

Comparative spectroscopic and electrochemical study of V(V) substituted Keggin-type phosphomolybdates and -tungstates

Supplementary Information

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1 Additional data

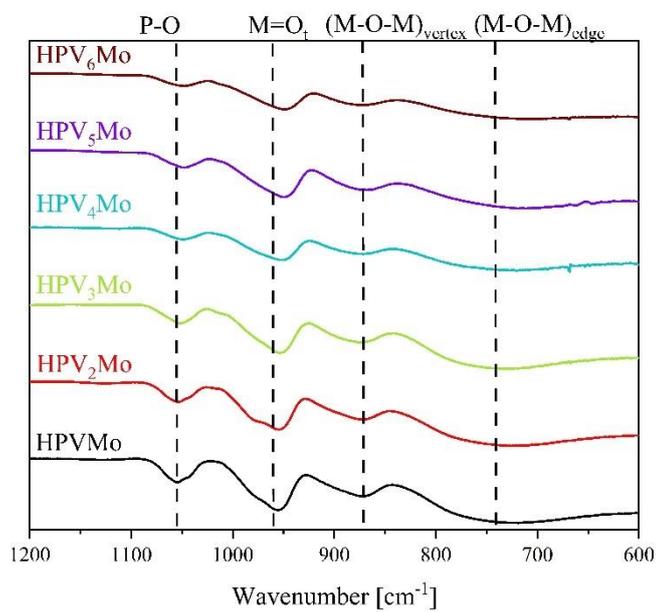


Figure S1: ATR-FT-IR spectra of the POMs HPV_xMo with $x = 1$ to 6.

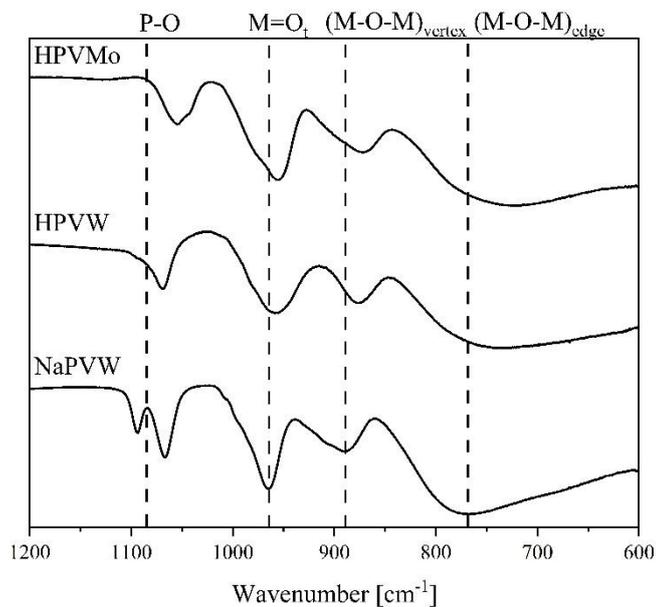


Figure S2: ATR-FT-IR spectra of the POMs NaPVW, HPVW and HPVMo.

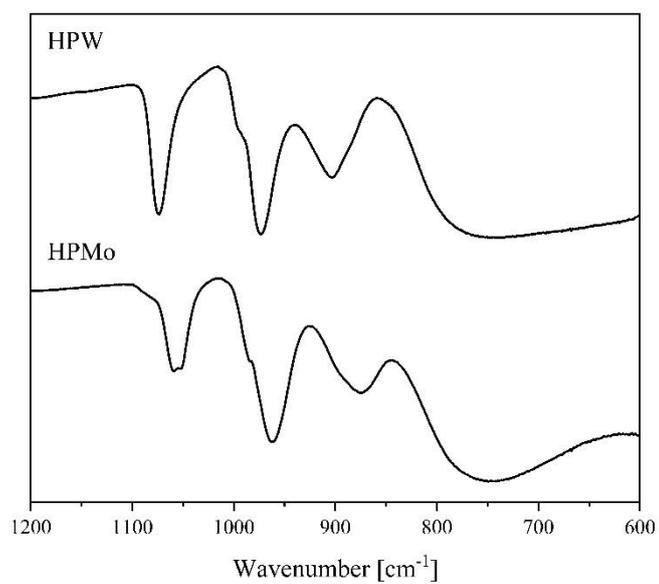


Figure S3: ATR-FT-IR spectra of the POMs HPMo and HPW.

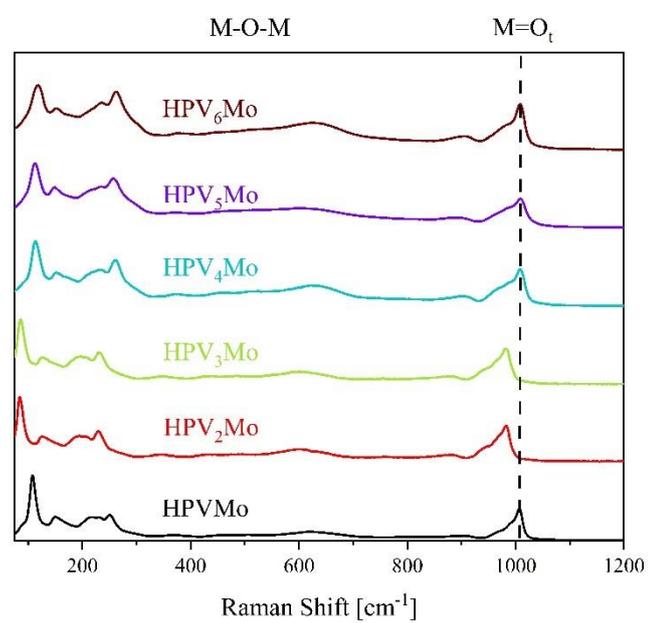


Figure S4: Raman spectra of the POMs HPV_xMo with $x = 1$ to 6.

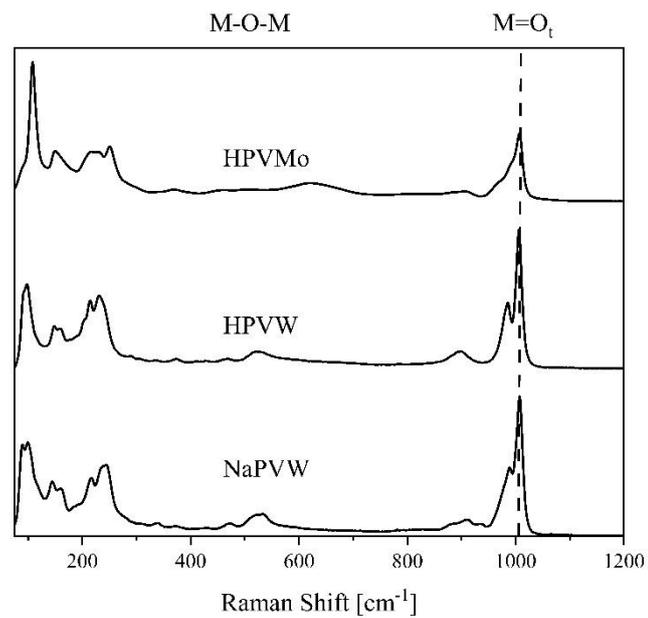


Figure S5: Raman spectra of the POMs NaPVW, HPVW and HPVMo.

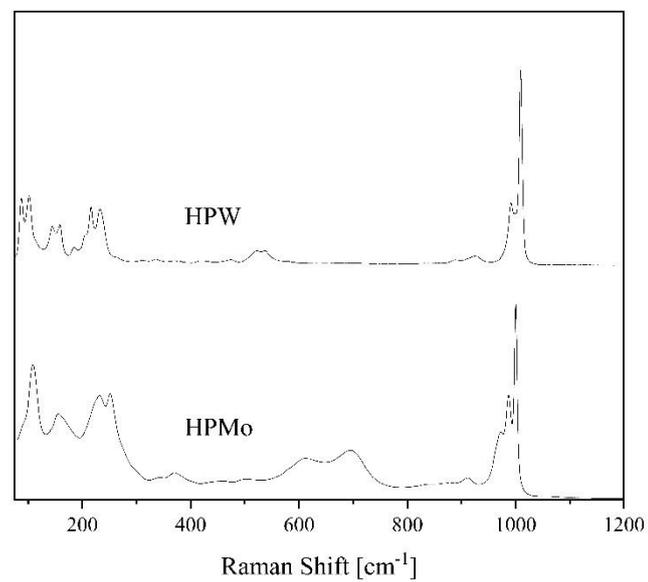


Figure S6: Raman spectra of the POMs HPMo and HPW.

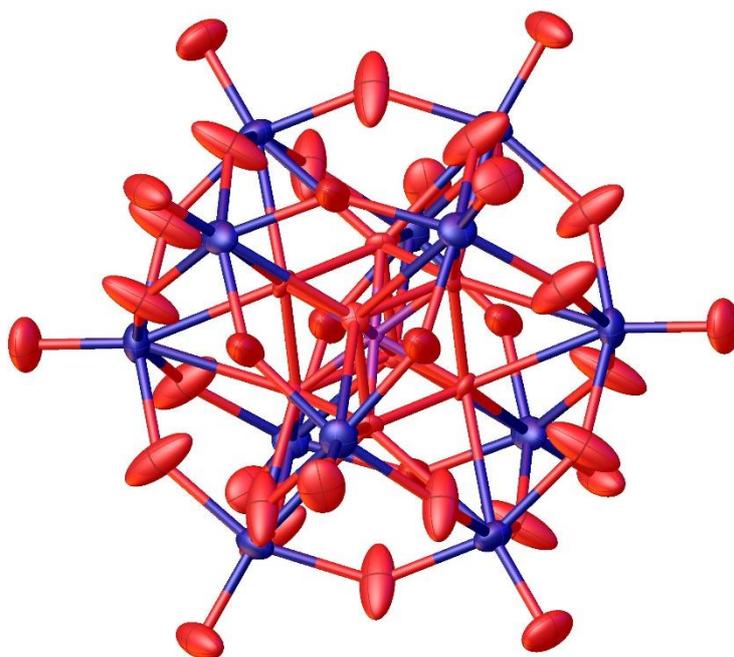


Figure S7: Solid-state structure of compound NaPV_2W determined by X-ray diffraction. The compound was crystallized in the space group $P4/mnc$ (128). Residual electron density attributed to hydration water has been refined with a solvent mask (aka SQUEEZE). R_1 : 2.86 %, wR_2 : 7.35 %, R_{int} : 5.21 %, GooF: 1.061. Colour code: Purple: phosphorous, red: oxygen, and blue: metals (W, V).

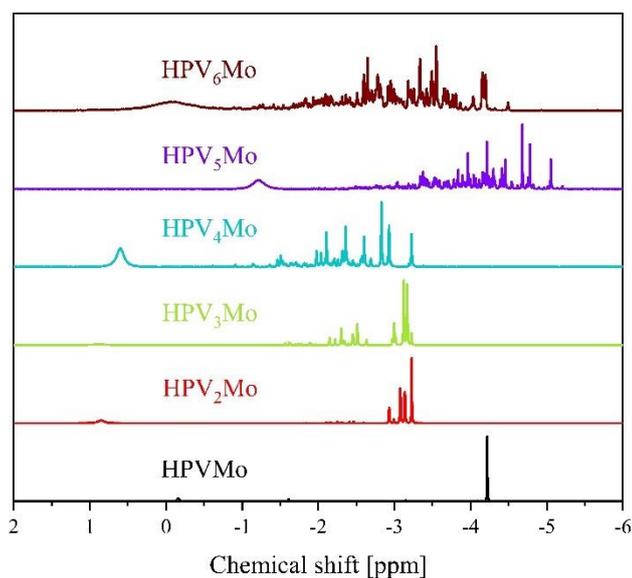


Figure S8: ^{31}P -NMR spectra of the POMs HPV_xMo with $x = 1$ to 6. All spectra were measured in a mixture of 90 % water (pH 1) and 10 % acetone- d_6 . Measurement frequency: 242.9 MHz. 85 % H_3PO_4 was used as external standard.

