Supporting information

Determination of α-Keggin structure of $[GeW_{11}O_{39}Ru^{III}(H_2O)]^{5-}$. Reaction of mono-ruthenium-substituted Keggin-type germanotungstate $[GeW_{11}O_{39}Ru^{III}(H_2O)]^{5-}$ with dimethyl sulfoxide to form $[GeW_{11}O_{39}Ru^{III}(dmso)]^{5-}$ and its structural characterization.

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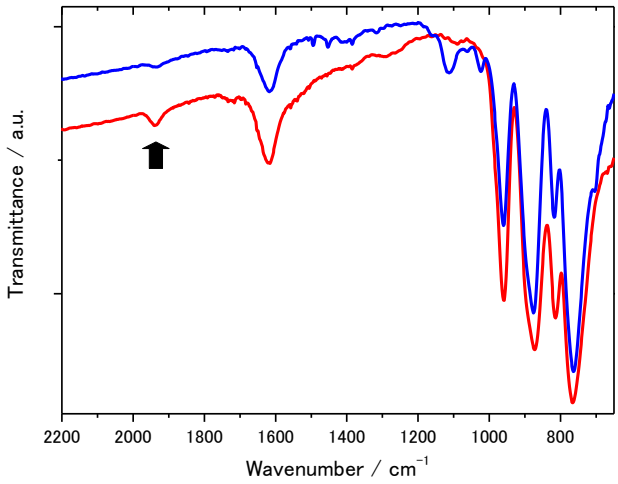

Figure S1. IR spectra of (blue line) $[GeW_{11}O_{39}Ru^{III}(dmso)]^{5-}$ (**2**) and (blue line) $[GeW_{11}O_{39}Ru^{III}(H_2O)]^{5-}$ (**1**). The black arrow indicates the peaks corresponding to the CO ligand bound to Ru^{II}.

