Supporting Information

Hydrothermal and Solid-state Transformation of Ruthenium-supported Keggin-type Heteropolytungstates $[XW_{11}O_{39}\{Ru(II)(benzene)(H_2O)\}]^{n-}$ (X = P (n = 5), Si (n = 6), Ge (n = 6)) to Ruthenium-substituted Keggin-type Heteropolytungstates.

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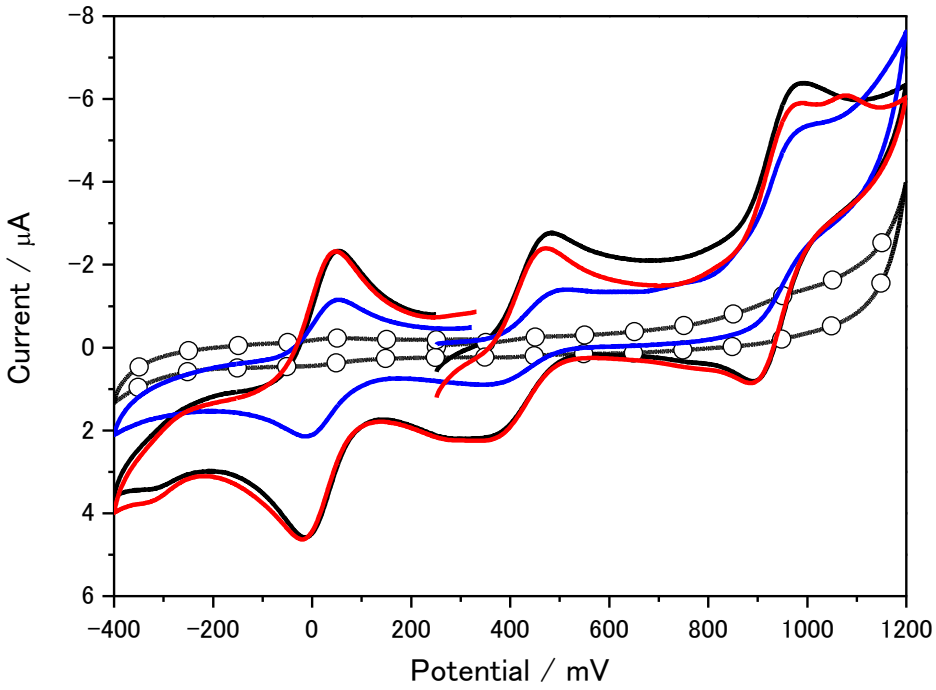


Figure S1. Cyclic voltammograms of reaction solutions obtained by reaction of $K_7[PW_{11}O_{39}]$ and $[Ru(benzene)Cl_2]_2$ at (red line) 215 ºC, (black line) 170 ºC, (blue line) 150 ºC and (solid line with open circles) 100 ºC for 5 hours. The reaction mixture (0.1 ml) was dissolved in 0.526 M KH_2PO_4 (1.9 ml) (pH ca. 4.3).

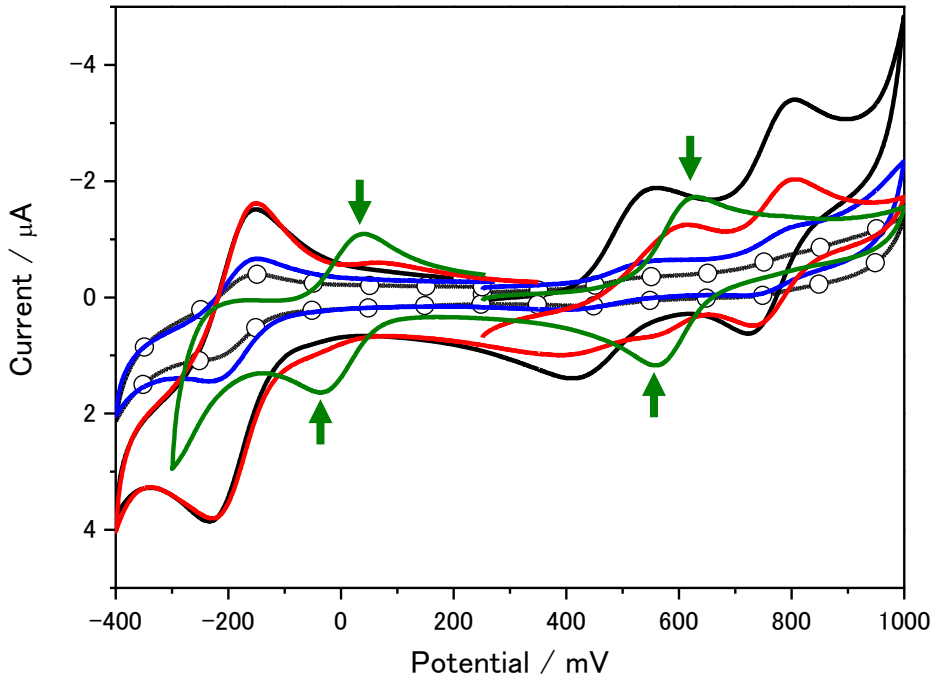


Figure S2. Cyclic voltammograms of reaction solutions obtained by reaction of $K_8[SiW_{11}O_{39}]$ and $[Ru(benzene)Cl_2]_2$ at (red line) 215 ºC, (black line) 170 ºC, (blue line) 150 ºC and (solid line with open circles) 100 ºC for 5 hours. The reaction mixture (0.1 ml) was dissolved in 0.526 M KH_2PO_4 (1.9 ml) (pH ca. 4.3). Green line is cyclic voltammogram of $[\{SiW_{11}O_{39}Ru(IV/III)\}_2O]^{11-}$ (**3b**) (0.45 mM) in 0.5 M KH_2PO_4 (pH 4.3). Arrows indicate peaks corresponding to redox peaks of **3b**.