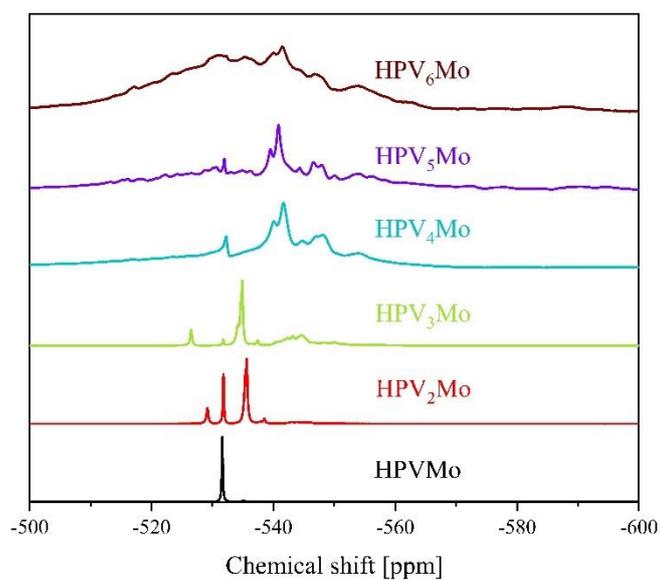


Figure S9: ^{51}V -NMR spectra of the POMs HPV_xMo with $x = 1$ to 6. All spectra were measured in a mixture of 90 % water (pH 1) and 10 % acetone- d_6 . Measurement frequency: 157.8 MHz. NaVO_3 was used as external standard.

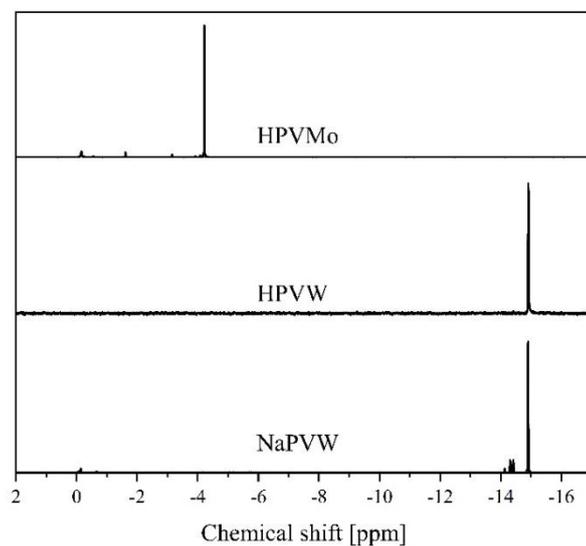


Figure S10: ^{31}P -NMR spectra of the POMs NaPVW, HPVW and HPVMo. Spectra for NaPVW and HPVW were measured in a mixture of 70 % water (pH 1) and 30 % D_2O and spectra for HPV $_2$ Mo were measured in a mixture of 90 % water (pH 1) and 10 % acetone- d_6 . Measurement frequency: 242.9 MHz. 85 % H_3PO_4 was used as external standard.

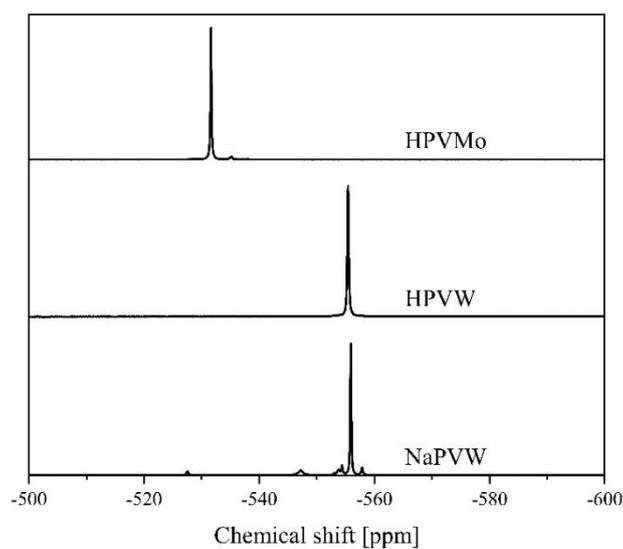


Figure S11: ^{51}V -NMR spectra of the POMs NaPVW, HPVW and HPV₂Mo. Spectra for NaPVW and HPVW were measured in a mixture of 70 % water (pH 1) and 30 % D₂O and spectra for HPV₂Mo were measured in a mixture of 90 % water (pH 1) and 10 % acetone-*d*₆. Measurement frequency: 157.8 MHz. NaVO₃ was used as external standard.

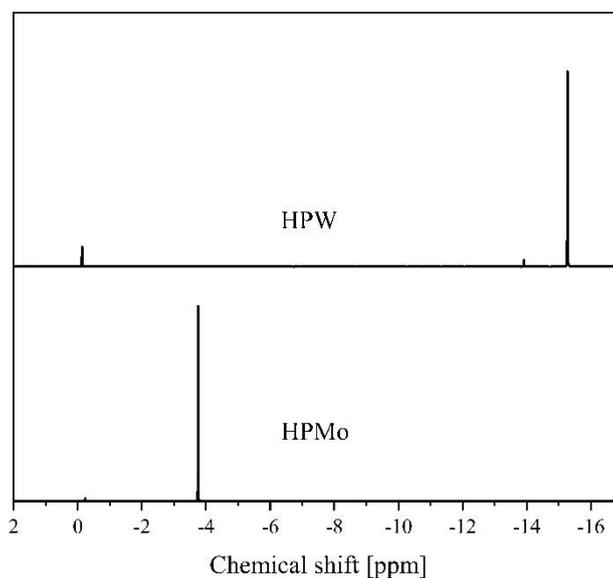


Figure S12: ^{31}P -NMR spectra of the HPMo and HPW. The spectrum for HPW was measured in a mixture of 70 % water (pH 1) and 30 % D₂O and the spectrum for HPMo was measured in a mixture of 90 % water (pH 1) and 10 % acetone-*d*₆. Measurement frequency: 242.9 MHz. 85 % H₃PO₄ was used as external standard.

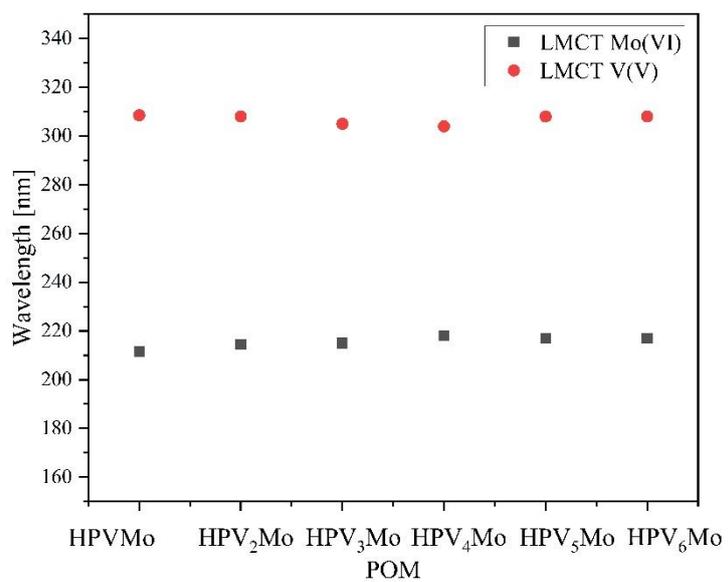


Figure S13: Plot of LMCT maxima vs. HPV_xMo.

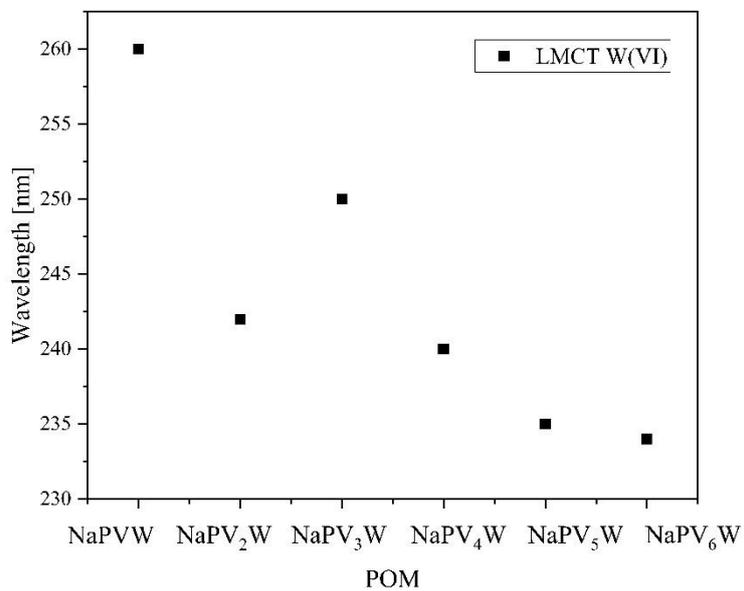


Figure S14: Plot of LMCT maxima vs. degree of substitution in NaPV_xW.

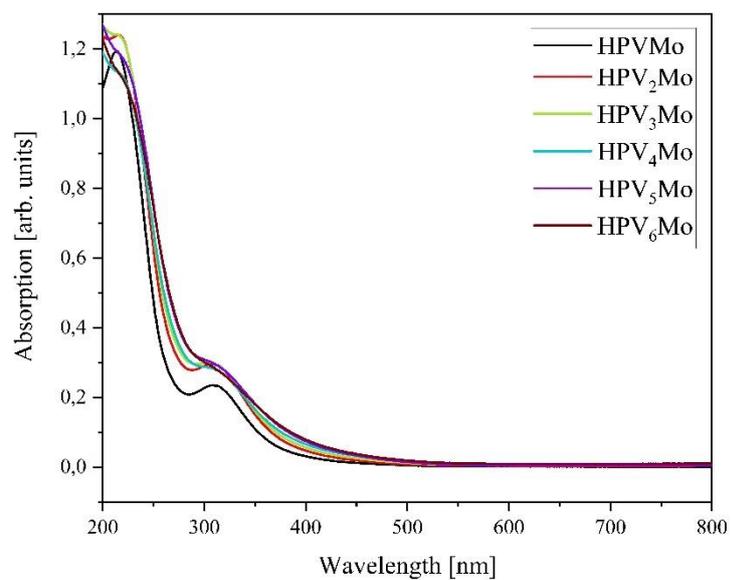


Figure S15: UV-Vis spectra of the POMs HPV_xMo with $x = 1$ to 6.

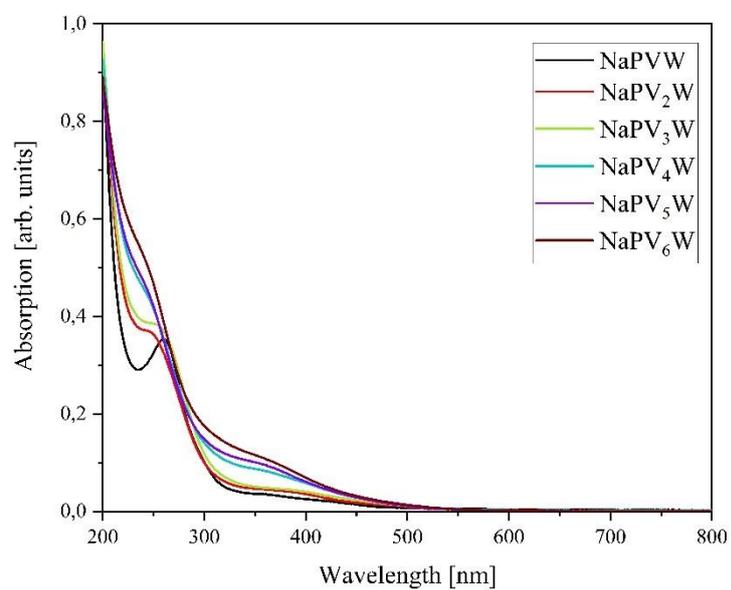


Figure S16: UV-Vis spectra of the POMs NaPV_xW with $x = 1$ to 6.

