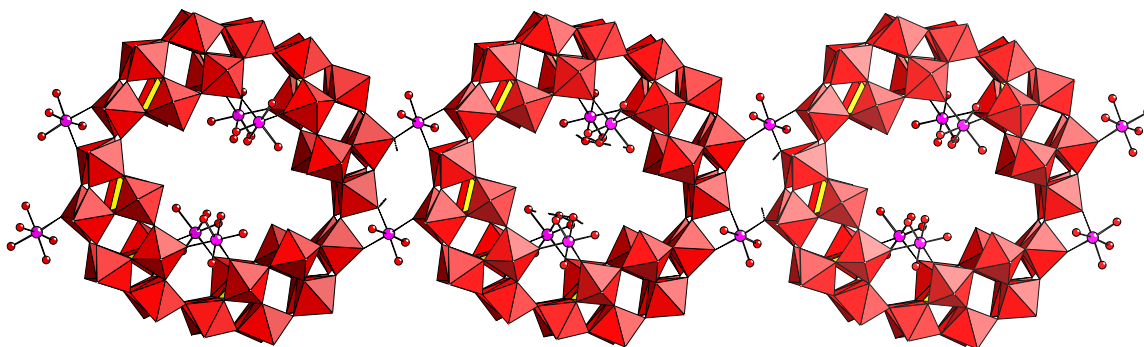


**Cobalt, Manganese, Nickel, and Vanadium Derivatives of the Cyclic 48-Tungsto-8-Phosphate [H<sub>7</sub>P<sub>8</sub>W<sub>48</sub>O<sub>184</sub>]<sup>33-</sup>**

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**Supplementary Information**



**Figure S1.** Arrangement of **1** in the solid state indicating that two ‘external’  $\text{Co}^{2+}$  ions link three neighboring polyanions forming a chain. Alkali cations and crystal waters not shown for clarity.

## Electrochemistry Studies

### *Stability*

The stabilities of **1**, **2** and **4** in solution were assessed by monitoring their UV-vis spectra as a function of pH over a period of at least 24 h. The behaviour of polyanion **1** is representative for the series and will be described in detail. The spectrum of **1** is characterized by a broad peak which remained located between 269 nm and 260 nm when the pH varied between 0.33 and 7. For each pH value, all the spectra were reproducible with respect to absorbance and wavelength locations. In addition, cyclic voltammetry (CV) experiments, lasting up to 10 hours, suggested also that **1** is stable in the pH domain explored. Such stability parallels that of the precursor crown heteropolyanion  $[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}]^{33-}$  (**P<sub>8</sub>W<sub>48</sub>**).<sup>1</sup>

