Electronic Supplementary Information for Dalton Transactions

Synthesis and Crystal Structure of the Pseudosandwich-Type Heteropolytungstates Functionalized by Organometallic Ruthenium(II)

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Figure S1. Combined polyhedral/ball and stick representation of the 2D structure of $KNa_6[(RuC_6H_6)AsW_9O_{34}]\cdot 17H_2O$ (**As-1**), and $Na_7[(RuC_6H_6)PW_9O_{34}]\cdot 14H_2O$ (**P-2**). The balls represent ruthenium (yellow), oxygen (red), sodium (blue) and carbon (gray). The AsO_4/PO_4 tetrahedron is green and the WO_6 octahedra are red. No hydrogens shown for clarity.

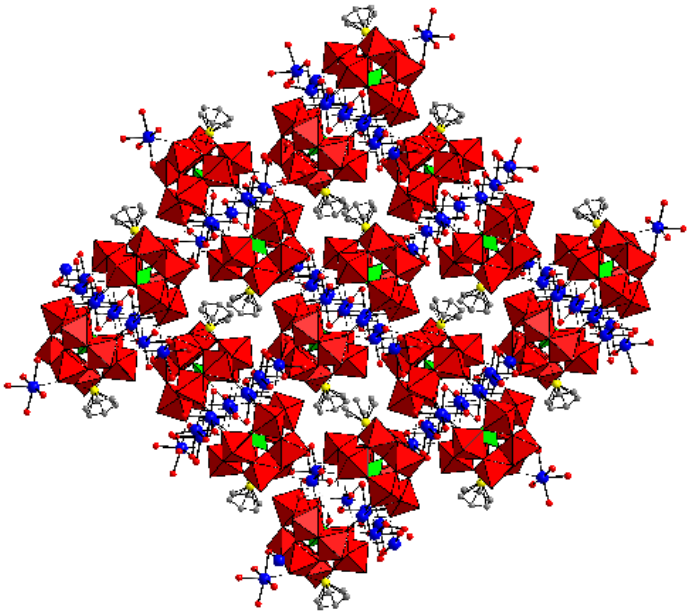


Figure S2. Combined polyhedral/ball and stick representation of the 3D structure of $KNa_6[(RuC_6H_6)AsW_9O_{34}]\cdot 17H_2O$ (**As-1**). The color code is same as in Figure S1. No hydrogens shown for clarity.

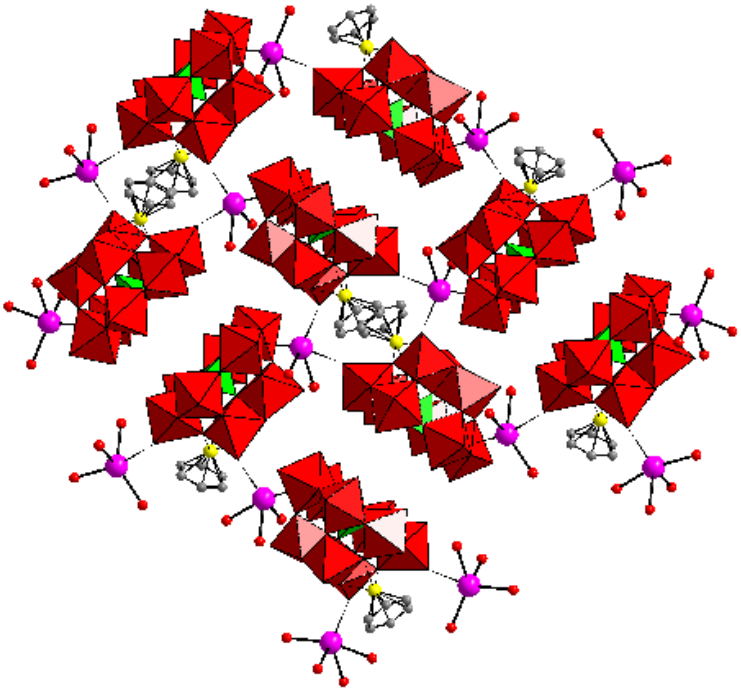


Figure S3. Combined polyhedral/ball and stick representation of the 3D structure of $Na_7[(RuC_6H_6)PW_9O_{34}]\cdot 14H_2O$ (**P-2**).