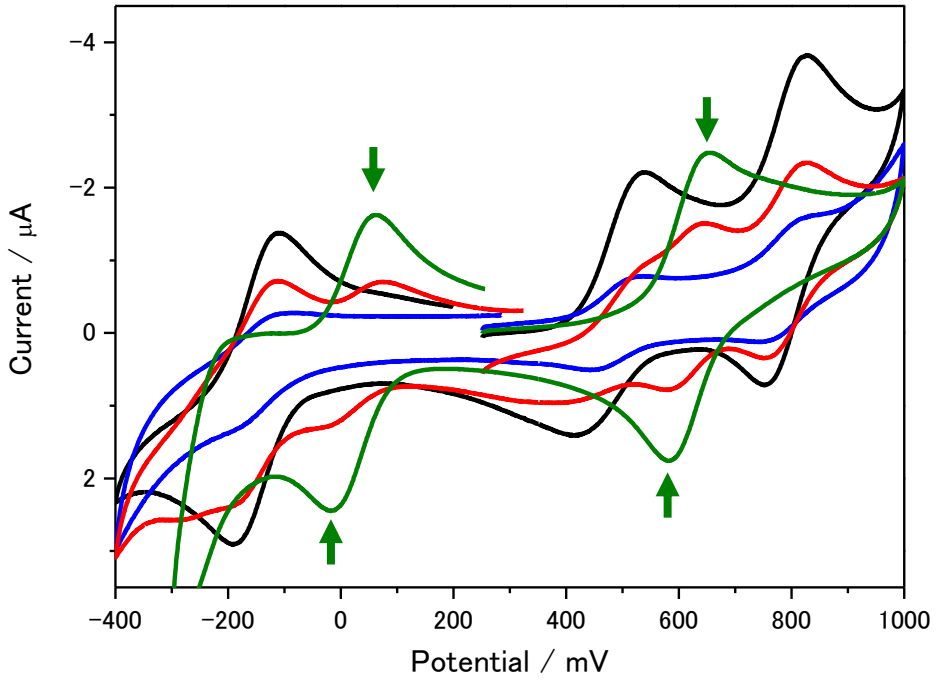


Figure S3. Cyclic voltammograms of reaction solutions obtained by reaction of $K_8[GeW_{11}O_{39}]$ and $[Ru(benzene)Cl_2]_2$ at (red line) 215 ºC, (black line) 170 ºC and (blue line) 150 ºC for 5 hours. The reaction mixture (0.1 ml) was dissolved in 0.526 M KH_2PO_4 (1.9 ml) (pH ca. 4.3). Green line is cyclic voltammogram of $[\{GeW_{11}O_{39}Ru(IV/III)\}_2O]^{11-}$ (**3c**) (0.45 mM) in 0.5 M KH_2PO_4 (pH 4.3). Arrows indicate peaks corresponding to redox peaks of **3c**.