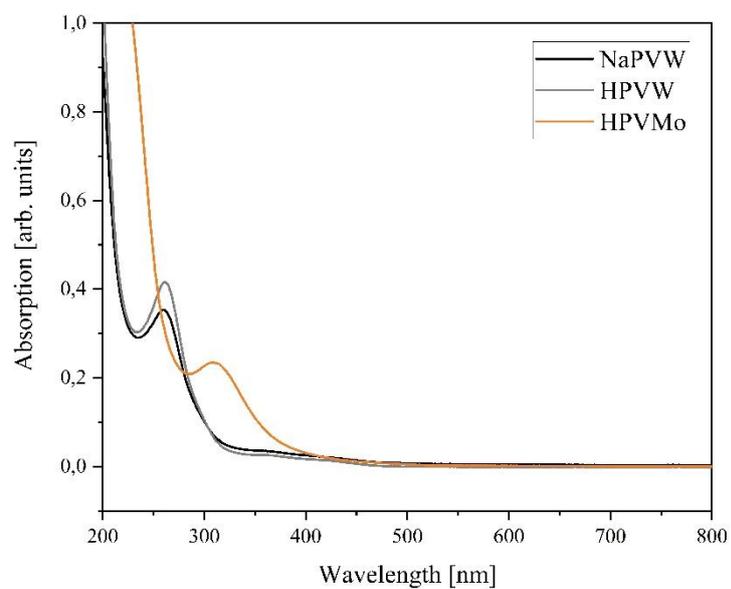


Figure S17: UV-Vis spectra of the POMs NaPVW, HPVW and HPVMo.

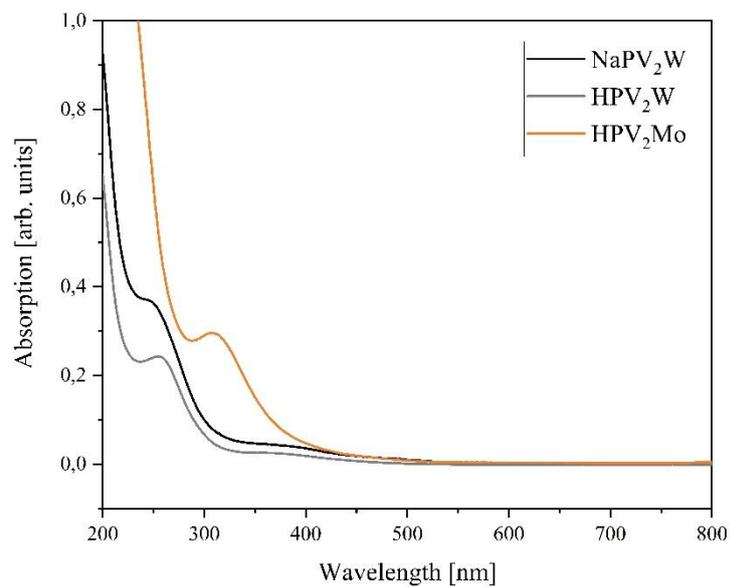


Figure S18: UV-Vis spectra of the POMs NaPV₂W, HPV₂W and HPV₂Mo.

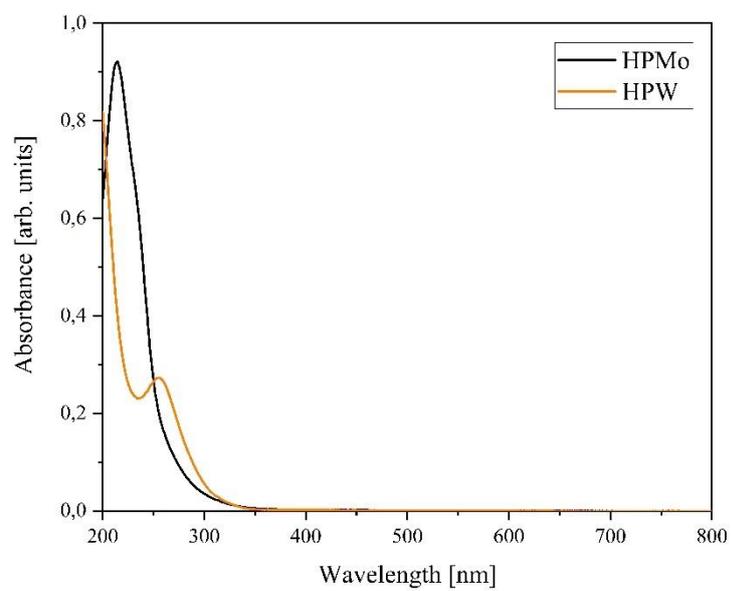


Figure S19: UV-Vis spectra of the POMs HPMo and HPW.

Lambert-Beer's law (equation 1):

$$Abs = \varepsilon_{\lambda} \cdot d \cdot c \quad (1)$$

Abs: Absorption

ε_{λ} : extinction coefficient (wavelength λ dependant) [$\text{l mol}^{-1} \text{cm}^{-1}$]

d: Cuvette layer thickness (1 cm) [cm]

c: concentration [mol/L]

Calibration line (equation 2):

$$Abs = a \cdot c + b \quad (2)$$

a: slope

b: Axis intercept

Determining the extinction coefficient:

$$a = \varepsilon_{\lambda} \cdot d \quad (3)$$

$$\varepsilon_{\lambda} = \frac{a}{d} \quad (4)$$

A detailed description for the measurement procedure can be found under 2.2 UV-Vis spectroscopy, extinction coefficients.

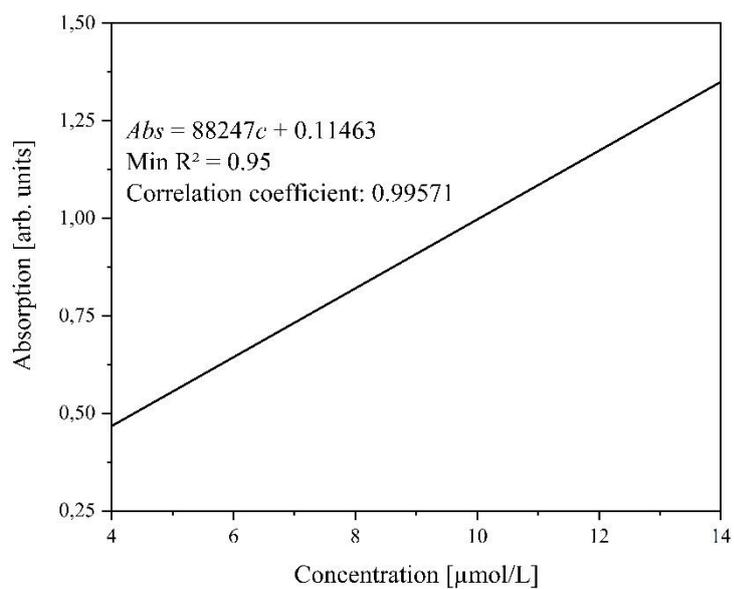


Figure S20: Calibration line for determining the extinction coefficient for HPV Mo at 211.5 nm (Mo(VI) LMCT).

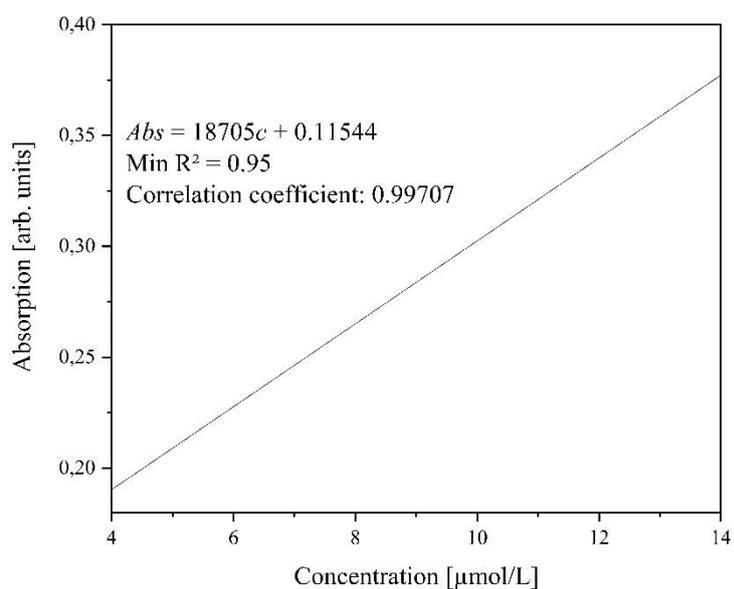


Figure S21: Calibration line for determining the extinction coefficient for HPV Mo at 308.5 nm (V(V) LMCT).

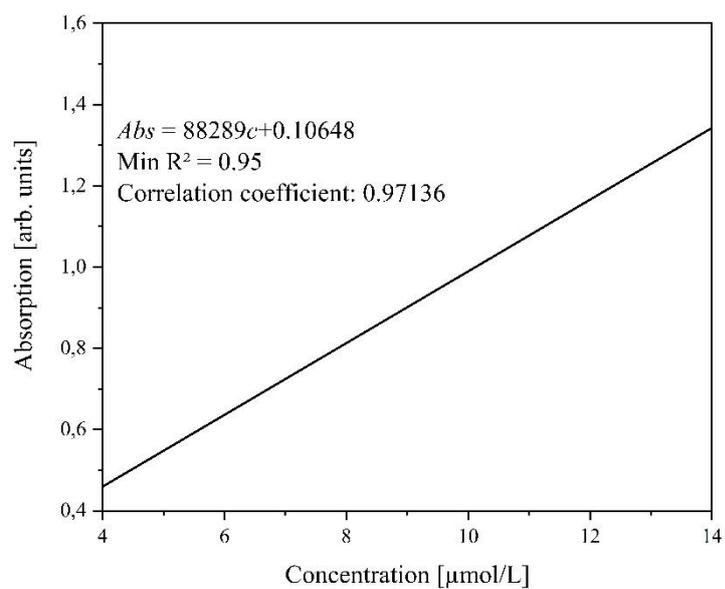


Figure S22: Calibration line for determining the extinction coefficient for HPV₂Mo at 214.5 nm (Mo(VI) LMCT).

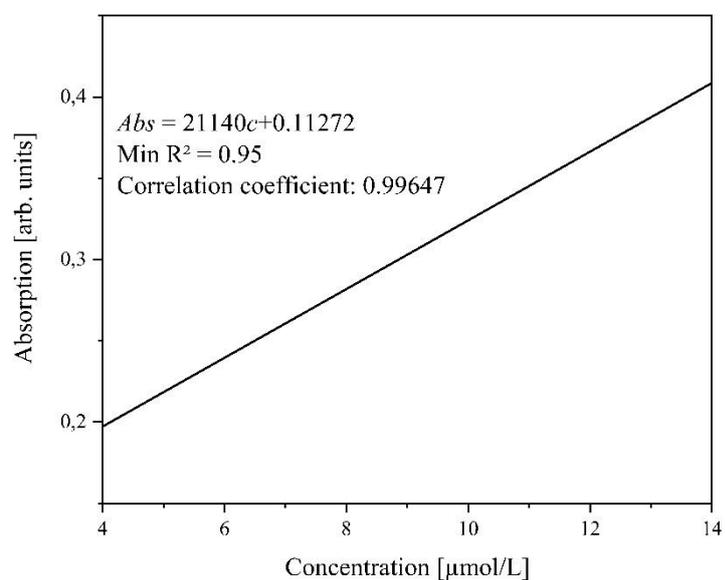


Figure S23: Calibration line for determining the extinction coefficient for HPV₂Mo at 308 nm (V(V) LMCT).

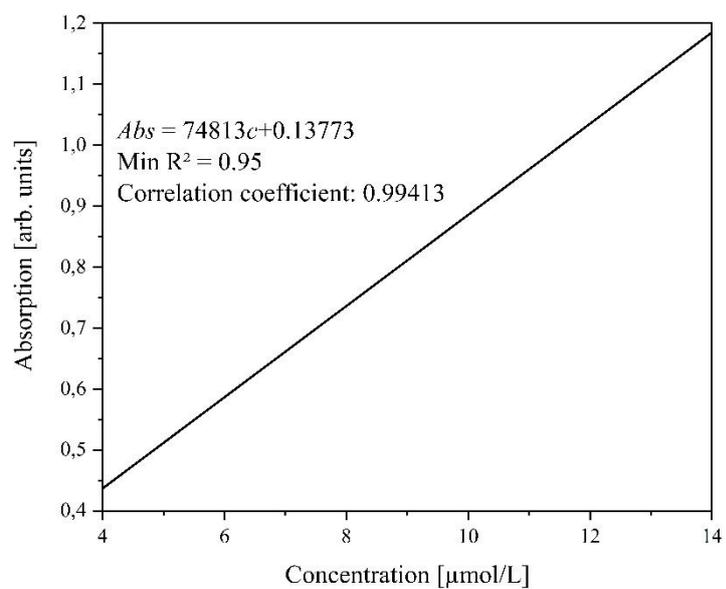


Figure S24: Calibration line for determining the extinction coefficient for HPV₃Mo at 215 nm (Mo(VI) LMCT).