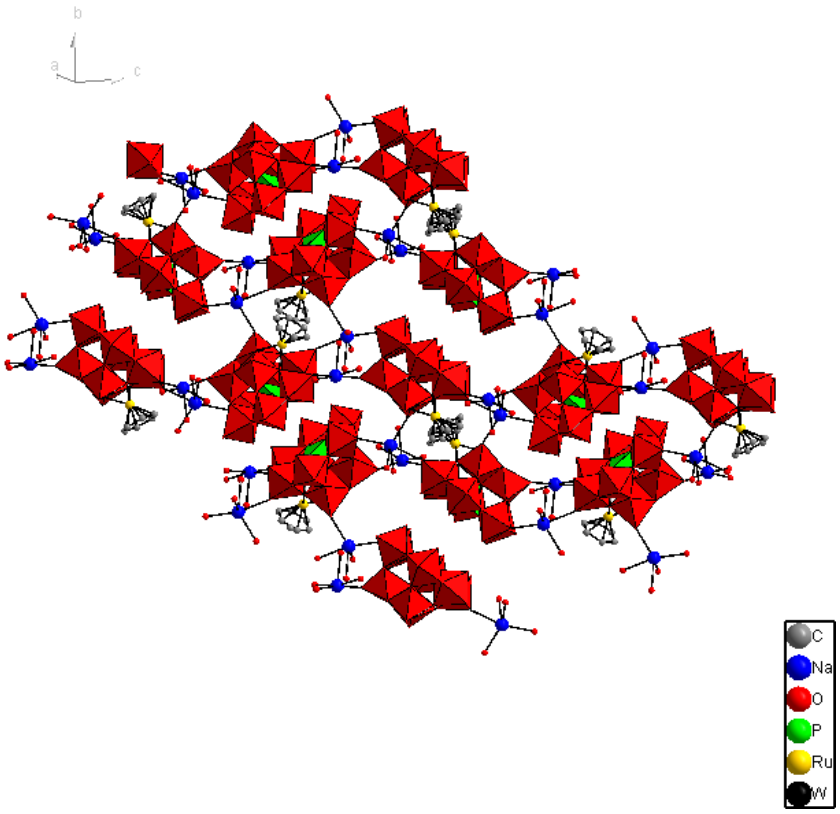


Figure S4. The TG curves for compounds **As-1** and **P-2**.