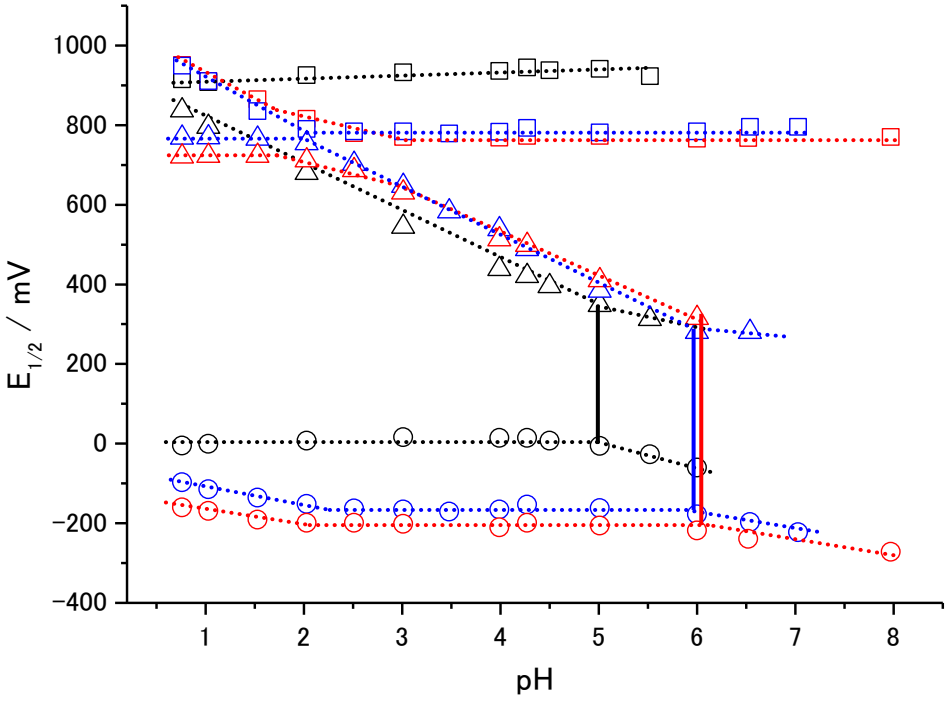
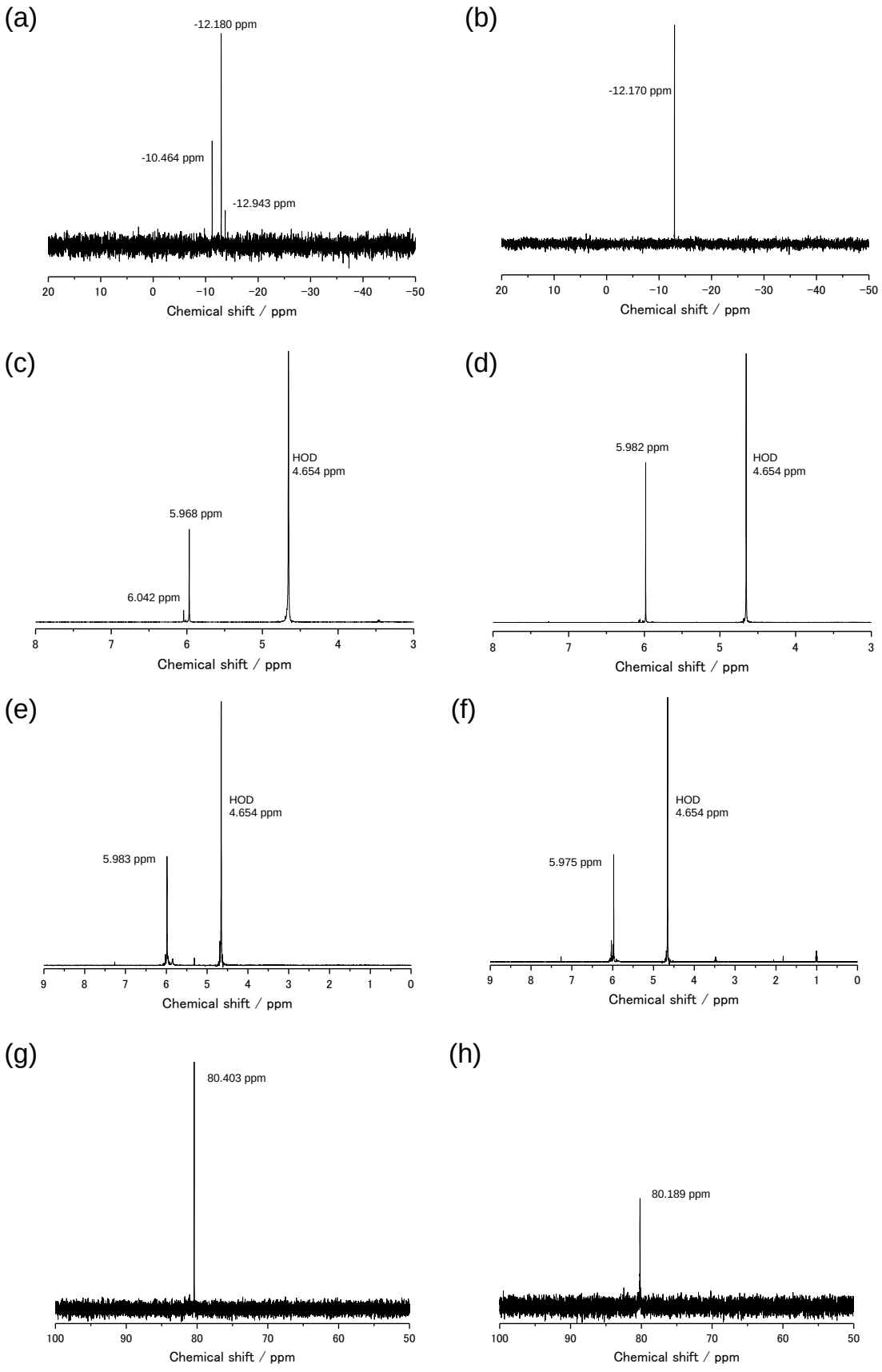


Figure S4. pH dependence on redox potentials $E_{1/2}$ (Pourbaix diagram) for (black) **1a**, (red) **1b** and (blue) **1c**. Squares, triangles and circles indicate redox potentials of Ru(V/IV), Ru(IV/III) and Ru(III/II), respectively.



(i)

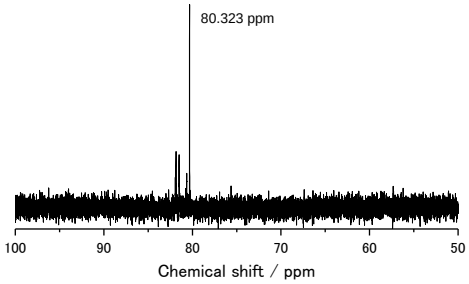


Figure S5. (a) ^{31}P-NMR and (c) ^{1}H-NMR of yellow solid obtained by a reaction of $[PW_{11}O_{39}]^{7-}$ and $[Ru(benzene)Cl_2]_2$ at 100 ºC for 5 hours. The solid was isolated by adding CsCl. (b) ^{31}P-NMR and (d) ^{1}H-NMR of $[PW_{11}O_{39}\{Ru(benzene)(H_2O)\}]^{5-}$ (**2a**) prepared at room temperature (Proust's group method, V. Artero, V. Lahootun, R. Villanneau, R. Thouvenot, P. Herson, P. Gouzerh and A. Proust, *Inorg. Chem.*, 2005, **44**, 2826-2835.). ^{1}H-NMR of (e) $[SiW_{11}O_{39}\{Ru(benzene)(H_2O)\}]^{6-}$ (**2b**) and (f) $[GeW_{11}O_{39}\{Ru(benzene)(H_2O)\}]^{6-}$ (**2c**) prepared at room temperature. ^{13}C-NMR of (g) **2a**, (h) **2b** and (i) **2c** prepared at room temperature.

