}) for 0.4 mM $[S_2W_{18}O_{62}]^{4-}$ in (---) dry CH_3CN and in (—) dry CH_2Cl_2/CH_3CN (80 : 20) containing 0.1 M Bu_4NClO_4 as the supporting electrolyte.

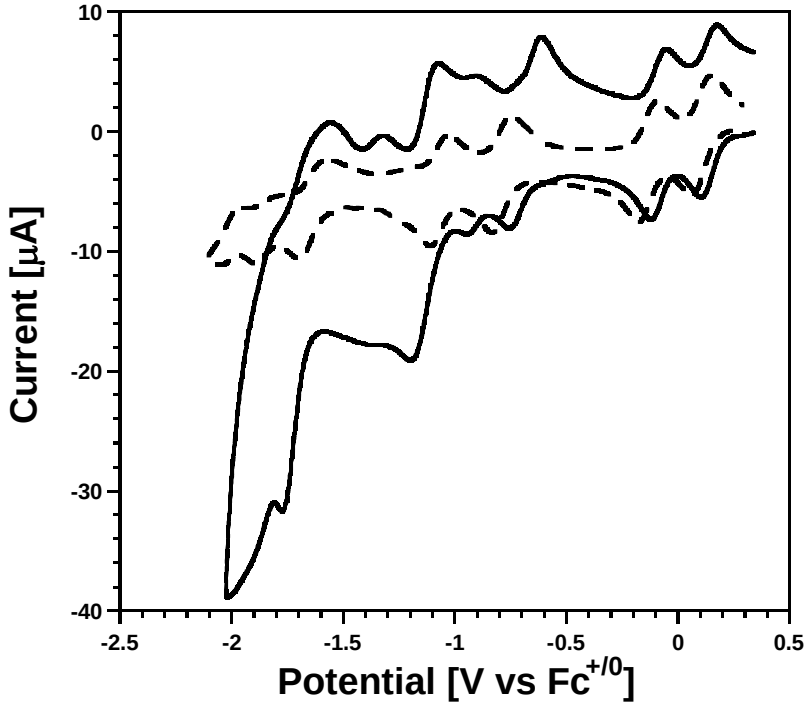


Figure S2 Cyclic voltammograms at a glassy carbon electrode (v = 0.1 V s^{-1}) for 0.4 mM $[S_2Mo_{18}O_{62}]^{4-}$ in (---) dry CH_3CN and in (—)CH_3CN solution containing 0.8 mM water and 0.1 M Bu_4NClO_4 as the supporting electrolyte.

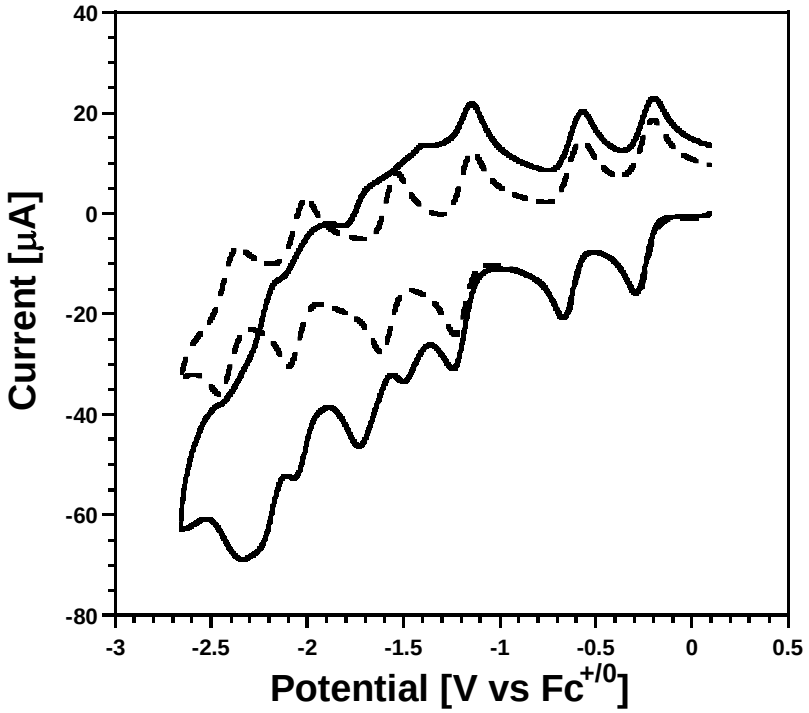


Figure S3 Cyclic voltammograms at a glassy carbon electrode (v = 0.1 V s^{-1}) for 0.3 mM $[S_2W_{18}O_{62}]^{4-}$ in CH_3CN (0.1 M Bu_4NClO_4) before (---) and after addition (—) of 50 mM triflic acid.