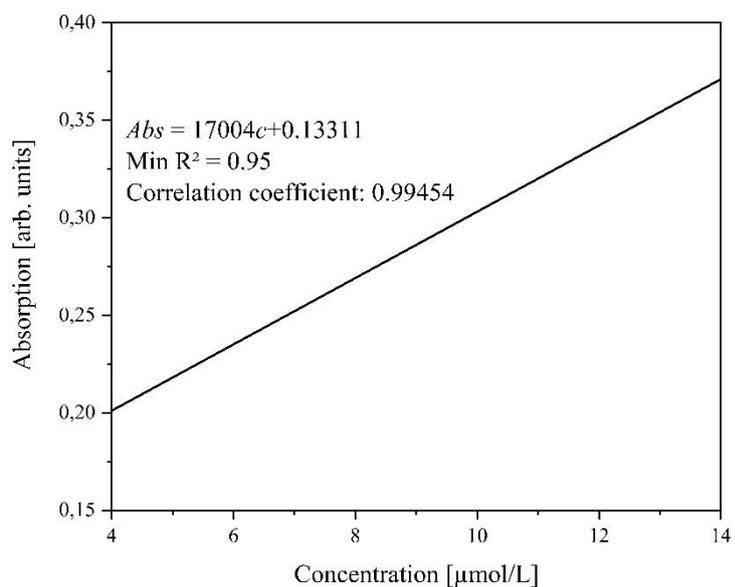


Figure S25: Calibration line for determining the extinction coefficient for HPV₃Mo at 305 nm (V(V) LMCT).

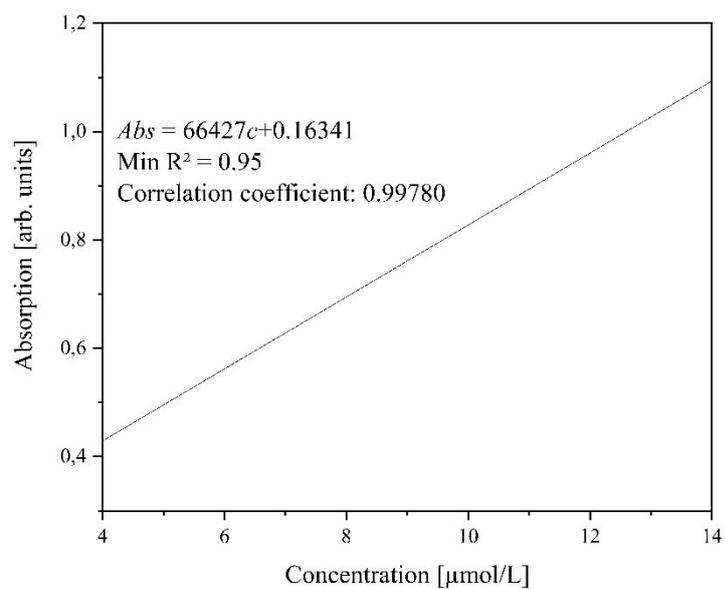


Figure S26: Calibration line for determining the extinction coefficient for HPV₄Mo at 218 nm (Mo(VI) LMCT).

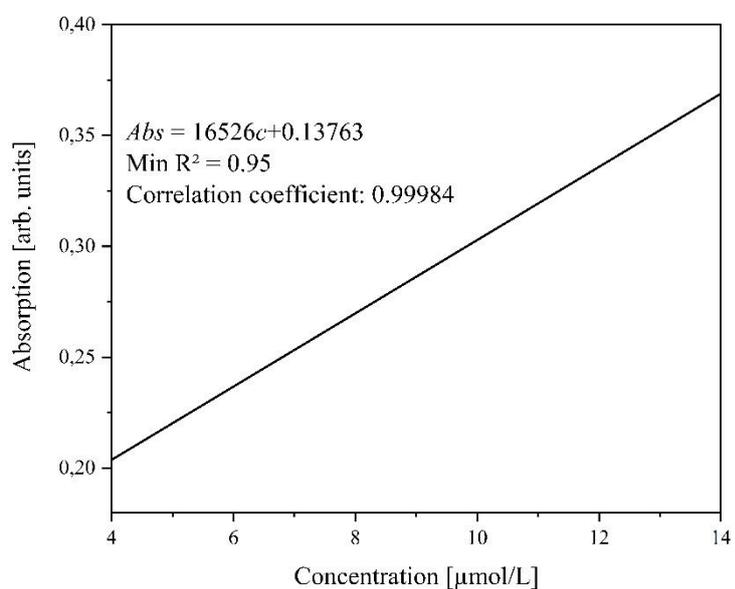


Figure S27: Calibration line for determining the extinction coefficient for HPV₄Mo at 304 nm (V(V) LMCT).

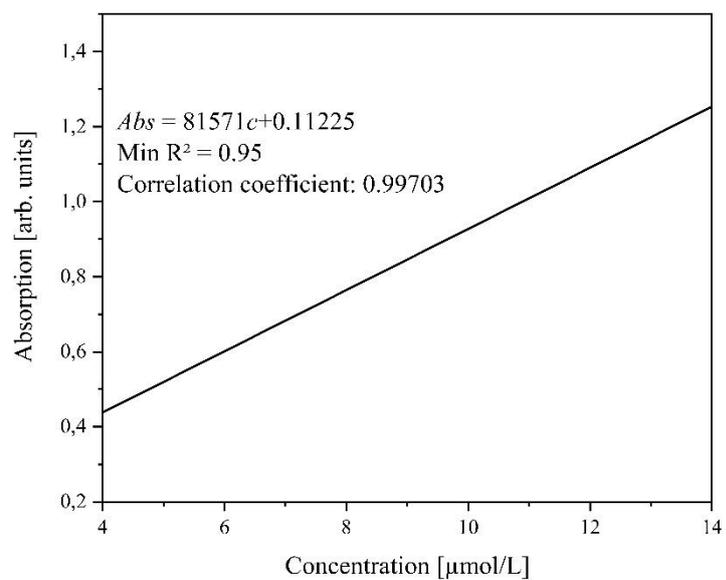


Figure S28: Calibration line for determining the extinction coefficient for HPV₅Mo at 217 nm (Mo(VI) LMCT).

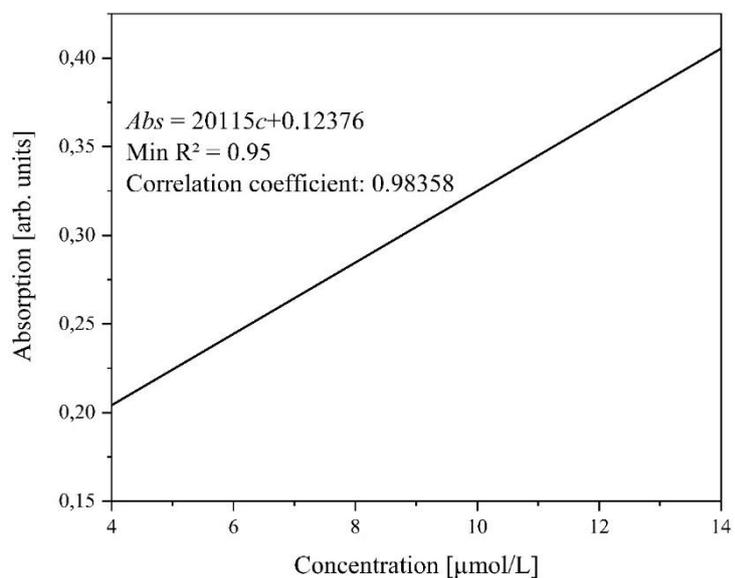


Figure S29: Calibration line for determining the extinction coefficient for HPV₅Mo at 308 nm (V(V) LMCT).

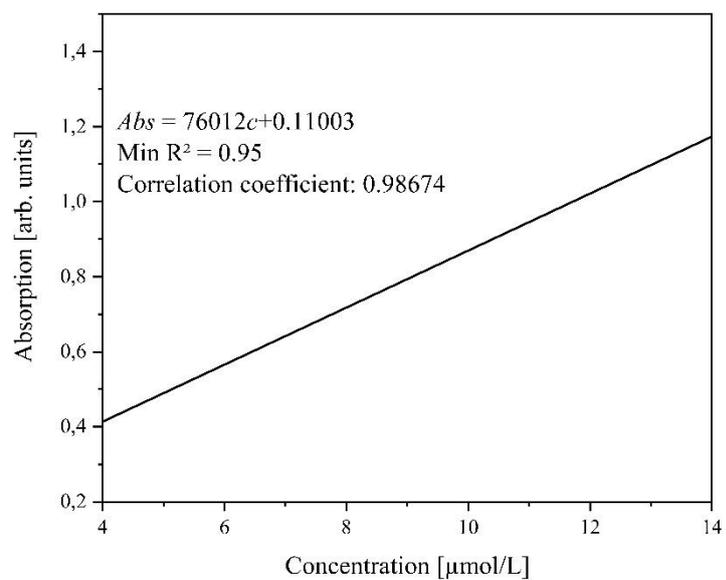


Figure S30: Calibration line for determining the extinction coefficient for HPV₆Mo at 217 nm (Mo(VI) LMCT).

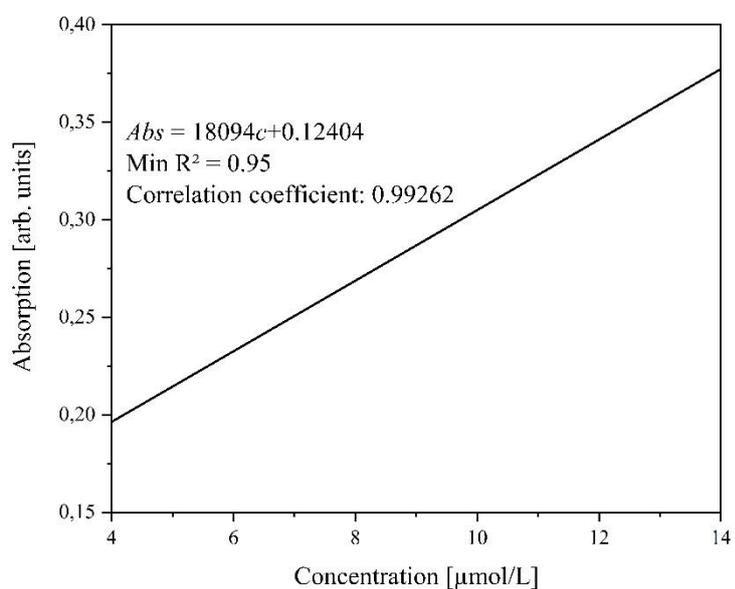


Figure S31: Calibration line for determining the extinction coefficient for HPV₆Mo at 308 nm (V(V) LMCT).

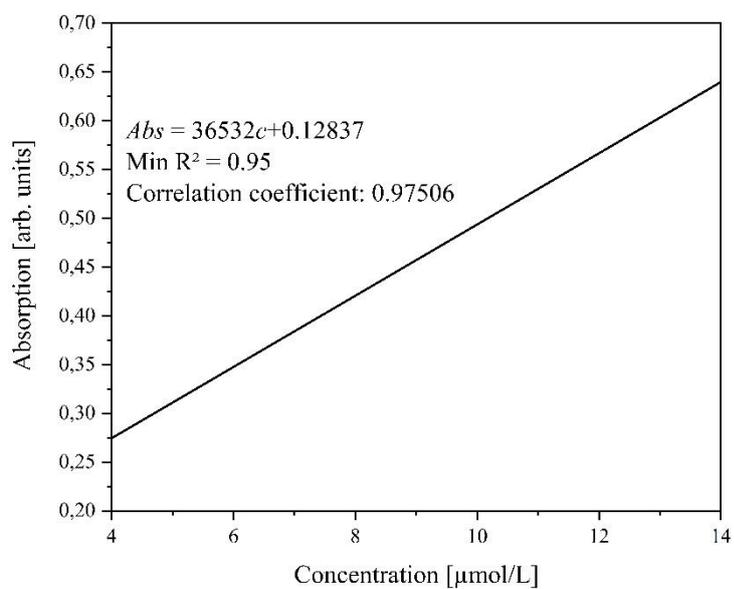


Figure S32: Calibration line for determining the extinction coefficient for NaPVW at 260 nm (W(VI) LMCT).

