

SUPPORTING INFORMATION ON

Electrochemical, electro-catalytic and magnetic properties of vanadium-containing polyoxometalates

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S1. Cyclic voltammetry characterisation at pH 3.0 (0.2M Na₂SO₄ + H₂SO₄)

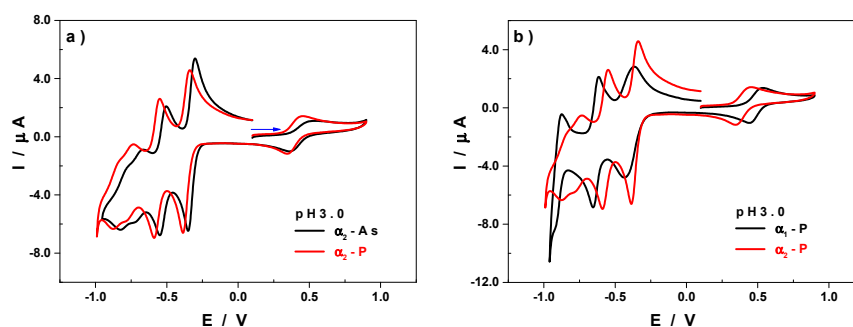


Figure S1. CVs of a) α_2 -As (black) and α_2 -P (red); b) α_1 -P (black) and α_2 -P (red) in 0.2M Na₂SO₄ + H₂SO₄ / pH3. Working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 10 mV s⁻¹.

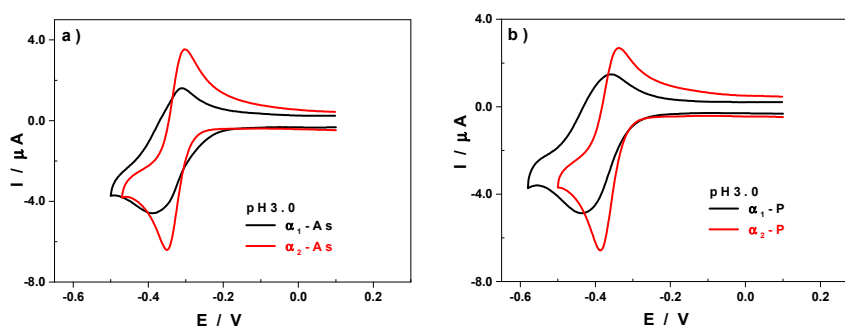


Figure S2. CVs of a) α_1 -As (black) and α_2 -As (red); b) α_1 -P (black) and α_2 -P (red) in 0.2M Na₂SO₄ + H₂SO₄ / pH3. Working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 10 mV s⁻¹.

S2. Cyclic voltammetry characterisation in three different media: 0.2M Na₂SO₄ + H₂SO₄ / pH 3.0 (black), 0.4M CH₃CO₂Na + CH₃CO₂H / pH 5.0 (red) and 0.2M Na₂HPO₄ + H₃PO₄ / pH 7.0