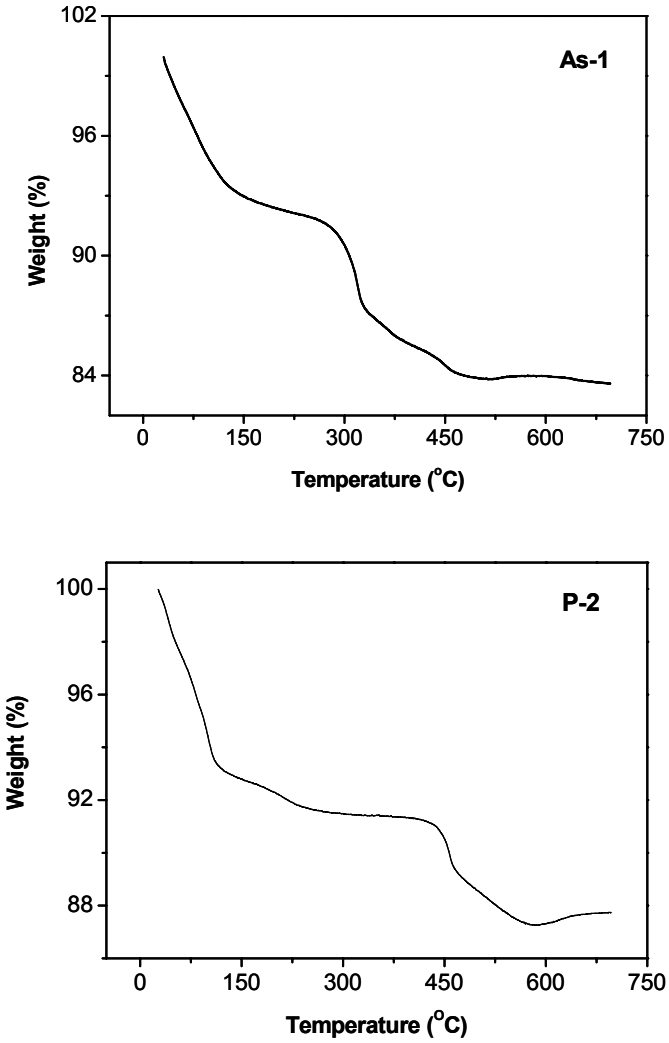


Figure S5. The simulative (red line) and experimental (black line) powder X-ray diffraction patterns for compounds **As-1** and **P-2.**

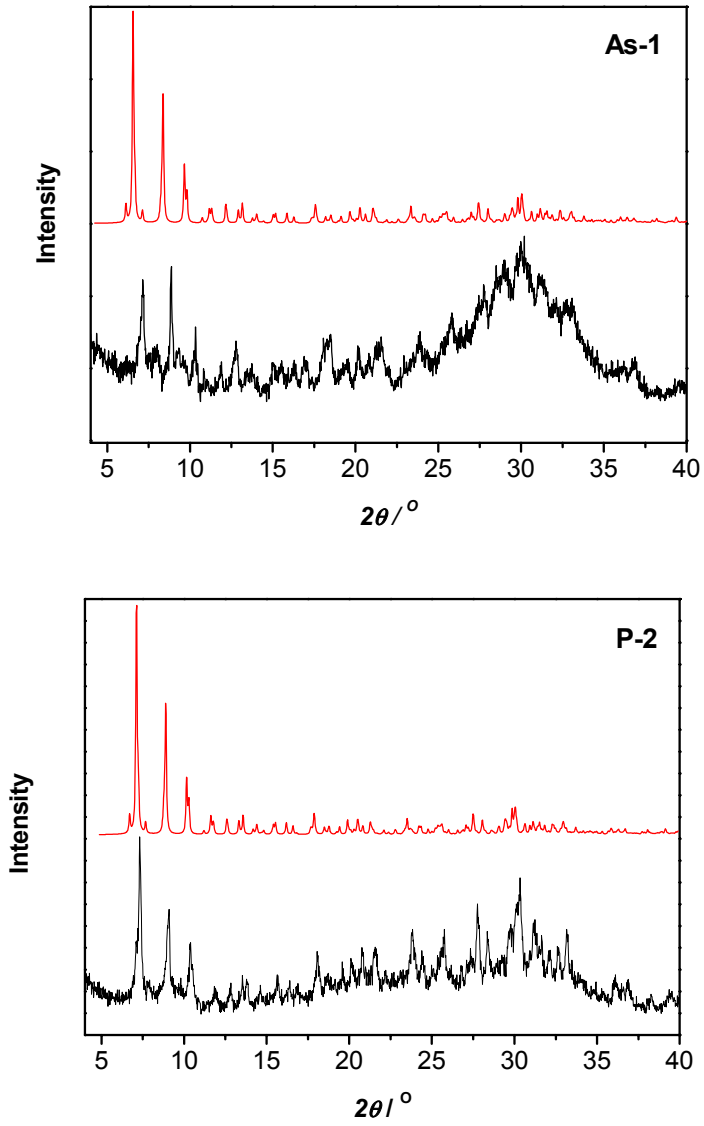
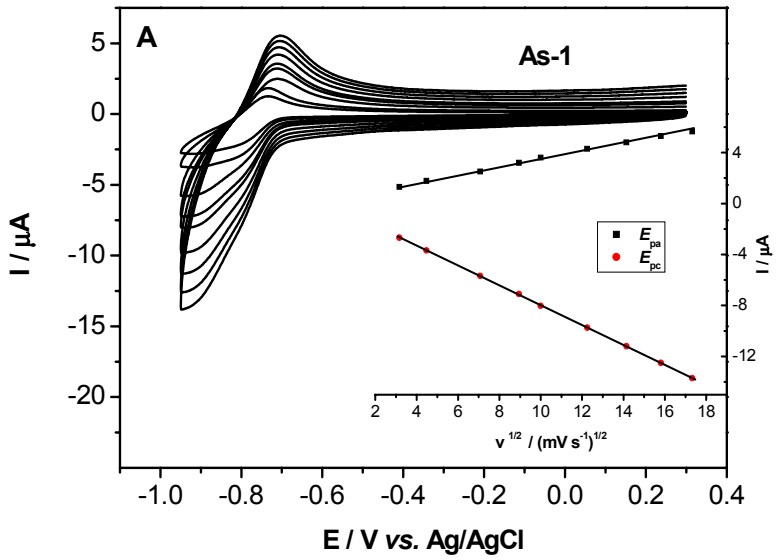