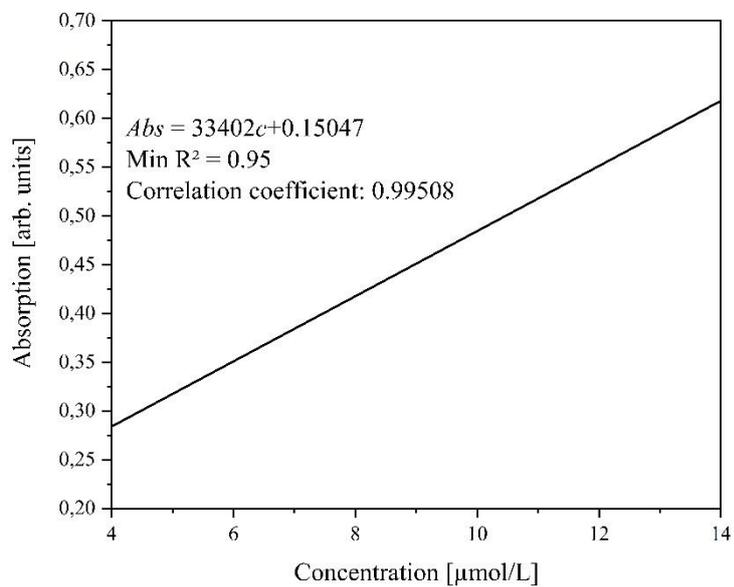


Figure S33: Calibration line for determining the extinction coefficient for NaPV₂W at 242 nm (W(VI) LMCT).

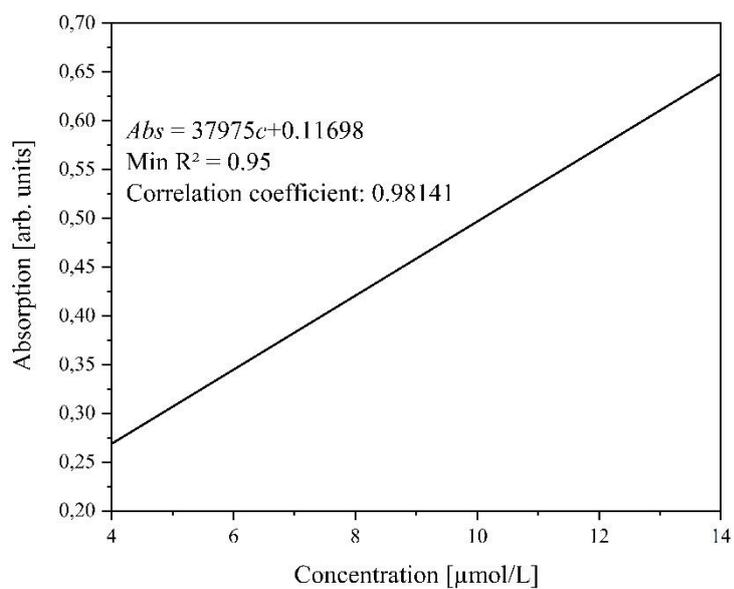


Figure S34: Calibration line for determining the extinction coefficient for NaPV₃W at 250 nm (W(VI) LMCT).

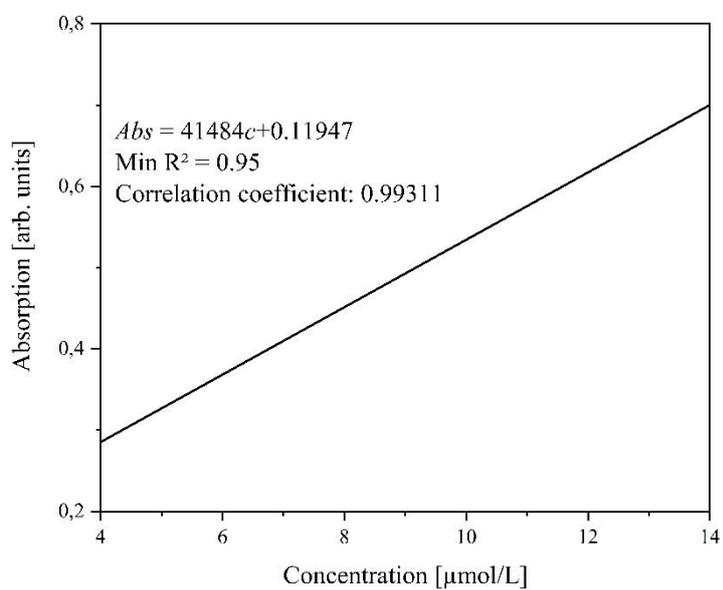


Figure S35: Calibration line for determining the extinction coefficient for NaPV₄W at 240 nm (W(VI) LMCT).

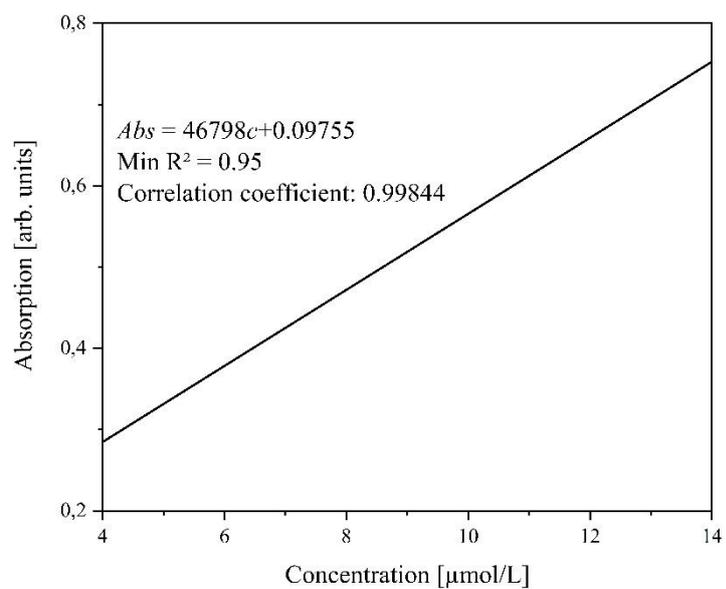


Figure S36: Calibration line for determining the extinction coefficient for NaPV₅W at 235 nm (W(VI) LMCT).

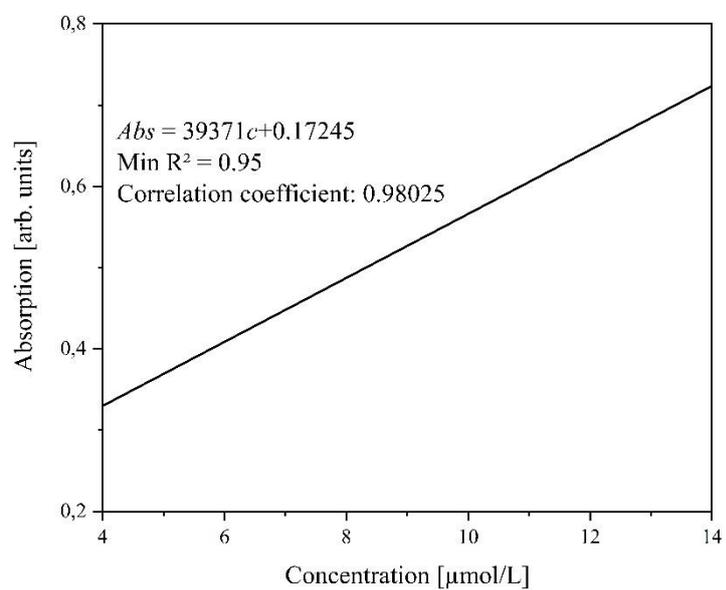


Figure S37: Calibration line for determining the extinction coefficient for NaPV₆W at 234 nm (W(VI) LMCT).

Table 1: Peak maxima (oxidation pathway) and peak minima (reduction pathway) from the CV data and maxima from the SWV data of the POMs in aqueous pH 1 solution (HCl): concentration 1 mmol/L; scan rate 100 mV/s (CV) and 5 mV/s (SWV).

Maximum oxidation pathway CV [mV]	Minimum reduction pathway CV [mV]	Mean value CV [mV]	Peak maxima SWV [mV]
H₃[PMo₁₂O₄₀]			
-	-	-	-570
-277	-	-	-370
-	-169	-	-150
-87.7	8.33	-39.7	-
-	-	-	50
218	167	193	205
-	-	-	340
H₄[PVMo₁₁O₄₀]			
-	-	-	-575
-485	-445	-465	-425
-270	-335	-303	-320
-120	-25	-73	-150
-	-	-	10
120	85	103	70
-	-	-	215
440	340	390	390
H₅[PV₂Mo₁₀O₄₀]			
-	-	-	-555
-	-	-	-425
-	-	-	-325
-275	-185	-230	-
-110	-30/-35	-73	-155
-	-	-	5
125	90	108	90
425	300	363	380
H₆[PV₃Mo₉O₄₀]			
-	-	-	-530
-	-	-	-420
-300	-340	-320	-325
-	-180	-	-150
-	-45	-	10
115	-	-	95
430	305	368	370
H₇[PV₄Mo₈O₄₀]			
-	-	-	-530
-305	-	-	-345
-	-200	-	-155
-	-	-	-55
60	-	-	-
-	270	-	-

410	-	-	350
H₈[PV₅Mo₇O₄₀]			
-	-	-	-525
-350	-	-	-350
-	-220	-	-175
105	-	-	-80
-	-	-	-40
-	285	-	-
400	-	-	340
H₉[PV₆Mo₆O₄₀]			
-	-	-	-535
-300	-	-	-350
-	-200	-	-165
105	-	-	-
-	-	-	-10
-	235	-	-
405	-	-	345
H₃[PW₁₂O₄₀]			
-345	-400	-373	-375
-65	-140	-103	-95
Na₄[PVW₁₁O₄₀]			
-	-	-	-575
525	410	468	475
Na₅[PV₂W₁₀O₄₀]			
-	-	-	-570
330	180	255	250
525	460	493	490
Na₆[PV₃W₉O₄₀]			
-	-	-	-580
-	120	-	150
280	-	-	255
435	-	-	385
Na_{6.6}H_{0.4}[PV₄W₈O₄₀]			
-	-	-	-580
330	180	-	255
Na_{6.8}H_{1.2}[PV₅W₇O₄₀]			
-	-	-	-580
345	180	263	255
Na_{6.7}H_{2.3}[PV₆W₆O₄₀]			
-	-	-	-570
335	160	248	245

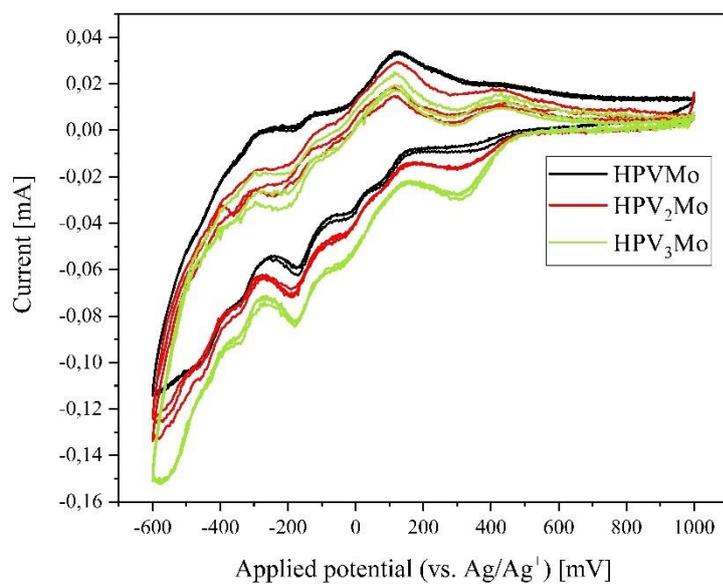


Figure S38: CV data of the POMs HPV_xMo with $x = 1$ to 3 (concentration 1 mmol/L, scan rate 100 mV/s and pH 1 (HCl as supporting electrolyte)).