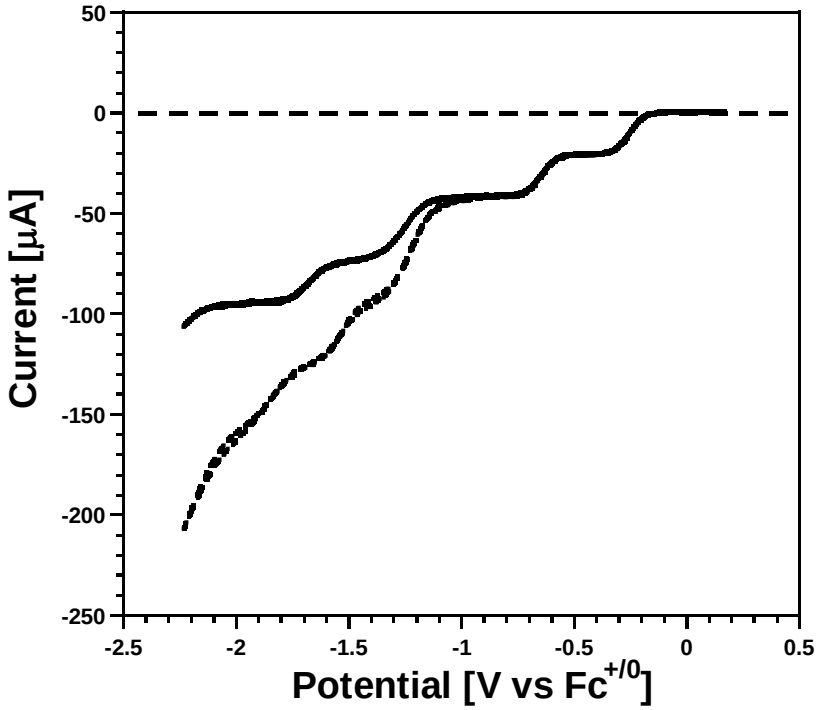


Figure S4 RDE voltammograms at a glassy carbon electrode (ω = 1790 rpm, v = 0.01 V s^{-1}) for 0.3 mM $[S_2W_{18}O_{62}]^{4-}$ in CH_3CN (0.1 M Bu_4NClO_4) before(—) and after (---) addition of 50 mM glacial acetic acid.