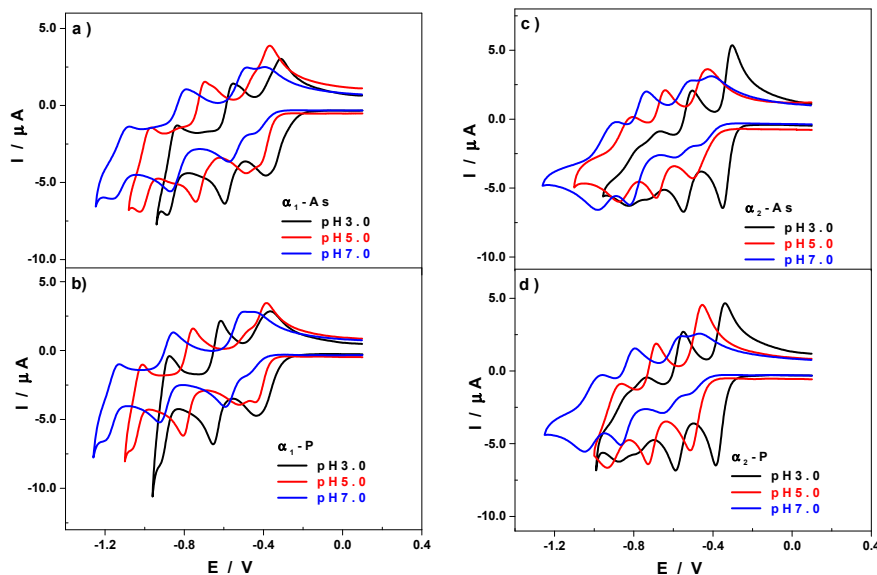


Figure S3. CVs of a) α_1 -As; b) α_1 -P; c) α_2 -As and d) α_2 -P in 0.2M Na₂SO₄ + H₂SO₄ / pH 3.0 (black), 0.4M CH₃CO₂Na + CH₃CO₂H / pH 5.0 (red) and 0.2M Na₂HPO₄ + H₃PO₄ / pH 7.0 (blue). Working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 10 mV s⁻¹.

Table S1. Oxidation peak potentials (E_a) and reduction peak potentials (E_c) measured from CVs recorded in 0.4M CH₃CO₂Na + CH₃CO₂H / pH 5.0 (see above for the conditions).

	V	W ₁	W ₂	W ₃	W ₄	
E_a	0.598	-0.370	-0.442	-0.698	-0.970	α_1-As
E_c	0.516	-0.416	-0.486	-0.742	-1.022	
$E_0' = (E_a + E_c)/2$						
# electrons	1	1	1	2	2	
	V	W ₁	W ₂	W ₃	W ₄	
E_a	0.550	-0.400	-0.628	-0.800	-	α_2-As
E_c	0.372	-0.514	-0.700	-0.884	-	
$E_0' = (E_a + E_c)/2$						
# electrons	1	2	2	2	-	
	V	W ₁	W ₂	W ₃	W ₄	
E_a	0.546	-0.384	-0.470	-0.756	-0.1012	α_1-P

E_c	0.432	-0.440	-0.520	-0.804	-1.070	
$E_0' = (E_a + E_c)/2$						
# electrons	1	1	1	2	2	
	V	W ₁	W ₂	W ₃	W ₄	
E_a	0.466	-0.432	-0.672	-0.860	-	
E_c	0.338	-0.532	-0.738	-0.942	-	α_2-P
$E_0' = (E_a + E_c)/2$						
# electrons	1	2	2	2	-	

Table S2. Oxidation peak potentials (E_a) and reduction peak potentials (E_c) measured from CVs recorded in 0.2M Na₂HPO₄ + H₃PO₄ / pH 7.0 (see above for the conditions).

	V	W ₁	W ₂	W ₃	W ₄	
E_a	0.624	-0.400	-0.488	-0.788	-1.080	
E_c	0.500	-0.440	-0.560	-0.870	-1.160	α_1-As
$E_0' = (E_a + E_c)/2$						
# electrons	1	1	1	2	2	
	V	W ₁	W ₂	W ₃	W ₄	
E_a	0.494	-0.414	-0.510	-0.734	-0.890	
E_c	0.390	-0.460	-0.586	-0.820	-0.978	α_2-As
$E_0' = (E_a + E_c)/2$						
# electrons	1	1	1	2	2	
	V	W ₁	W ₂	W ₃	W ₄	
E_a	0.550	-0.466	-0.500	-0.857	-1.130	
E_c	0.428	-0.480	-0.593	-0.923	-1.214	α_1-P
$E_0' = (E_a + E_c)/2$						
# electrons	1	1	1	2	2	
	V	W ₁	W ₂	W ₃	W ₄	
E_a	0.450	-0.466	-0.570	-0.800	-0.968	
E_c	0.388	-0.530	-0.648	-0.860	-1.044	α_2-P
$E_0' = (E_a + E_c)/2$						
# electrons	1	1	1	2	2	

S3. Preparation of the Britton-Robinson buffer solution

The Britton-Robinson buffer solution has a composition such that its pH varies linearly with the amount of hydroxide ions added to it.