Figure S6. Cyclic voltammograms of $[(RuC_6H_6)XW_9O_{34}]^{7-}$ (X = As, **1;** P, **2**) in a pH 3 medium (1.0 M LiCl + HCl) at scan rates of 10, 20, 50, 80, 100, 150, 200, 250, and 300 mV· s^{-1}. The inset shows the relationship of the square roots of the scan rates *vs*. the oxidation peak currents of W and reduction peak currents of W. Polyanion concentration: 4.4×10^{-4} M. The scan rate was 50 mV · s^{-1}. The working electrode was glassy carbon, and the reference electrode was Ag/AgCl. (A) $[(RuC_6H_6)AsW_9O_{34}]^{7-}$ (**1**). (B) $[(RuC_6H_6)PW_9O_{34}]^{7-}$ (**2**).



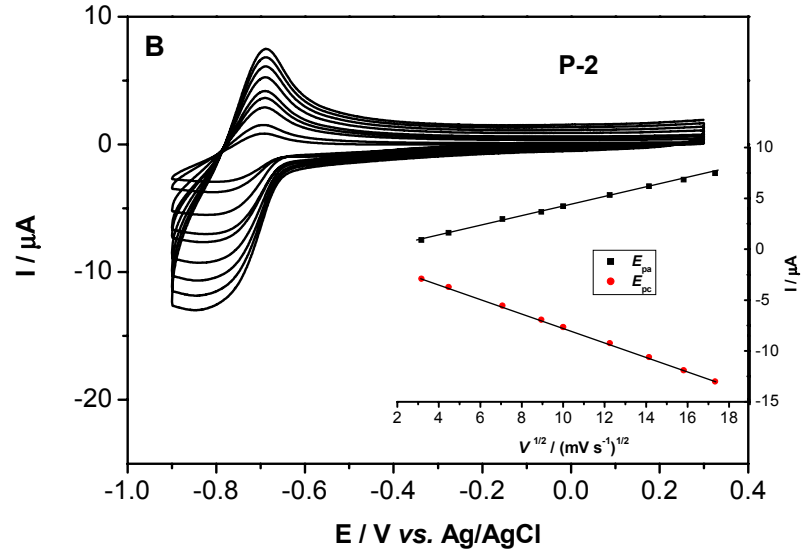


Figure S7. Cyclic voltammograms of 4.4×10^{-4} M **As-1** in pH 3 medium (1M LiCl + HCl) in the absence (dot) and presence of nitrate (1M) (solid). The scan rate was 2 $mV \cdot s^{-1}$; the working electrode was glassy carbon and the reference electrode a Ag/AgCl electrode.