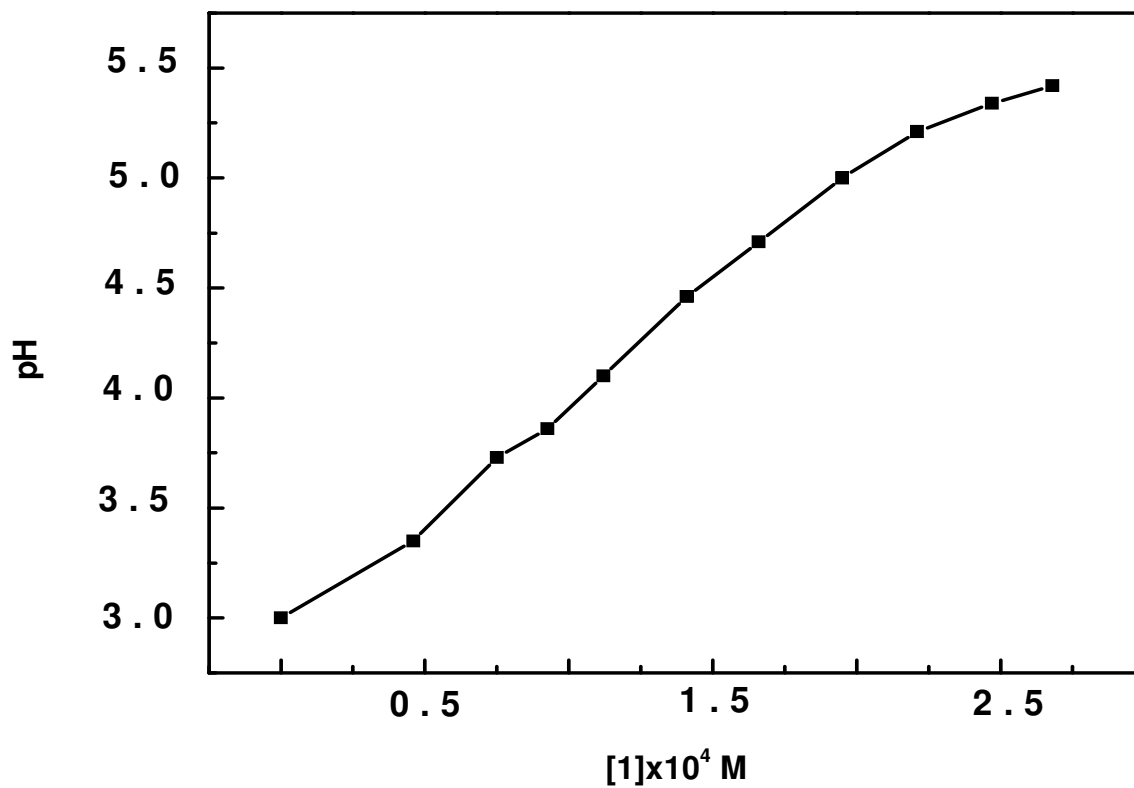
### *pH Variations for Solutions of 1*

Based on the knowledge of the solution behaviour of **P<sub>8</sub>W<sub>48</sub>**,<sup>2</sup> it was anticipated that redissolution of the current polyanions in several aqueous media might be accompanied by an important proton consumption. Polyanion **1** was again selected as a representative example. Typically, a solution containing 1M LiCl + HCl (pH = 3) was chosen to illustrate this behaviour. The pH of the solution was then monitored accurately as a function of the amount of **1** added. Figure S2 shows the pH variations. In short, addition of 0.27 mM **1** to the supporting electrolyte drives the final pH to roughly 5.5. Analogous observations were made previously for several POMs,<sup>1,3</sup> including the satellite-shaped Co(II) containing tungstosilicate  $[\text{Co}_6(\text{H}_2\text{O})_{30}\{\text{Co}_9\text{Cl}_2(\text{OH})_3(\text{H}_2\text{O})_9(\beta\text{-SiW}_8\text{O}_{31})_3\}]^{5-}$  (**Co15**).<sup>4</sup> These behaviours are explained by taking into account the buffer capacity of the medium and the pK<sub>a</sub>'s of the relevant POM in its oxidized state. The observed fast increase of the pH in the chloride medium is a result of the absence of any buffer capacity. These remarks are particularly important for electrochemistry and electrocatalysis studies with POMs where, in addition to the existence of protonable sites in the oxidized state, electron transfers are usually accompanied by acid-base equilibria. As a consequence of these observations, media with a high acidity as pH = 0.33 and buffers with a large capacity such as 1 M CH<sub>3</sub>COOLi + CH<sub>3</sub>COOH (pH 5) were

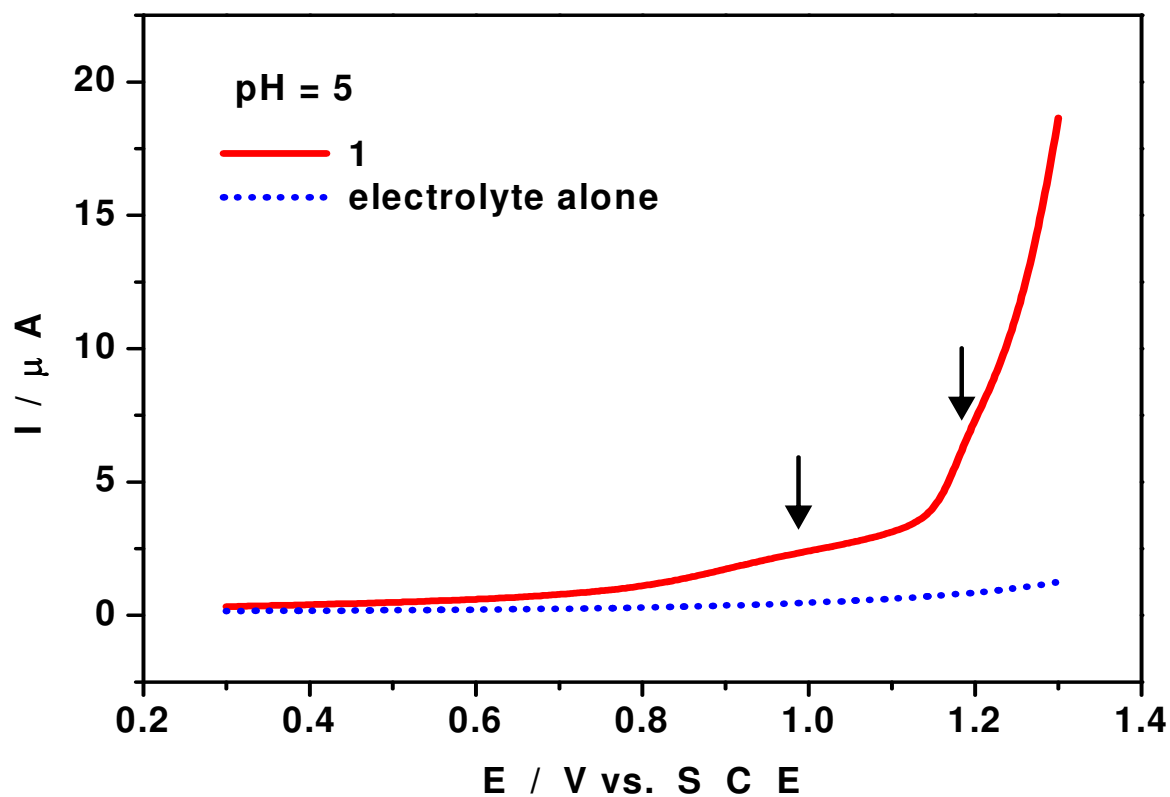
necessary for further work and were selected to avoid important pH variations upon mere dissolution of **1**.