In a 1 L calibrated flask, mix 12.5 mL of phosphoric acid 1.00 mol.L⁻¹, 12,5 mL of acetic acid 1.00 mol.L⁻¹ and 125 mL of boric acid 0.1 mol.L⁻¹ (6,19 g.L⁻¹) and add water up to 1L. The three components H₃PO₄, CH₃CO₂H and H₃BO₃ are all at a concentration of 1.25.10⁻² mol.L⁻¹.

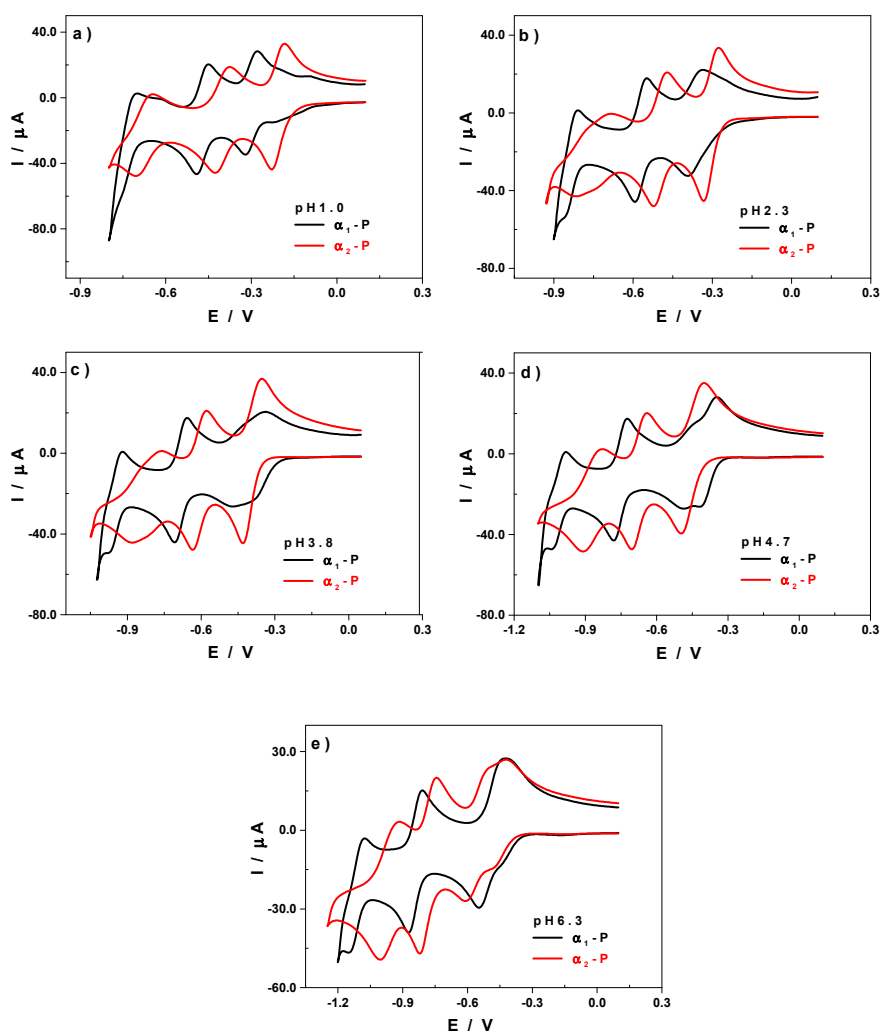


Figure S4. CVs of α_1 -P (black) and α_2 -P (red) in Britton-Robinson buffer. a) pH 1.0; b) pH 2.3; c) pH 3.8; d) pH 4.7; e) pH 6.3. Working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 10 mV s⁻¹.