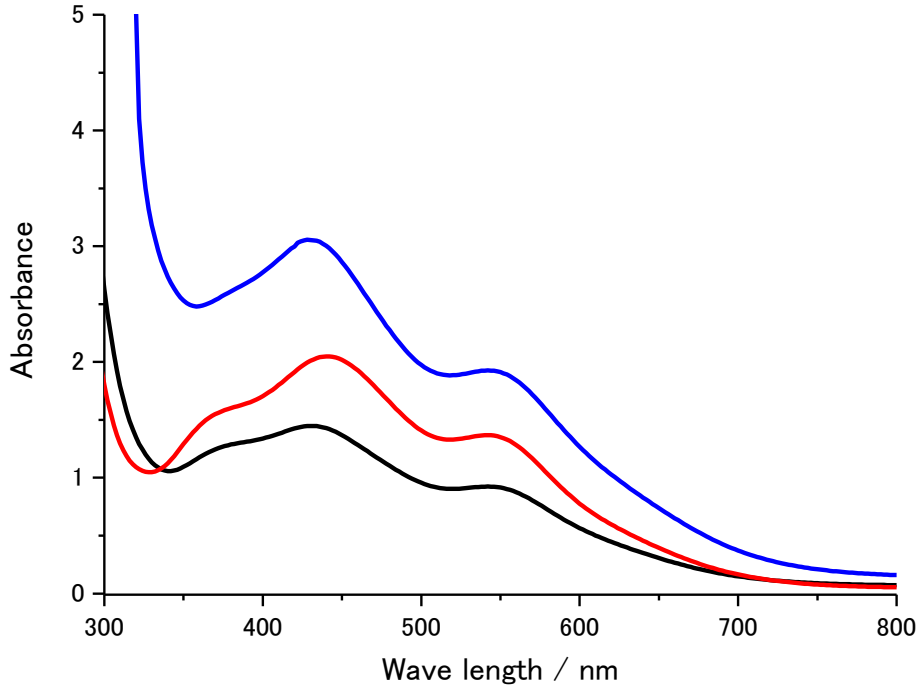


Figure S6. UV-Vis spectra of reaction solution obtained by reaction of (blue) $K_8[SiW_{11}O_{39}]$ or (black) $K_8[GeW_{11}O_{39}]$ with $[Ru(benzene)Cl_2]_2$ at 215 ºC for 5 hours. The reaction mixture (0.1 ml) was dissolved in 0.526 M KH_2PO_4 (1.9 ml) (pH ca. 4.3). Concentration of Ru is ca. 0.85 mM. Red line is UV-Vis spectrum of $[\{SiW_{11}O_{39}Ru(IV/III)\}_2O]^{11-}$ (**3b**) (0.18 mM) in 0.5 M KH_2PO_4.

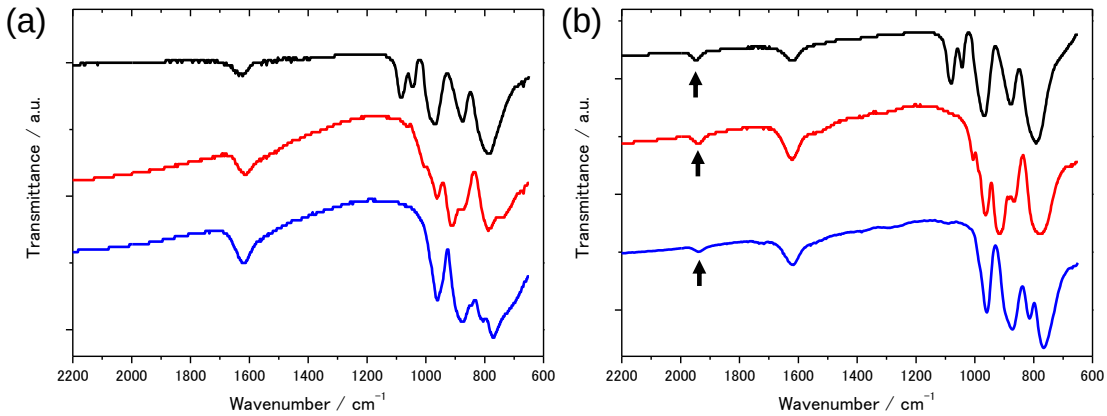


Figure S7. IR spectra of Ru-substituted heteropolytungstates produced by reactions of (black) $[PW_{11}O_{39}]^{7-}$, (red) $[SiW_{11}O_{39}]^{8-}$ or (blue) $[GeW_{11}O_{39}]^{8-}$ with (a) $[Ru(benzene)Cl_2]_2$ or (b) $Ru(acac)_3$ as a Ru source. Reaction temperature was 170 ºC and reaction time was 5 hours or 20 hours for reactions with $[Ru(benzene)Cl_2]_2$ or $Ru(acac)_3$, respectively. The solid was isolated by adding CsCl. Arrows in (b) indicate peaks corresponding to CO of $[PW_{11}O_{39}Ru(II)(CO)]^{5-}$, $[SiW_{11}O_{39}Ru(II)(CO)]^{6-}$ or $[GeW_{11}O_{39}Ru(II)(CO)]^{6-}$.