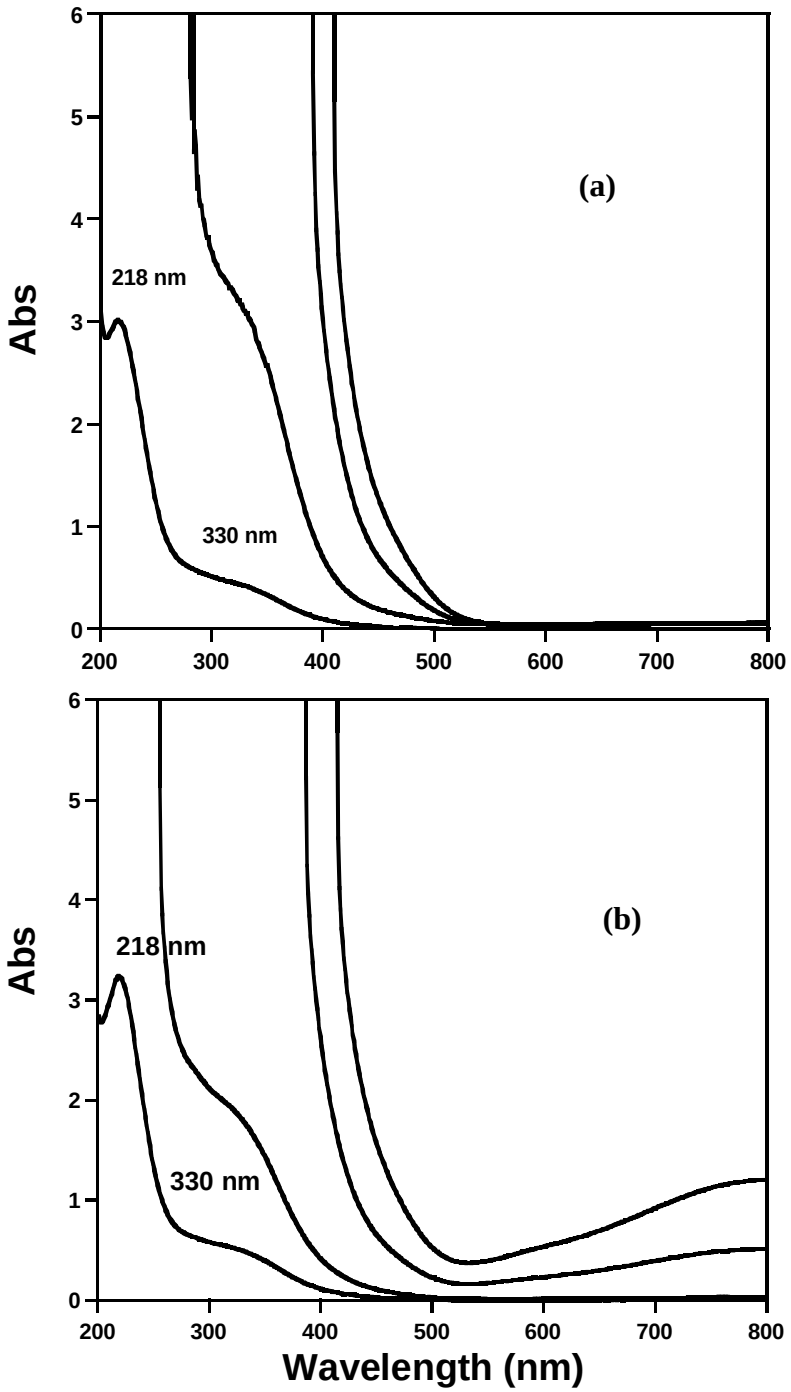
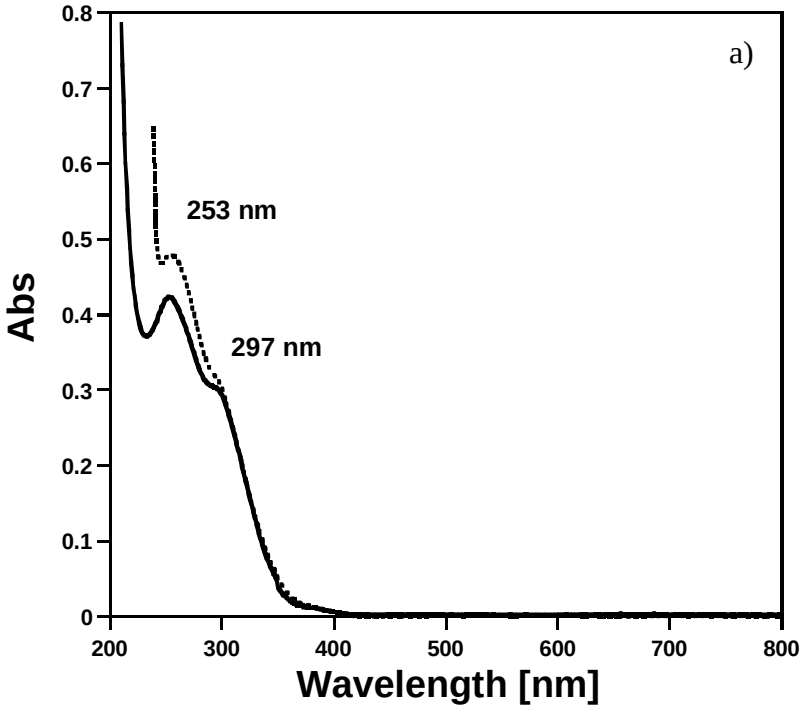
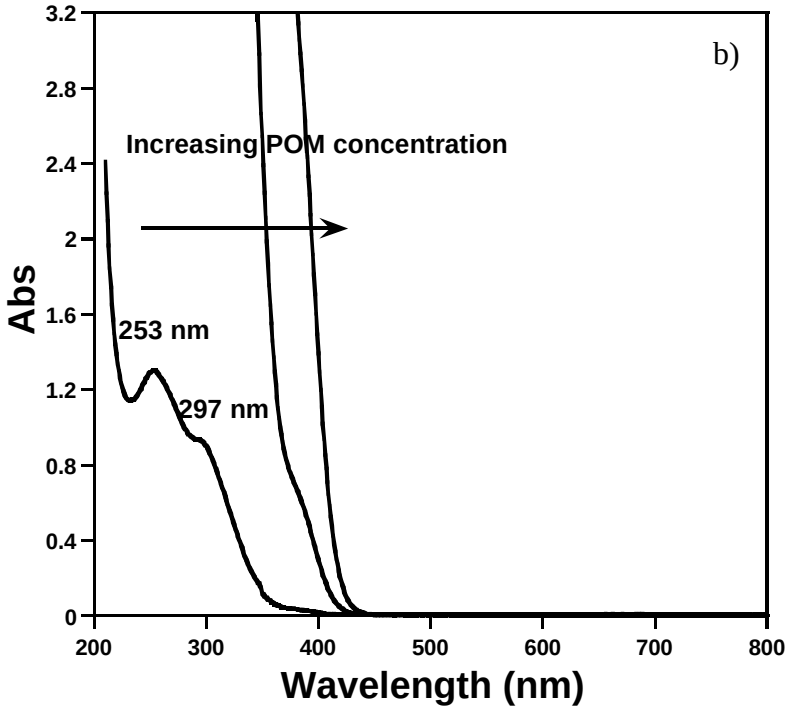