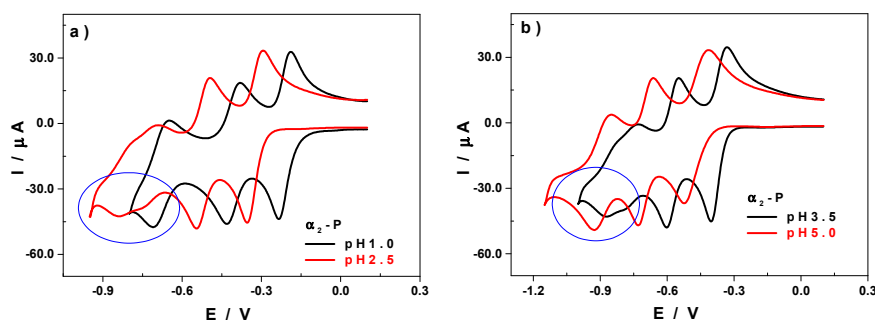


Figure S5. CVs of α_2 -P in Britton-Robinson buffer at a) pH 1.0 (black) and pH 2.5 (red); b) pH 3.5 (black) and pH 5.0 (red). Working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 10 mV s⁻¹.

Law of variation of the reduction peak potential of the third wave as a function of the pH

- $W_3(\alpha_1) = -0.47 - 0.064 \text{ pH}$
- $W_3(\alpha_2) = -0.37 - 0.072 \text{ pH}$

S4 Electro-catalytic properties

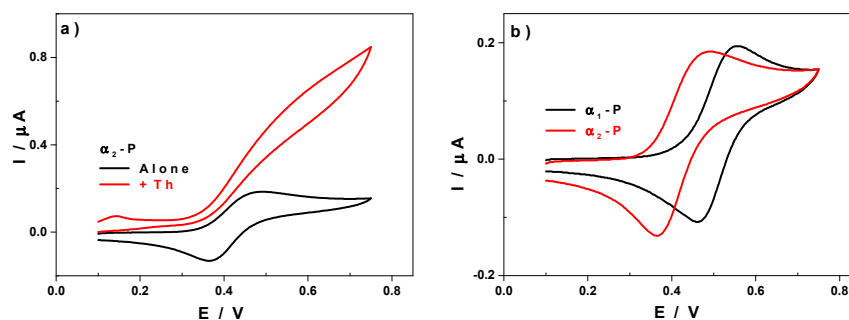


Figure S6 a) CVs of α_2 -P alone (black) and in the presence of thiol (red); b) CVs of α_1 -P (black) and α_2 -P (red), both alone. Electrolyte: 0.2M Na₂HPO₄ + H₃PO₄ / pH 7.0. Working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 2 mV s⁻¹.

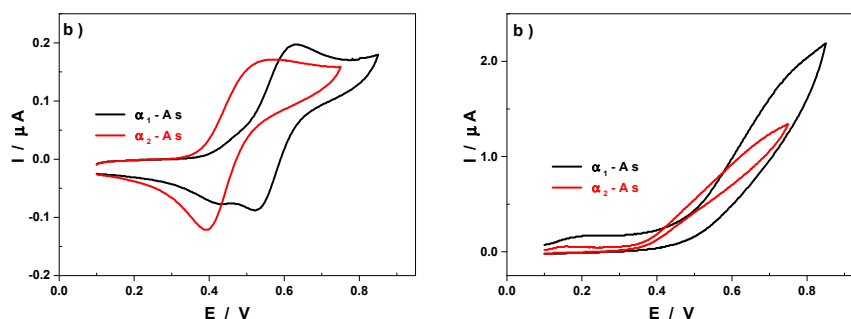


Figure S7. CVs of α_1 -As (black) and α_2 -As (red): a) alone and b) in presence of thiol. Electrolyte: 0.2M Na₂HPO₄ + H₃PO₄ / pH 7.0. Working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 2 mV s⁻¹.