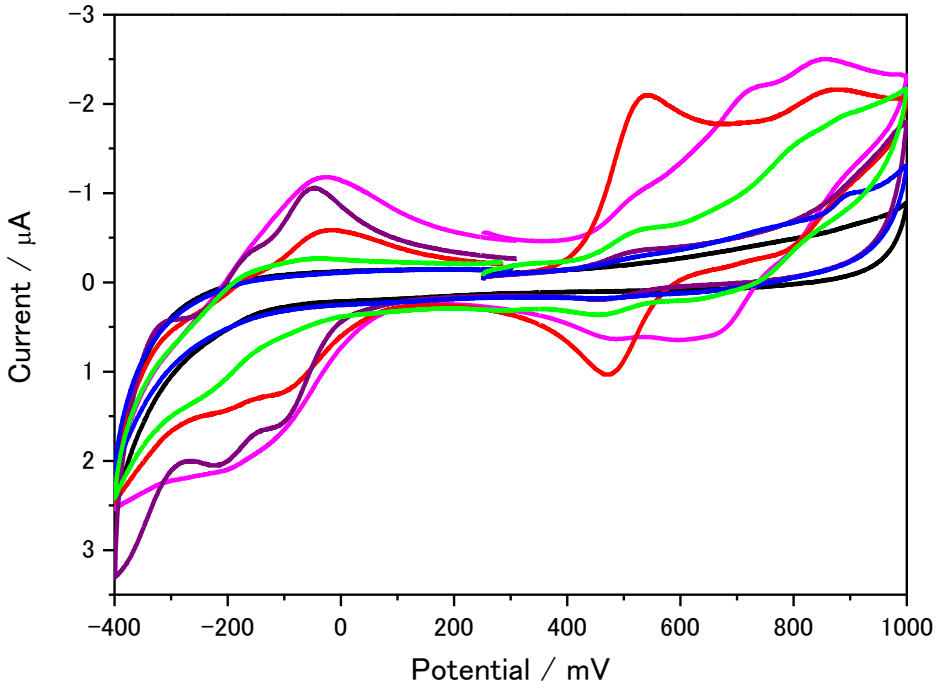


Figure S8. Cyclic voltammograms of the complex **2b** after calcination at (blue) 100 ºC, (green) 200 ºC, (pink) 400 ºC, (red) 450 ºC, (purple) 500 ºC and (black) 600 ºC. The sample was heated with a ramp of 5 ºC/min. CV was measured in 0.5 M KH_2PO_4 (pH 4.3).

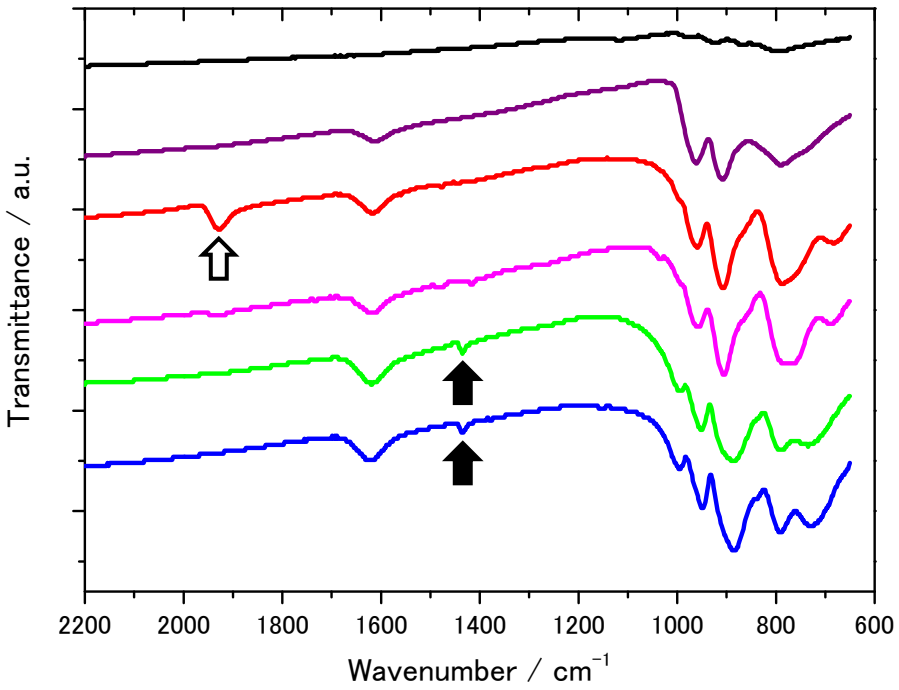


Figure S9. IR of the complex **2b** after calcination at (blue) 100 ºC, (green) 200 ºC, (pink) 400 ºC, (red) 450 ºC, (purple) 500 ºC and (black) 600 ºC. The sample was heated with a ramp of 5 ºC/min. The black arrow indicates the peak corresponding to benzene and the white arrow indicates the peak corresponding to CO coordinating to Ru(II).