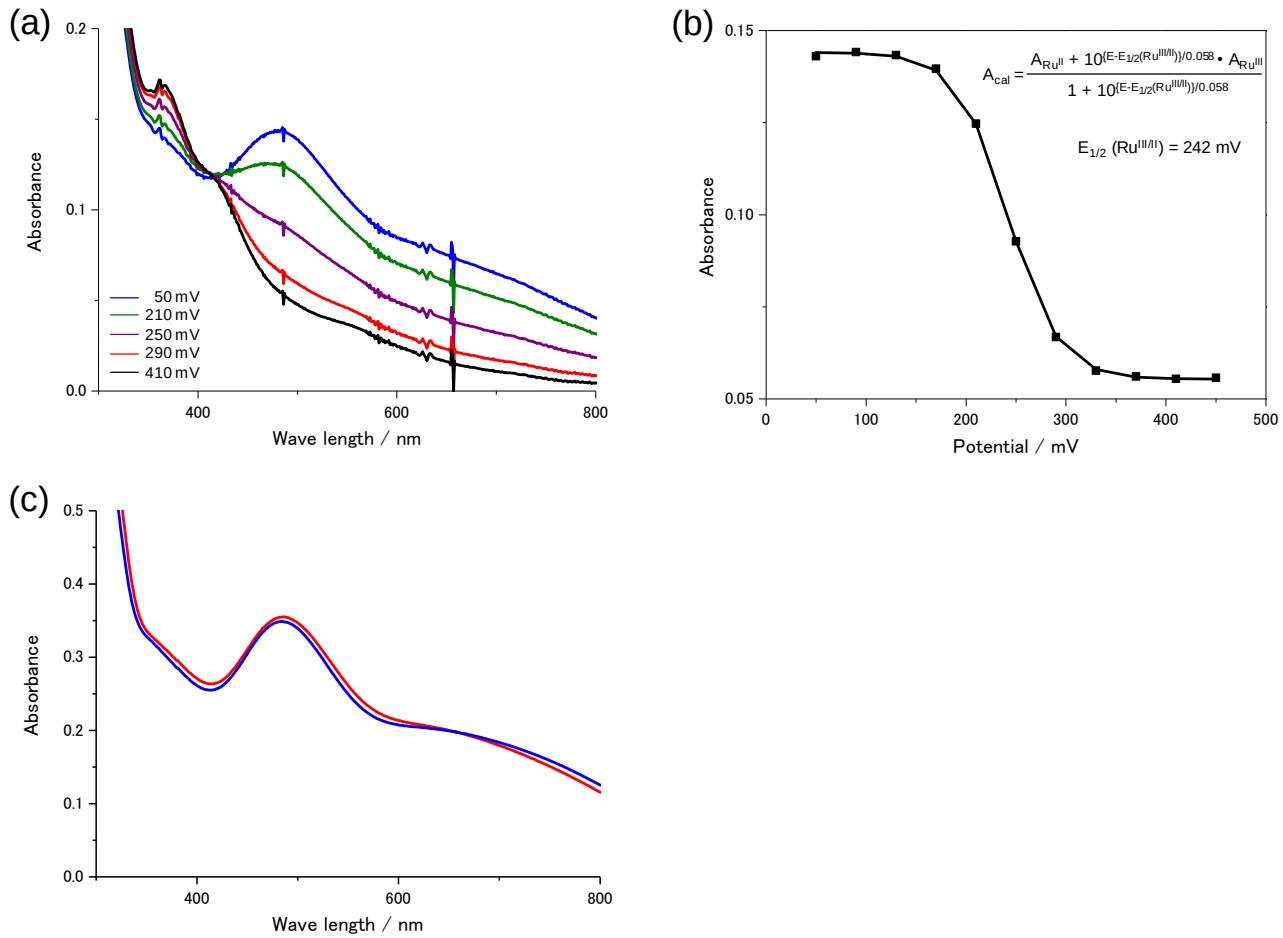

Figure S2. (a) UV-Vis spectra measured at different electrode potentials during the redox of **2** in 0.5 M KH_2PO_4 (pH 4.3). Cell length was 0.5 mm. (b) Changes in absorbance of UV-Vis spectra at 480 nm against applied voltage. Closed square and solid line indicated the observed and calculated values, respectively. (c) UV-Vis spectra of one-electron-reduced species of (red) **2** and (blue) $[SiW_{11}O_{39}Ru^{III}(dmso)]^{5-}$ (ca. 6 mg) by adding ascorbic acid (10 eq.) in D_2O (0.6 mL). Cell length was 0.5 mm.

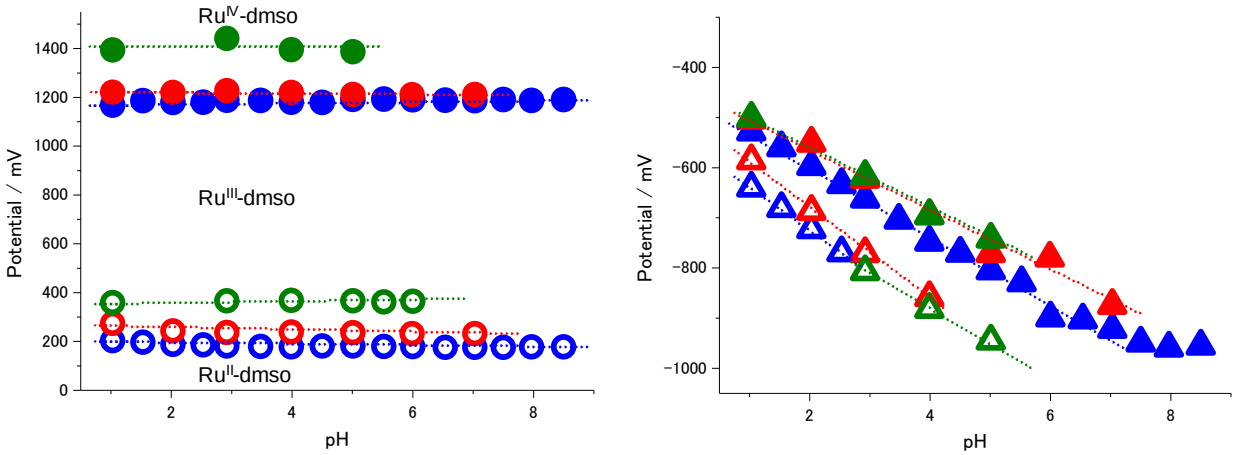

Figure S3. pH dependence on redox potentials $E_{1/2}$ for (red) **2**, (blue) $[SiW_{11}O_{39}Ru^{III}(dmso)]^{5-}$ and (green) $[PW_{11}O_{39}Ru^{III}(dmso)]^{4-}$. Closed circle, open circle, closed triangle and open triangle indicate redox potentials of $Ru^{IV/III}$, $Ru^{III/II}$, the first 2-electron reduction and the second 2-electron reduction, respectively.

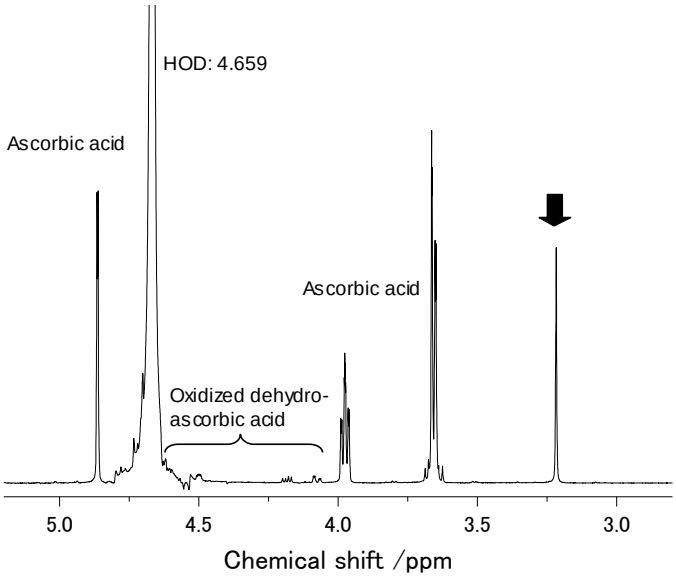

Figure S4. ^{1}H-NMR spectrum of the $[SiW_{11}O_{39}Ru^{III}(dmso)]^{5-}$ after reduction using ascorbic acid. The black arrow indicates a peak corresponding to the proton of the methyl group of dmso coordinated to Ru^{II}.