S5 Magnetic properties

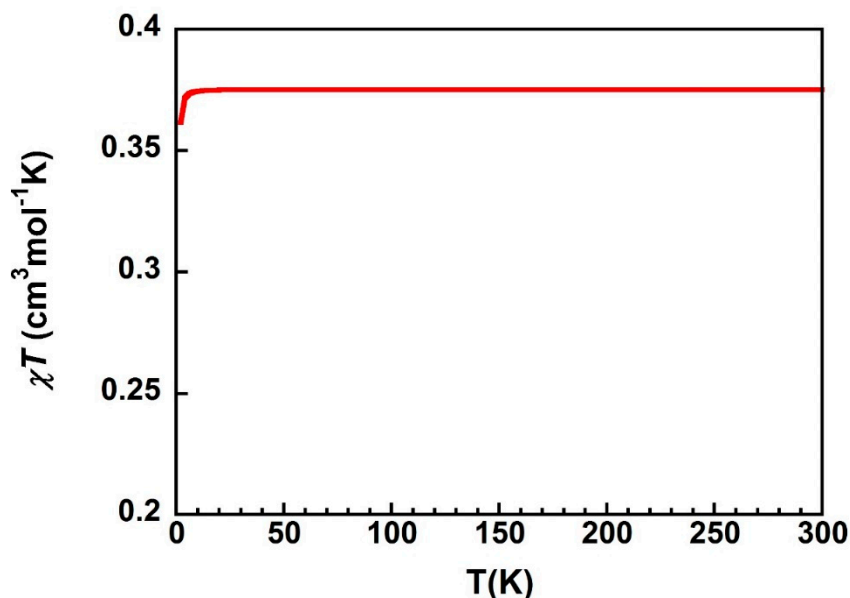


Figure S8: Theoretical susceptibility under an applied field of 1T in the form of a $\chi_m T$ *vs* T plot for a $S=1/2$ ion.

S6. Syntheses of different POMs

α_1 -K₈[As₂V^{IV}W₁₇O₆₂].18H₂O (MW 4955.09)

A sample of VOSO₄.5H₂O (0.76 g; ~ 3.0 mmol) is dissolved in 90 mL of millipore water; the solution is acidified by the addition of hydrochloric acid (2 mL; 4M HCl); then α_1 -K₁₀As₂W₁₇O₆₁.19H₂O (15.0 g; 3.0 mmol) is added in small portions with stirring. After 30 minutes of evolution at room temperature, the resulting black solution is filtered and treated with solid potassium chloride (10 g). The grey-black precipitate that formed is collected by filtration, washed with ethanol and dried in the open air. This material is re-crystallised in a minimum of acidified water (HCl solution of pH < 1). Mass obtained, m = 12.32 g; yield = 83%.g

α_2 -K₈[As₂V^{IV}W₁₇O₆₂].18H₂O (MW 4955.09)

The same method as described for the compound α_1 -K₈[As₂V^{IV}W₁₇O₆₂].18H₂O is used, this time starting from α_2 -K₁₀As₂W₁₇O₆₁.19H₂O (15.0 g; 3.0 mmol). This material is re-crystallised in a minimum of acidified water (HCl solution of pH < 1). Mass obtained, m = 13.54 g; yield = 91 %.

α_1 -K₈[P₂V^{IV}W₁₇O₆₂].18H₂O (MW 4867.19)

The same method as described for the compound α_1 -K₈[As₂V^{IV}W₁₇O₆₂].16H₂O is used, this time starting from α_1 -K₁₀P₂W₁₇O₆₁.19H₂O (15.0 g; 3.0 mmol). This material is re-crystallised in a minimum of acidified water (HCl solution of pH < 1). Mass obtained, m = 13.05 g; yield = 89 %.