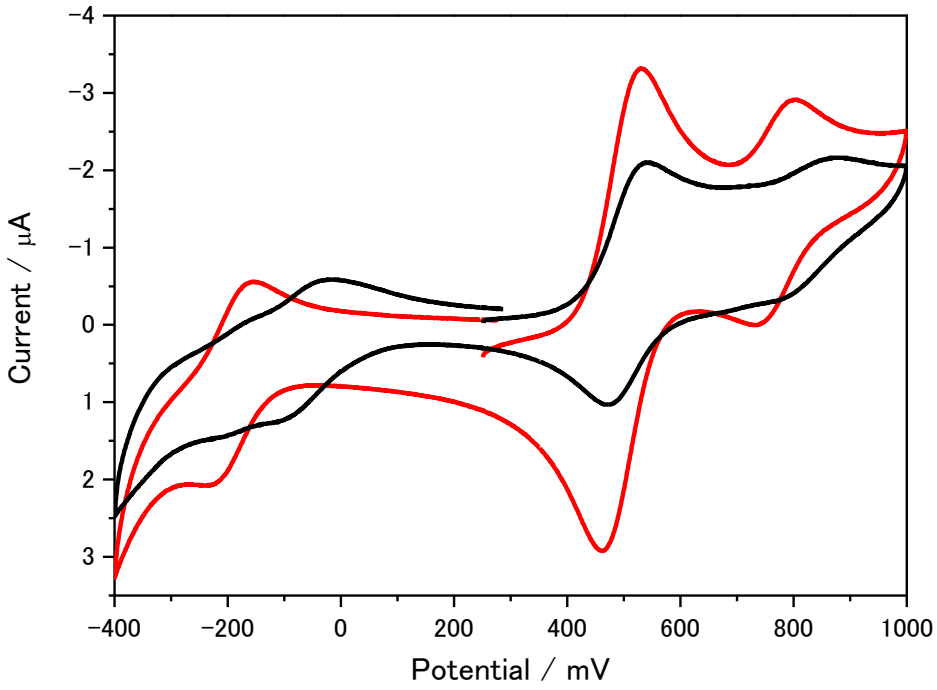


Figure S10. Cyclic voltammograms of sample obtained (black) after calcination of **2b** at 450 ºC and (red) after recrystallization of the calcined **2b** (450 ºC) from water.

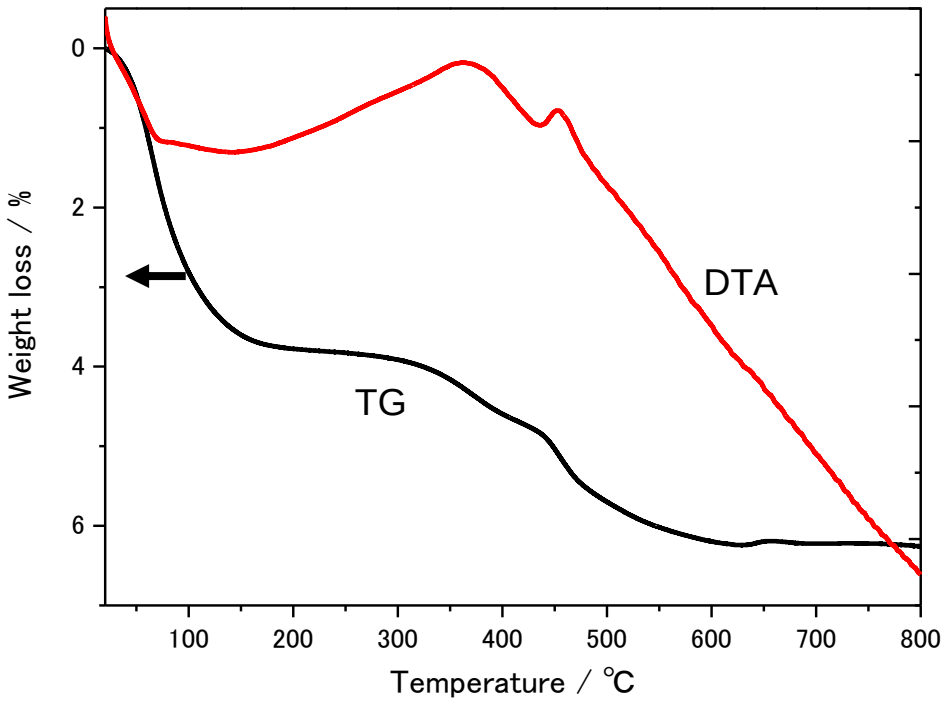


Figure S11. TG-DTA profile of **2a**.