## References

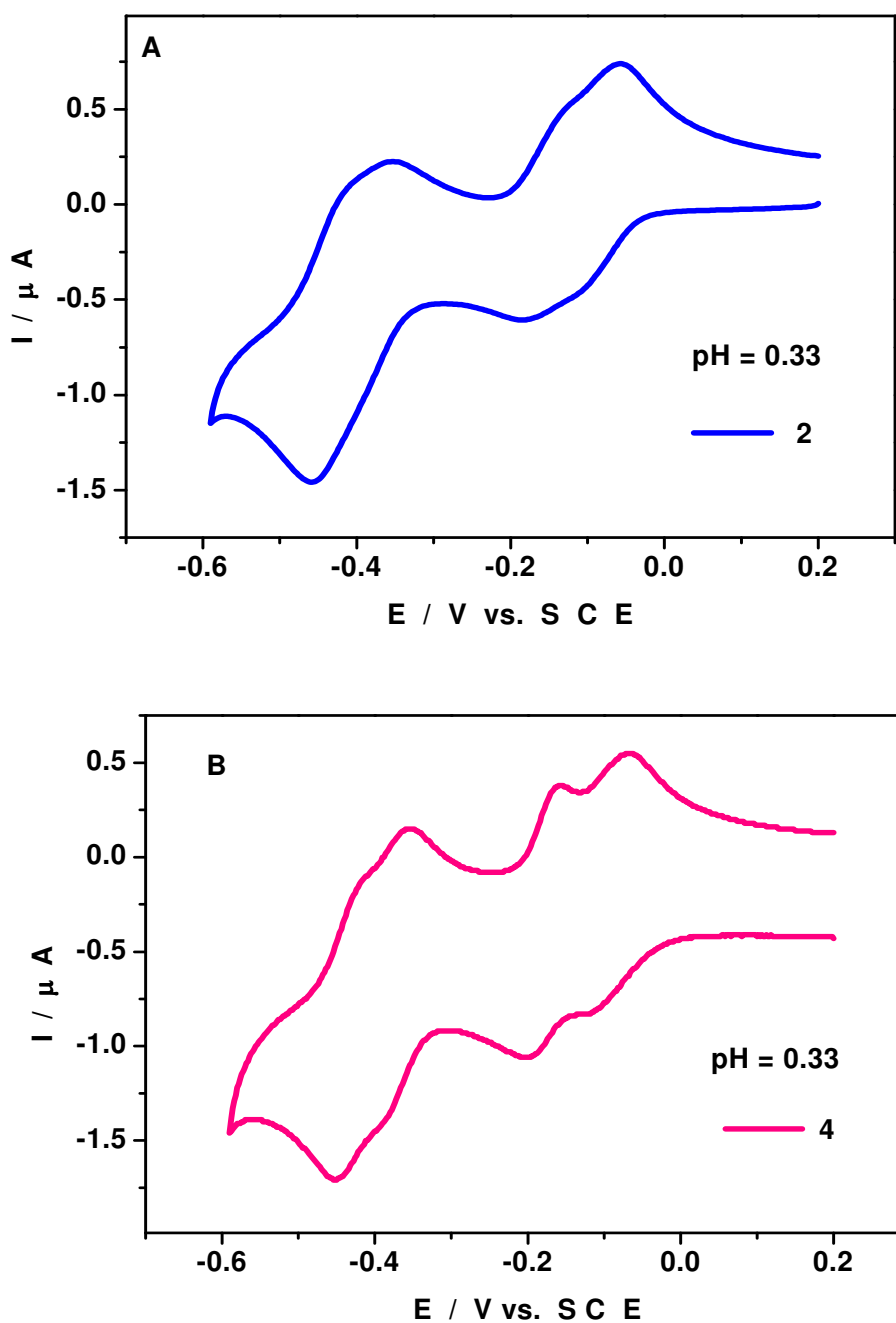
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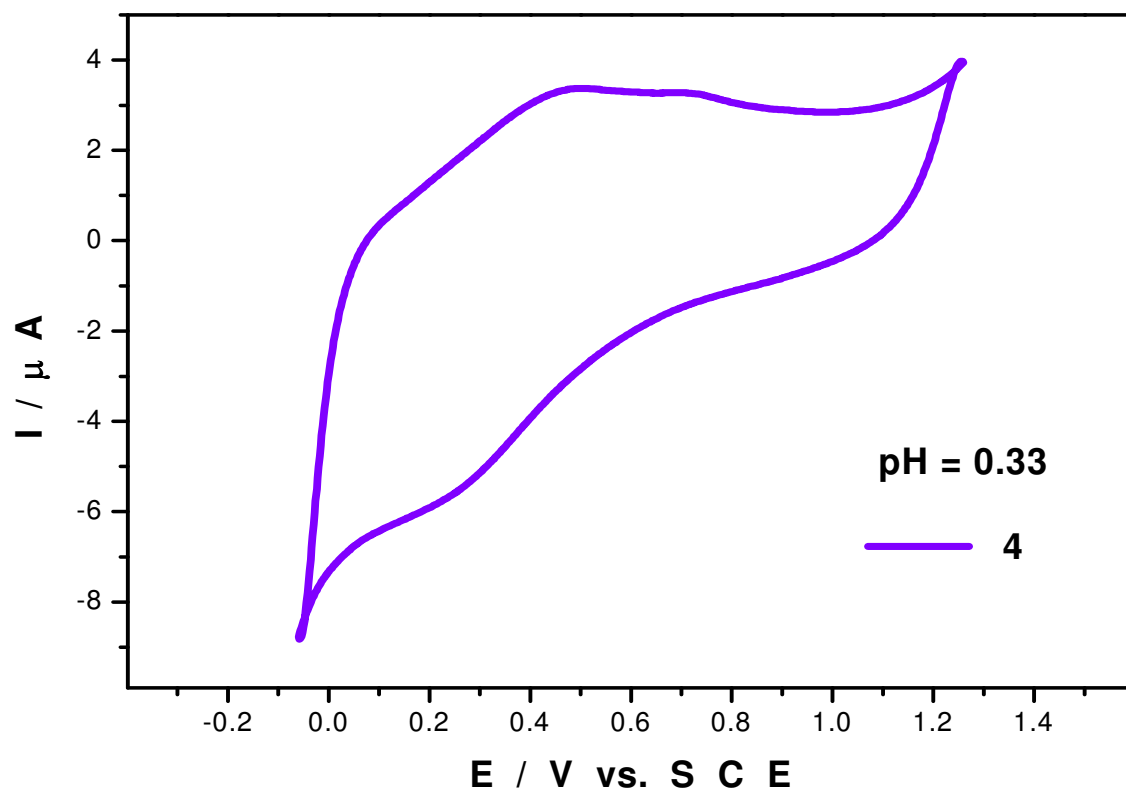
**Figure S2.** Evolution of the pH of an initially pH 3 solution (1 M LiCl + HCl) as a function of the concentration of polyanion **1**.



**Figure S3.** Voltammetric studies of  $4 \times 10^{-5}$  M polyanion **1** restricted to its  $\text{Co}^{2+}$ -waves in pH 0.33 (0.5 M  $\text{H}_2\text{SO}_4$ ) medium. The working electrode was glassy carbon and the reference electrode was SCE. The scan rate was  $10 \text{ mV s}^{-1}$ .



**Figure S4.** Cyclic voltammetric studies of  $4 \times 10^{-5}$  M polyanions **2** and **4** restricted to their reversible  $W^{VI}$ -waves in pH 0.33 (0.5 M H<sub>2</sub>SO<sub>4</sub>) medium. The working electrode was glassy carbon and the reference electrode was SCE. The scan rate was 10 mV s<sup>-1</sup>.



**Figure S5.** Cyclic voltammetric studies of  $4 \times 10^{-5}$  M polyanion **4** restricted to its reversible  $V^V$ -waves in pH 0.33 (0.5 M  $H_2SO_4$ ) medium. The working electrode was glassy carbon and the reference electrode was SCE. The scan rate was  $600 \text{ mV s}^{-1}$ .