α_2 -K₈[P₂V^{IV}W₁₇O₆₂].16H₂O (MW 4867.19)

The same method as described for the compound $\alpha_1\text{-K}_8[\text{As}_2\text{V}^{\text{IV}}\text{W}_{17}\text{O}_{62}]\cdot 16\text{H}_2\text{O}$ is used, this time starting from $\alpha_2\text{-K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}\cdot 19\text{H}_2\text{O}$ (15.0 g; 3.0 mmol). This material is re-crystallised in a minimum of acidified water (HCl solution of pH < 1). Mass obtained, m = 13.88 g; yield = 95 %.

$\alpha_1\text{-K}_7[\text{As}_2\text{V}^{\text{V}}\text{W}_{17}\text{O}_{62}]\cdot 18\text{H}_2\text{O}$ (MW 4915.99)

To a solution containing 6 mL of 0.5 M NaVO_3 (3 mmol), 18 mL of molar HCl and 75 mL of millipore water, 15 g of $\alpha_1\text{-K}_{10}\text{As}_2\text{W}_{17}\text{O}_{61}\cdot 19\text{H}_2\text{O}$ (3 mmol) is added. After 30 minutes of evolution at room temperature, the resulting intense yellow solution is filtered and treated with solid potassium chloride (10 g). The yellow precipitate that appears is collected by filtration, washed with ethanol and dried in the open air. This material is re-crystallised in a minimum of acidified water (HCl solution of pH < 1). Mass obtained, m = 12.02 g; yield = 81 %.

$\alpha_2\text{-K}_7[\text{As}_2\text{V}^{\text{V}}\text{W}_{17}\text{O}_{62}]\cdot 18\text{H}_2\text{O}$ (MW 4915.99)

The same method as described for the compound $\alpha_1\text{-K}_7[\text{As}_2\text{V}^{\text{V}}\text{W}_{17}\text{O}_{62}]\cdot 18\text{H}_2\text{O}$ is used, this time starting from $\alpha_2\text{-K}_{10}\text{As}_2\text{W}_{17}\text{O}_{61}\cdot 19\text{H}_2\text{O}$ (15.0 g; 3.0 mmol). This material is re-crystallised in a minimum of acidified water (HCl solution of pH < 1). Mass obtained, m = 12.50 g; yield = 85 %.

$\alpha_1\text{-K}_7[\text{P}_2\text{V}^{\text{V}}\text{W}_{17}\text{O}_{62}]\cdot 18\text{H}_2\text{O}$ (MW 4828.10)

The same method as described for the compound $\alpha_1\text{-K}_7[\text{As}_2\text{V}^{\text{V}}\text{W}_{17}\text{O}_{62}]\cdot 18\text{H}_2\text{O}$ is used, this time starting from $\alpha_1\text{-K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}\cdot 19\text{H}_2\text{O}$ (15.0 g; 3.0 mmol). This material is re-crystallised in a minimum of acidified water (HCl solution of pH < 1). Mass obtained, m = 13.25 g; yield = 92 %.

$\alpha_2\text{-K}_7[\text{P}_2\text{V}^{\text{V}}\text{W}_{17}\text{O}_{62}]\cdot 18\text{H}_2\text{O}$ (MW 4828.10)

The same method as described for the compound $\alpha_1\text{-K}_7[\text{As}_2\text{V}^{\text{V}}\text{W}_{17}\text{O}_{62}]\cdot 18\text{H}_2\text{O}$ is used, this time starting from $\alpha_2\text{-K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}\cdot 19\text{H}_2\text{O}$ (15.0 g; 3.0 mmol). This material is re-crystallised in a minimum of acidified water (HCl solution of pH < 1). Mass obtained, m = 13.70 g; yield = 95 %.