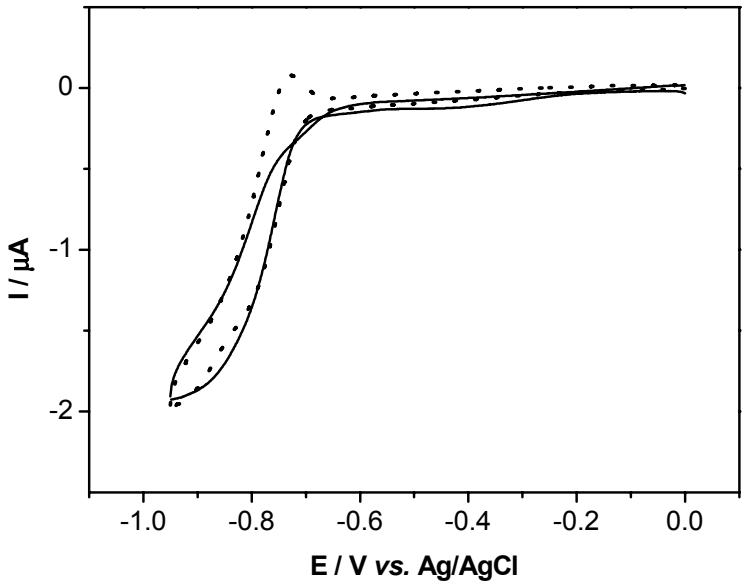
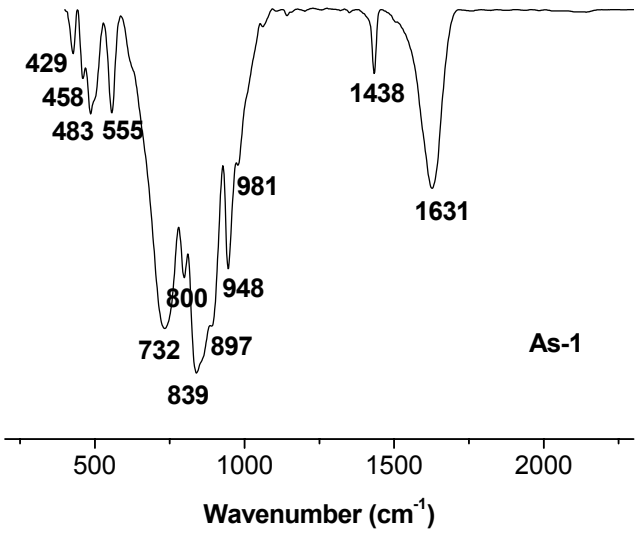
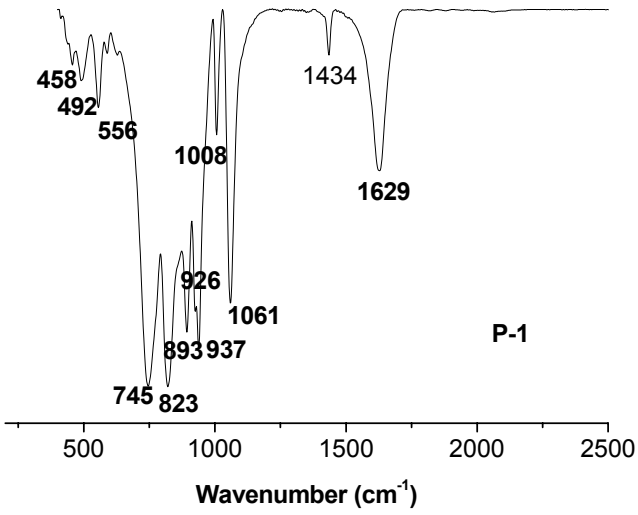


Figure S8. IR spectra for compounds **As-1** and **P-2**.





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