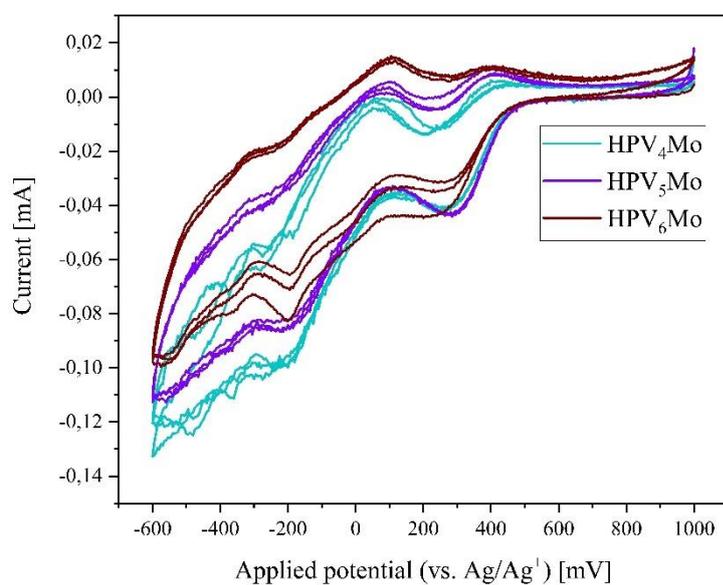


Figure S39: CV data of the POMs HPV_xMo with $x = 4$ to 6 (concentration 1 mmol/L, scan rate 100 mV/s and pH 1 (HCl as supporting electrolyte)).

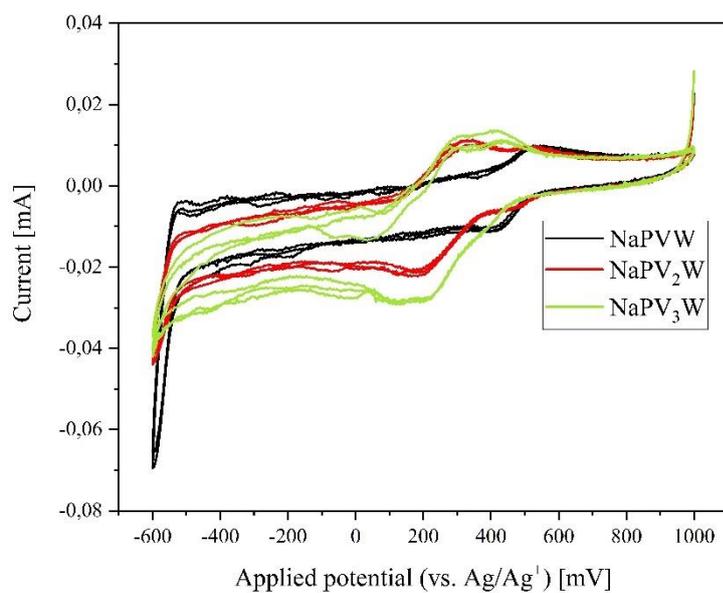


Figure S40: CV data of the POMs NaPV_xW with $x = 1$ to 3 (concentration 1 mmol/L, scan rate 100 mV/s and pH 1 (HCl as supporting electrolyte)).

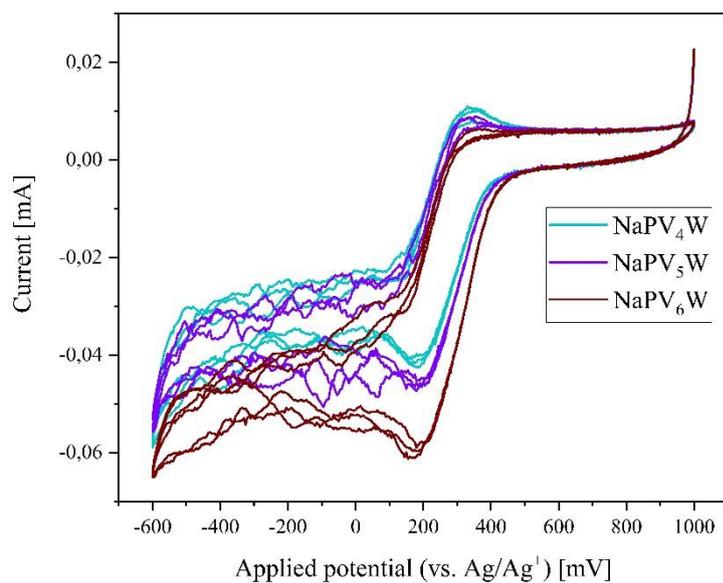


Figure S41: CV data of the POMs NaPV_xW with $x = 4$ to 6 (concentration 1 mmol/L, scan rate 100 mV/s and pH 1 (HCl as supporting electrolyte)).

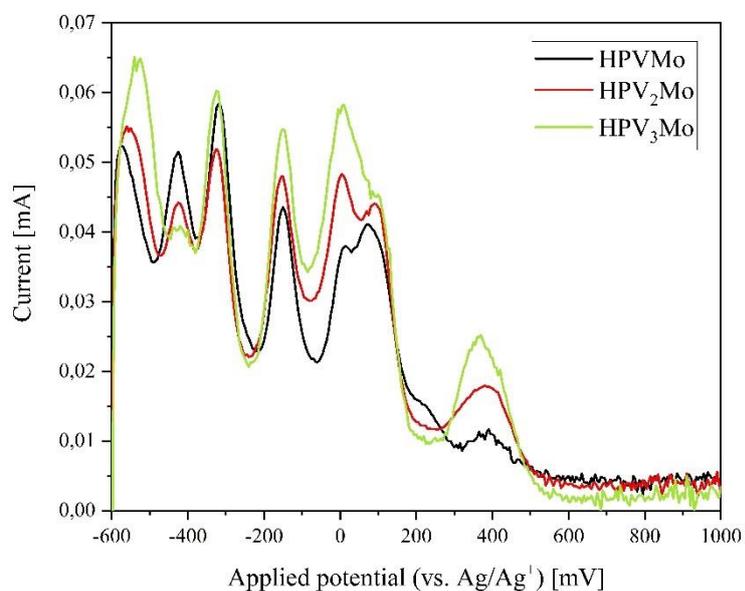


Figure S42: SWV data of the POMs HPV_xMo with $x = 1$ to 3 (concentration 1 mmol/L, scan rate 5 mV and pH 1 (HCl as supporting electrolyte)).

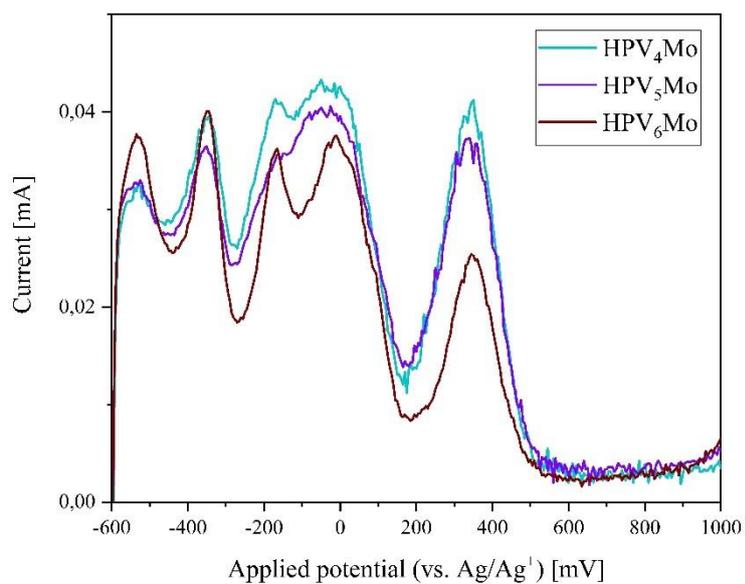


Figure S43: SWV data of the POMs HPV_xMo with $x = 4$ to 6 (concentration 1 mmol/L, scan rate 5 mV and pH 1 (HCl as supporting electrolyte)).

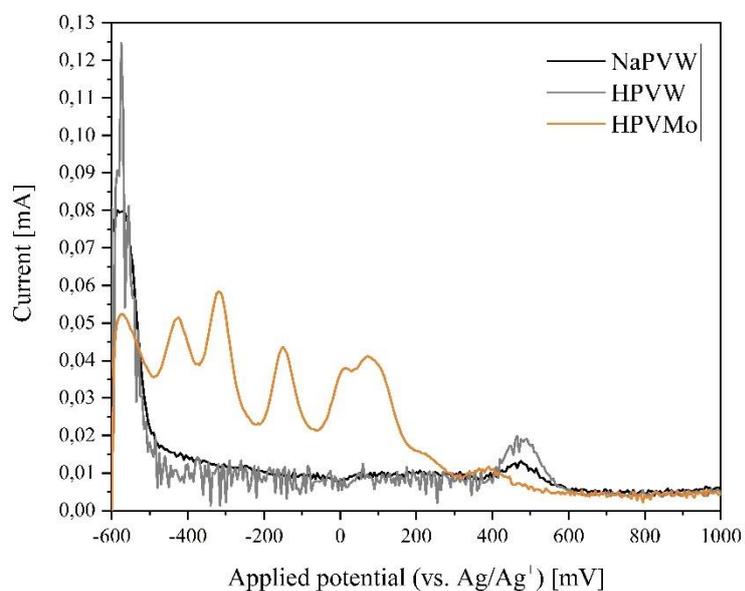


Figure S44: SWV data of the POMs NaPVW, HPVW and HPVMo (concentration 1 mmol/L, scan rate 5 mV and pH 1 (HCl as supporting electrolyte)).

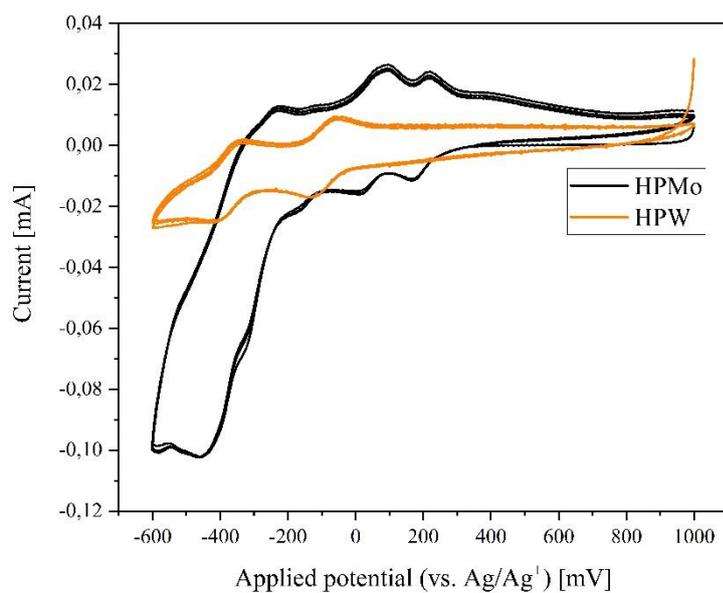


Figure S45: CV data of the POMs HPMo and HPW (concentration 1 mmol/L, scan rate 100 mV/s and pH 1 (HCl as supporting electrolyte)).

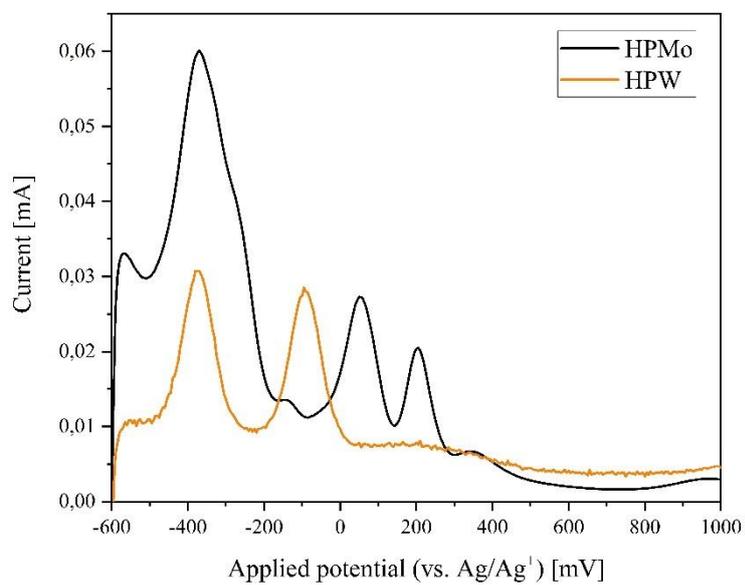


Figure S46: SWV data of the POMs HPMo and HPW (concentration 1 mmol/L, scan rate 5 mV and pH 1 (HCl as supporting electrolyte)).