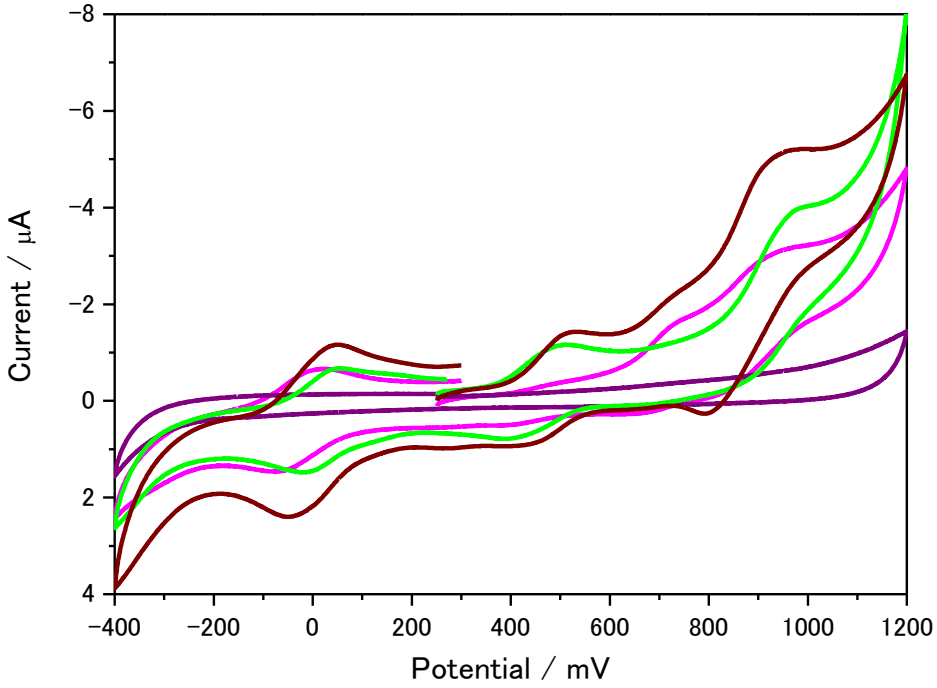


Figure S12. Cyclic voltammograms of the complex **2a** after calcination at (green) 200 ºC, (brown) 300 ºC, (pink) 400 ºC and (purple) 500 ºC. The sample was heated with a ramp of 5 ºC/min. CV was measured in 0.5 M KH_2PO_4 (pH 4.3).

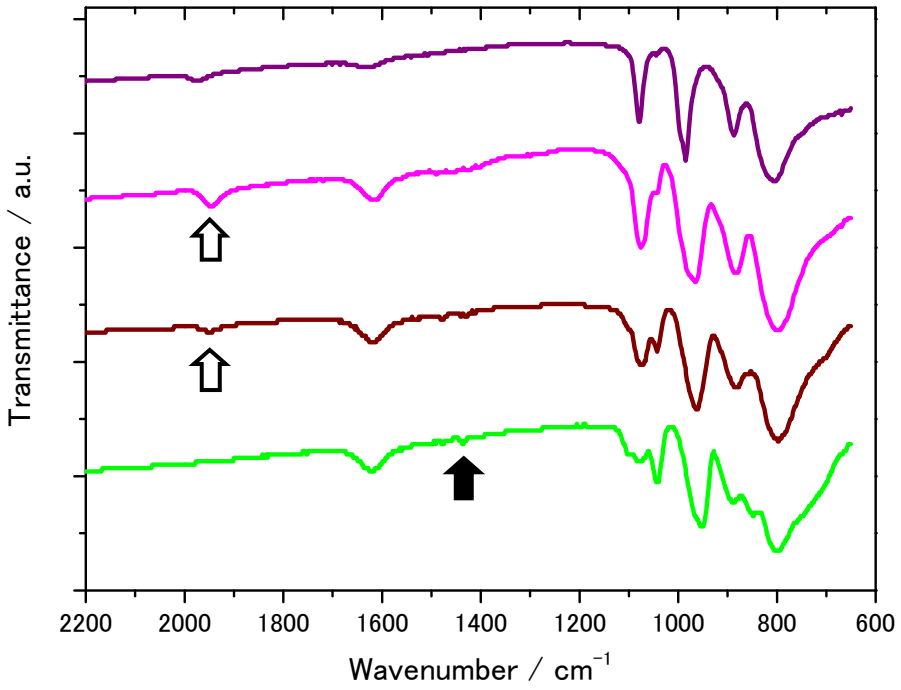


Figure S13. IR of the complex **2a** after calcination at (green) 200 ºC, (brown) 300 ºC, (pink) 400 ºC and (purple) 500 ºC. The sample was heated with a ramp of 5 ºC/min. The black arrow indicates the peak corresponding to benzene and the white arrow indicates the peak corresponding to CO coordinating to Ru(II).

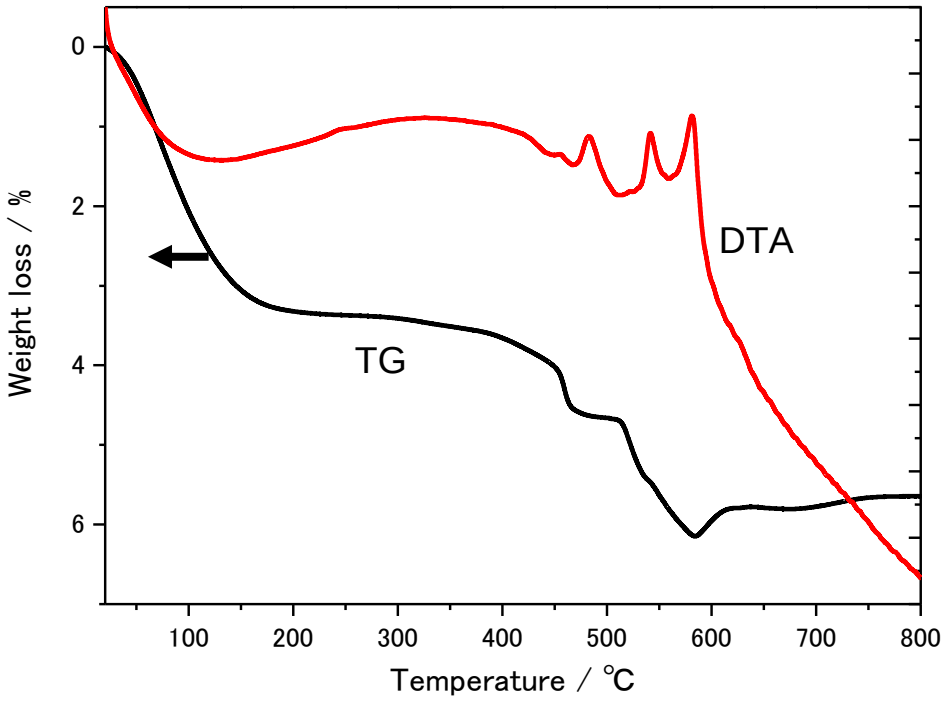


Figure S14. TG-DTA profile of **2c**.