Figure S5 UV-vis spectra in CH_3CN (0.1 M Bu_4NClO_4) for (a) 0.02, 0.06, 0.1 and 0.2 mM $[S_2Mo_{18}O_{62}]^{4-}$ (no absorbance is found in the visible region for λ > 520 nm) and (b) as for (a) but after a one-electron bulk electrolysis showing that $[S_2Mo_{18}O_{62}]^{5-}$ absorbs light in the visible region at λ > 520 nm.





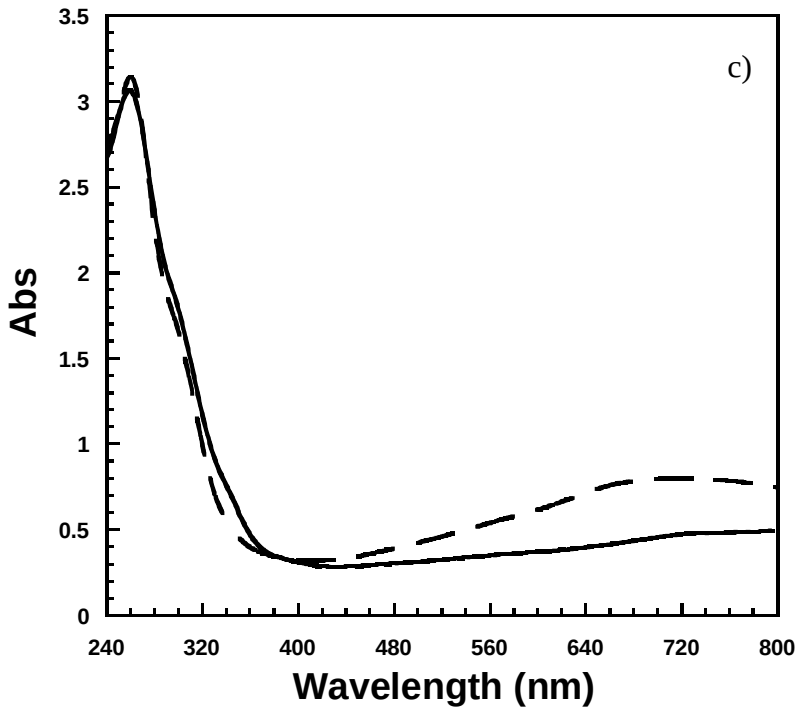


Figure S6 UV-visible spectra for (a) 0.01 mM $[S_2W_{18}O_{62}]^{4-/5-/6-}$in (—) CH_3CN (0.1M $Bu_4N\ ClO_4$) and (---) [Bmim][PF_6], (b) $[S_2W_{18}O_{62}]^{4-}$ in CH_3CN (0.1M Bu_4NClO_4) at concentrations of 0.03 to 2 mM, (c) after bulk electrolysis of 0.02 mM $[S_2W_{18}O_{62}]^{4-}$ in CH_3CN (0.1 M Bu_4NClO_4) to generate the one (—) $[S_2W_{18}O_{62}]^{5-}$ and two (---) $[S_2W_{18}O_{62}]^{6}$ electron reduced species.