2 Experimental Details

2.1 Chemicals

- Phosphotungstic acid hydrate: > 99 %, Sigma-Aldrich
- Sodium tungstate dihydrate: 99 %, AlanaR NORMAPUR
- Sodium metavanadate: 96 % Alfa Aesar
- Molybdenum trioxide: 99 %, Alfa Aesar
- Divanadium pentoxide: 99 %, Alfa Aesar
- Phosphoric acid: 85 % in water, Grüssing
- Hydrochloric acid: 37 % in water, VWR chemicals
- Hydrogen peroxide: 30 % in water, VWR chemicals
- Acetic acid glacial: > 99 %, VWR International
- Sodium acetate: 99 %, Merck
- Sodium carbonate: 99 % Grüssing
- Deuterium oxide: 99.9 %, Deutero GmbH

2.2 Analytics

All POMs presented here were characterized for four significantly important properties using selected methods:

1. Composition: Knowledge of the chemical and stoichiometric composition of the POM materials makes it possible to assess the extent to which the desired degree of substitution has been achieved and to estimate the purity of the POM samples. Wet chemical, elemental analytical methods such as AAS or ICP-OES are used for this purpose. Thermogravimetric analyses (TGA) is used in this work to determine the hydrate water content.^[21]
2. Characterization of the POM in the solid-state: Characterization of the POM in the solid-state generates information on the purity, information on the structure type (e.g. Keggin-type) and indirectly information on the degree of substitution, since spectroscopic shifts are known to be generated by mass differences between elements from the periodic table. The methods used for this are essentially vibrational spectroscopic techniques such as attenuated total reflection Fourier transform infrared (ATR-FT-IR) or Raman spectroscopy.^[24]
3. Characterization of the POM in aqueous solution: Spectroscopic analysis of POMs in aqueous solutions allows the behaviour of a POM species in solution to be described. POMs in solutions are known for the pH-dependent formation of numerous dissociation fragments. Likewise, information can be derived about the electronic transitions responsible for the colour of the POM anions. The main methods used for this purpose are nuclear magnetic resonance (NMR) and ultraviolet-visible (UV-Vis) spectroscopy.^[25]

RedOx activity: Electrochemical methods such as cyclic voltammetry (CV) or square wave voltammetry (SWV) are suitable for determining the RedOx activity of a POM species. The information generated from this methods is suitable for estimating the extent to which defined POMs are suitable for RedOx catalytic applications.^[26]

AAS/ICP-OES (elemental analysis)

Samples were analyzed using an ICP-OES-spectrometer for elemental analysis (Fa. Spectro, type ARCOS) for the elements Mo, W, V and P (method ICP-OES). Na was measured with an AAS-F (Fa. Thermo, type Solaar S Series) (method: F-AES without HKL).

TGA analysis:

TGA measurements were performed with a NETZSCH TG 209 F1 220-10-039-K at the Fraunhofer-Zentrum für Angewandte Nanotechnologie CAN. The data were processed with the software Proteus Analysis from NETZSCH. About 20 mg of the sample was weighed into a duran-glas crucible and the change in mass was measured at the following temperature program:

- Tare
- 1 minute waiting time
- Heating to 30 °C with maximum heating rate
- Stay at 30 °C for 15 minutes
- Heating to 350 °C with a heating rate of 10 K/min
- Stay at 350 °C for 30 minute
- The sample was then cooled to room temperature

IR spectroscopy

IR spectra were measured in attenuated total reflection (ATR) measurement mode on a QATR™-S single-reflection ATR (with a diamond prism) from Shimadzu. From the raw data obtained, the baseline was corrected, and the peaks were determined manually. The IR data were then exported as an *x/y* text document.

Raman spectroscopy

Raman spectra were measured on a SENTERRA Raman microscope from Bruker Optik GmbH. The aperture was set to 50 x 1000 μm. A 20 objective was used on the microscope. The excitation laser has a wavelength of 785 nm and the measurement range used was between 75 cm⁻¹ and 1525 cm⁻¹. The integration time was 16 seconds, the number of scans was 8 and the Raman laser power was 10 mW.

NMR-spectroscopy

Samples were measured with a Bruker AVANCEII 600 MHz. Sample preparation: POM (70 mg) was dissolved in deionized water, which had previously been adjusted to the desired pH value using a 2 M hydrochloric acid solution in deionized water. D₂O or acetone-*d*₆ was added. ³¹P spectra: Time Domain Data Sizes (TD) of 32 K, the Number of Scans (NS) were set to 2k (= 2048), the Transmitter Frequency Offset for Channel F1 (O1) and the Spectral Width (SW) were -1 and 40 ppm. The Delay D1 was set to 1 s. ⁵¹V spectra: TD was 32 K, O1 and SW

-520 and 400 ppm, D1 0.5 s and NS was set to 4 K. The NMR analyses were carried out with the software MestReNova®. In MestReNova®, the peaks were first determined, and the data subsequently exported in .csv format.

UV-Vis spectroscopy

Stock solution: The respective POM (0.250 g) was dissolved in deionized water (250 mL) → 1 g/L.

Spectra measurement: All UV-Vis spectra were measured with a Cary 60 UV-Vis spectrometer (Agilent Technologies) in a 3 mL Quartz cuvette (QS). Measurements were carried out using the Cary WinUV software. Measuring range between 200 nm and 800 nm. The absorbance was measured in the slow measurement mode. The data were then exported as a .csv data set. All samples were prepared as follows: Stock solution 1 g/L. From the stock solution 80 µL were filled into the cuvette and 2920 µL were added to reach the final measuring volume of 3 mL.

Extinction coefficients: For determining the extinction coefficients the software Cary concentrations was used. Five calibration standards were prepared from the stock solution (1 g/L) with a final volume of 3 mL for the cuvette:

- 20 µL stock solution + 2980 µL deionized water
- 40 µL stock solution + 2960 µL deionized water
- 50 µL stock solution + 2950 µL deionized water
- 60 µL stock solution + 2940 µL deionized water
- 80 µL stock solution + 2920 µL deionized water

For evaluation equations 1 to 3 were used.

Electrochemistry (CV and SWV):

All CV/SWV measurements were performed in aqueous, hydrochloric acid medium at pH 1 and a concentration of 1 mmol/L on a Metrohm - Autolab PGSTAT101. During the measurement, the solution was purged with nitrogen gas. Working electrode: glassy carbon electrode (diameter: 3 mm); Reference electrode: Ag/Ag⁺ electrode; Counter electrode: platinum electrode. Measurements were taken in the measuring range between -600 and 1000 mV with a scan rate (for CV) of 100 mV/s for 3 scans. All SWV measurements were taken with a scan rate of 5 mV/s, a modulation amplitude of 20 mV and a frequency of 25 Hz. The

measurements were carried out with the software Ivium and the data was subsequently exported as an *x/y* text document.

Origin® 2019b:

All *x/y* files of all analytical data were plotted in Origin® 2019b.

2.3 Synthesis of $\text{Na}_{9-x}\text{H}_x[\text{PW}_9\text{O}_{34}] \cdot x \text{H}_2\text{O}$ according to Domaille *et al.*^[1]

Sodium tungstate dihydrate (20.01 g, 60 mmol, 6 equivalents) was dissolved in deionized water (40 mL) and an 85 % phosphoric acid solution in water (1.17 g, 10 mmol, 1 equivalent) was added. The final pH value was 8.9. Under stirring glacial acetic acid (4.05 g, 70 mmol, 7 equivalents) was added dropwise and during addition a colourless precipitate was formed. The pH changed to 7.4 after complete addition. After two hours of stirring the colourless precipitate was removed by vacuum filtration and was dried in a desiccator for 24 hours. The product was used without further purification. A colourless solid (7.46 g) was obtained.

Characterisation:

Literature hydration water content is seven molecules of water per POM molecule.^[1]

³¹P-NMR (242.9 MHz, $\text{H}_2\text{O}/\text{D}_2\text{O}$, 20 °C): δ [ppm] = -10.82, 2.07.

FT-IR (ATR): $\tilde{\nu}[\text{cm}^{-1}]$ = 3459 (w), 1630 (w, O–H, lattice H_2O), 1056 (s, P–O), 1014 (m, P–O), 932 (s), 882 (m), 812 (s), 760–730 (s, broad).

Elemental analysis calculated for $\text{Na}_9[\text{PW}_9\text{O}_{34}] \cdot 7 \text{H}_2\text{O}$: m/m [%] = Na: 8.07; P: 1.21; W: 64.57. Found: m/m [%] = Na: 7.52; P: 1.32; W: 59.6. Data normalised to tungsten, Na/P/W ratio: 9.06/1.18/9.

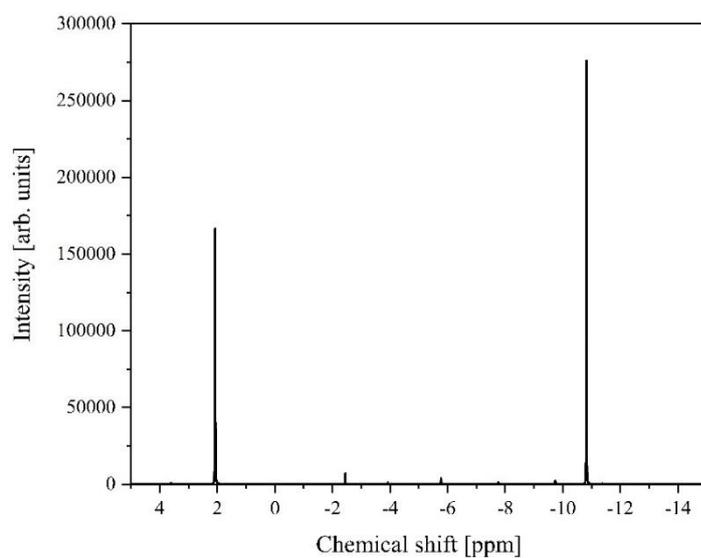


Figure S47: ³¹P-NMR spectrum of [PW₉O₃₄]⁹⁻ in a mixture of 70 % water (pH 5) and 30 % D₂O. Measurement frequency: 242.9 MHz. 85 % H₃PO₄ was used as external standard.

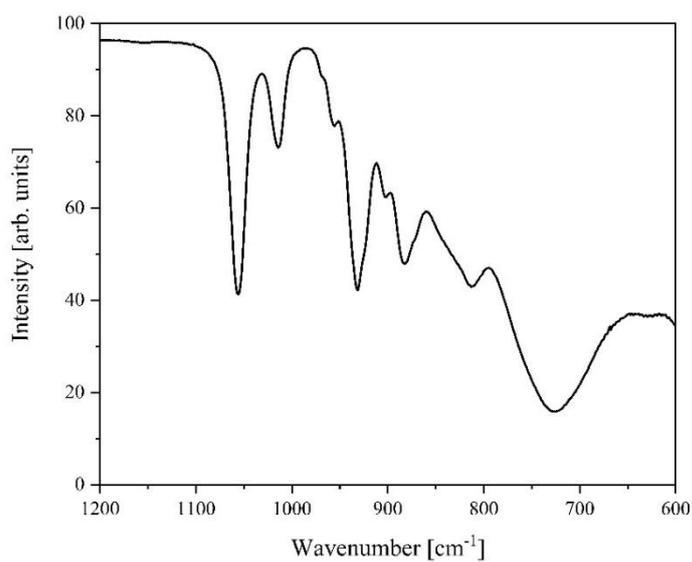


Figure S48: ATR-FT-IR spectrum of [PW₉O₃₄]⁹⁻.

2.4 Synthesis of $\text{Na}_4[\text{PVW}_{11}\text{O}_{40}] \cdot 9 \text{H}_2\text{O}$ according to Domaille *et al.*^[1]

Phosphotungstic acid (11.4 g, 3.6 mmol, 1 equivalent) was dissolved in deionized water (25 mL). The pH value of this solution was 0.5 and was adjusted to 4.8 by addition of small portions sodium carbonate. In parallel sodium metavanadate (0.57 g, 4.5 mmol, 1.25 equivalents) was dissolved in deionized water at 80 °C and added to the $[\text{PW}_{11}\text{O}_{39}]^{7-}$ solution. The pH value of the combined reaction mixture was adjusted to 2.0 by adding a 2 M hydrochloric acid solution in water and then heated up to 60 °C. After cooling to room temperature the pH value was 3.5 and was readjusted to 2.0 using a 2 M hydrochloric acid solution in water. The solution was then reheated to 60 °C. This procedure was repeated once, until upon cooling down to room temperature the pH value remained stable around 2.0. It was filtered and the solution was desalinated using a nanofiltration approach. A yellow solid (9.07 g) was obtained.