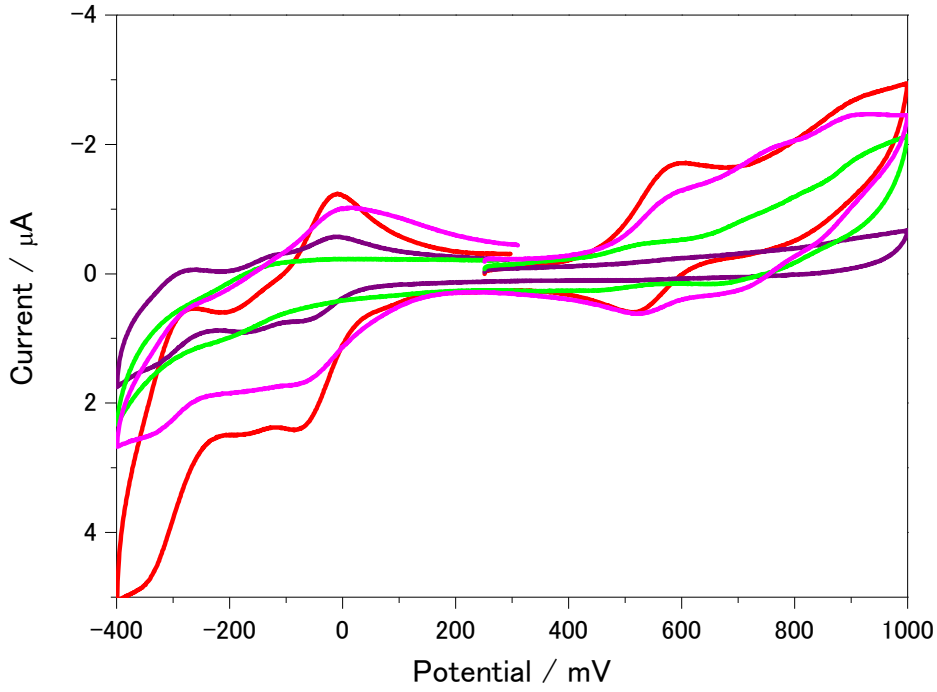


Figure S15. Cyclic voltammograms of the complex **2c** after calcination at (green) 200 ºC, (pink) 400 ºC, (red) 450 ºC and (purple) 500 ºC. The sample was heated with a ramp of 5 ºC/min. CV was measured in 0.5 M KH_2PO_4 (pH 4.3).

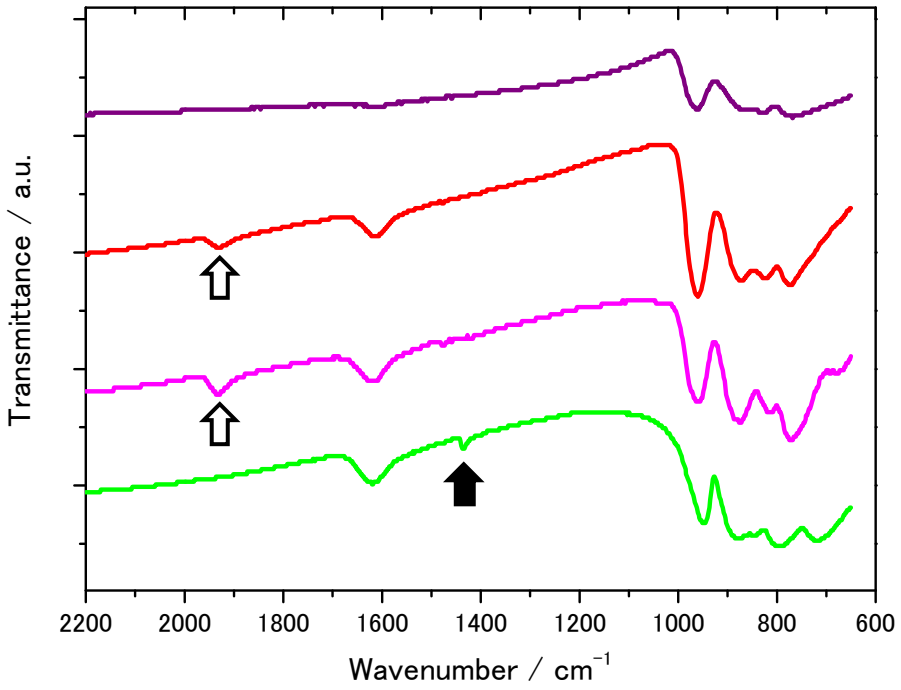


Figure S16. IR of the complex **2c** after calcination at (green) 200 ºC, (pink) 400 ºC, (red) 450 ºC and (purple) 500 ºC. The sample was heated with a ramp of 5 ºC/min. The black arrow indicates the peak corresponding to benzene and the white arrow indicates the peak corresponding to CO coordinating to Ru(II).