Characterisation:

^{31}P -NMR (242.9 MHz, $\text{H}_2\text{O}/\text{D}_2\text{O}$, 20 °C): δ [ppm] = -14.9.

^{51}V -NMR (157.8 MHz, $\text{H}_2\text{O}/\text{D}_2\text{O}$, 20 °C): δ [ppm] = -555.9.

FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1616 (w, O–H, lattice H_2O), 1094, 1066 (s, P–O), 965 (s, M=O_t), 890 (m, (M–O–M)_{vertex}), 764 (s, broad, (M–O–M)_{edge}).

Elemental analysis calculated for $\text{Na}_4[\text{PVW}_{11}\text{O}_{40}] \cdot 9 \text{H}_2\text{O}$: m/m [%] = Na: 3.07; P: 1.03; V: 1.70; W: 67.45. Found: m/m [%] = Na: 2.96; P: 1.13; V: 1.91; W: 64.2. Data normalised to tungsten, Na/P/V/W ratio: 4.05/1.15/1.18/11.

TGA: 5.45 % weight loss upon drying, this corresponds to 9 mol lattice water per mol of the POM.

2.5 Synthesis of $\text{Na}_5[\text{PV}_2\text{W}_{10}\text{O}_{40}] \cdot 14 \text{H}_2\text{O}$ according to a modified procedure of Domaille *et al.*^[1]

Sodium acetate (2.73 g, 33.3 mmol, 12.2 equivalents) was dissolved in deionized water (30 mL) and after dissolution acetic acid was added until the pH value of the solution reached 4.8. In the next step sodium metavanadate (0.71 g, 5.56 mmol, 2.02 equivalents) and sodium tungstate dihydrate (0.92 g, 2.78 mmol, 1.01 equivalents) were added and after dissolution, $\text{Na}_{9-x}\text{H}_x[\text{PW}_9\text{O}_{34}] \cdot x \text{H}_2\text{O}$ (6.67 g, 2.73 mmol, 1 equivalent) was added and stirred for 48 hours. The colour of the solution changed to dark red. It was filtered and then desalinated using a nanofiltration approach. An orange solid (6.25 g) was obtained.

Characterisation:

³¹P-NMR (242.9 MHz, $\text{H}_2\text{O}/\text{D}_2\text{O}$, 20 °C): δ [ppm] = -12.8 to -14.9.

⁵¹V-NMR (157.8 MHz, $\text{H}_2\text{O}/\text{D}_2\text{O}$, 20 °C): δ [ppm] = -527.0 to -565.0.

FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3424 (w), 1620 (w, O–H, lattice H_2O), 1083, 1054 (s, P–O), 952 (s, M=O_t), 876 (m, (M–O–M)_{vertex}), 774 (s, broad, (M–O–M)_{edge}).

Elemental analysis calculated for $\text{Na}_5[\text{PV}_2\text{W}_{10}\text{O}_{40}] \cdot 14 \text{H}_2\text{O}$: m/m [%] = Na: 3.86; P: 1.04; V: 3.42; W: 61.73. Found: m/m [%] = Na: 4.71; P: 1.18; V: 3.69; W: 57.7. Data normalised to tungsten, Na/P/V/W ratio: 6.52/1.21/2.31/10.

TGA: 8.53 % weight loss upon drying, this corresponds to 14 mol lattice water per mol of the POM.

2.6 Synthesis of $\text{Na}_6[\text{PV}_3\text{W}_9\text{O}_{40}] \cdot 13 \text{H}_2\text{O}$ according to Domaille *et al.*^[1]

Sodium acetate (2.73 g, 33.3 mmol, 12.2 equivalents) was dissolved in deionized water (30 mL) and after dissolution acetic acid was added until the pH value of the solution reached 4.8. In the next step sodium metavanadate (1.06 g, 8.33 mmol, 3.05 equivalents) and $\text{Na}_{9-x}\text{H}_x[\text{PW}_9\text{O}_{34}] \cdot x \text{H}_2\text{O}$ (6.67 g, 2.73 mmol, 1 equivalent) were added and stirred for 48 hours. The colour of the solution changed to dark red. It was filtered and then desalinated using a nanofiltration approach. A red solid (6.00 g) was obtained.

Characterisation:

³¹P-NMR (242.9 MHz, $\text{H}_2\text{O}/\text{D}_2\text{O}$, 20 °C): δ [ppm] = -12.1 to -14.9.

⁵¹V-NMR (157.8 MHz, $\text{H}_2\text{O}/\text{D}_2\text{O}$, 20 °C): δ [ppm] = -505.0 to -566.0.

FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3542, 3459, 3361 (w), 1620 (w, O–H, lattice H_2O), 1084, 1053 (s, P–O), 950 (s, M=O_t), 876 (m, (M–O–M)_{vertex}), 765 (s, broad, (M–O–M)_{edge}).

Elemental analysis calculated for $\text{Na}_6[\text{PV}_3\text{W}_9\text{O}_{40}] \cdot 13 \text{H}_2\text{O}$: m/m [%] = Na: 4.84; P: 1.09; V: 5.36; W: 58.1. Found: m/m [%] = Na: 5.22; P: 1.16; V: 5.40; W: 52.8. Data normalised to tungsten, Na/P/V/W ratio: 7.12/1.17/3.32/9.

TGA: 8.16 % weight loss upon drying, this corresponds to 13 mol lattice water per mol of the POM.

2.7 Synthesis of $\text{Na}_y\text{H}_z[\text{PV}_x\text{W}_{12-x}\text{O}_{40}]$ with $x = 4$ to 6 according to a modified procedure of Odyakov *et al.*^[2-4]

Sodium metavanadate was dissolved in deionized water at a temperature of 60 °C. Parallel to this step sodium tungstate dihydrate was dissolved in deionized water and a 85 % solution of phosphoric acid in water was added. The solution was boiled and the aqueous sodium metavanadate solution was added dropwise. After the addition the solution turned into light brown and the final pH value was 7.5 which was adjusted to 1.5 using a 2 M hydrochloric acid solution in water. The dark brown solution was refluxed for 60 min. After cooling to room temperature, the solution was filtered and desalinated using a nanofiltration approach. An intense red coloured solid was obtained.

Characterisation:

NaPV₄W:

³¹P-NMR (242.9 MHz, H₂O/D₂O, 20 °C): δ [ppm] = -10.0 to -13.5.

⁵¹V-NMR (157.8 MHz, H₂O/D₂O, 20 °C): δ [ppm] = -542.0 to -573.0.

FT-IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3342 (w), 1616 (w, O-H, lattice H₂O), 1072, 1053 (s, P-O), 948 (s, M=O_t), 868 (m, (M-O-M)_{vertex}), 756 (s, broad, (M-O-M)_{edge}).

Elemental analysis calculated for $\text{Na}_7[\text{PV}_4\text{W}_8\text{O}_{40}] \cdot 11 \text{H}_2\text{O}$: m/m [%] = Na: 5.95; P: 1.15; V: 7.53; W: 54.4. Found: m/m [%] = Na: 5.06; P: 1.20; V: 6.95; W: 48.9. Data normalised to tungsten, Na/P/V/W ratio: 6.62/1.17/4.11/8.

TGA: 7.55 % weight loss upon drying, this corresponds to 11 mol lattice water per mol of the POM.

NaPV₅W:

³¹P-NMR (242.9 MHz, H₂O/D₂O, 20 °C): δ [ppm] = -6.18 to -14.4.

⁵¹V-NMR (157.8 MHz, H₂O/D₂O, 20 °C): δ [ppm] = -523.0 to -624.0.

FT-IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3500 (w), 1600 (w, O-H, lattice H₂O), 1070, 1052 (s, P-O), 945 (s, M=O_t), 865 (m, (M-O-M)_{vertex}), 751 (s, broad, (M-O-M)_{edge}).

Elemental analysis calculated for $\text{Na}_8[\text{PV}_5\text{W}_7\text{O}_{40}] \cdot 11 \text{H}_2\text{O}$: m/m [%] = Na: 7.09; P: 1.19; V: 9.82; W: 49.6. Found: m/m [%] = Na: 5.78; P: 1.26; V: 9.66; W: 47.6. Data normalised to tungsten, Na/P/V/W ratio: 6.79/1.10/5.13/7.

TGA: 7.49 % weight loss upon drying, this corresponds to 11 mol lattice water per mol of the POM.

NaPV₆W:

³¹P-NMR (242.9 MHz, H₂O/D₂O, 20 °C): δ [ppm] = -7.21 to -13.6.

⁵¹V-NMR (157.8 MHz, H₂O/D₂O, 20 °C): δ [ppm] = -525.1 to -621.0.

FT-IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3500 (w), 1600 (w, O–H, lattice H₂O), 1071, 1059 (s, P–O), 944 (s, M=O_t), 864 (m, (M–O–M)_{vertex}), 748 (s, broad, (M–O–M)_{edge}).

Elemental analysis calculated for $\text{Na}_9[\text{PV}_6\text{W}_6\text{O}_{40}] \cdot 13 \text{H}_2\text{O}$: m/m [%] = Na: 8.21; P: 1.23; V: 12.1; W: 43.8. Found: m/m [%] = Na: 5.69; P: 1.20; V: 11.55; W: 40.68. Data normalised to tungsten, Na/P/V/W ratio: 6.71/1.05/6.15/6.

TGA: 9.65 % weight loss upon drying, this corresponds to 13 mol lattice water per mol of the POM.

See table 2 for details:

Table 2: Experimental details used to synthesize the POMs NaPV_xW with $x = 1$ to 6.

	Sodium metavanadate	Sodium tungstate dihydrate	Phosphoric acid (85 %)	Water for vanadate	Water for tungstate
NaPV₄W	2.03 g 16.6 mmol 4 equivalents	10.53 g 31.9 mmol 8 equivalents	0.51 g 4.4 mmol 1 equivalents	50 mL	50 mL
NaPV₅W	2.65 g 21.7 mmol 5 equivalents	9.64 g 29.2 mmol 7 equivalents	0.54 g 4.68 mmol 1 equivalents	60 mL	50 mL
NaPV₆W	3.33 g 27.3 mmol 6 equivalents	8.66 g 26.3 mmol 6 equivalents	0.57 g 4.94 mmol 1 equivalents	50 mL	50 mL

2.8 Etherate method

The sodium salt NaPV_xW was dissolved in deionized water and a hydrochloric acid solution in water was added. In a separation funnel the acidified solution was mixed with diethyl ether. Upon separation of the phases a third new, oily, and heavy phase with an intense colour was formed at the bottom. The POM ether phase was separated. New acid fractions were added to the aqueous phase and the process was repeated until formation of the third, heavy phase is no longer observed. Combined POM ether phases were dried under reduced pressure to yield a solid product.

See table 3 for details

Table 3: Experimental details for the POM etherate method.

	POM [g]	Water [mL]	Hydrochloric acid (37 %) [mL]	Diethyl ether [mL]
NaPVW → HPVW	2.00	50	20	50
NaPV₂W → HPV₂W	2.01	50	20	50

Characterisation:

HPVW:

³¹P-NMR (242.9 MHz, H₂O/D₂O, 20 °C): δ [ppm] = -14.9.

⁵¹V-NMR (157.8 MHz, H₂O/D₂O, 20 °C): δ [ppm] = -555.9.

FT-IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 1620 (w, O–H, lattice H₂O), 1070 (s, P–O), 959 (s, M=O_t), 876 (m, (M–O–M)_{vertex}), 735 (s, broad, (M–O–M)_{edge}).

Elemental analysis calculated for H₄[PVW₁₁O₄₀] · 18 H₂O: m/m [%] = Na: 0.00; P: 1.01; V: 1.66; W: 65.8. Found: m/m [%] = Na: < 0.02; P: 1.04; V: 1.70; W: 63.0. Data normalised to tungsten, Na/P/V/W ratio: 0.00/1.08/1.07/11.

TGA: 10.33 % weight loss upon drying, this corresponds to 18 mol lattice water per mol of the POM.

HPV₂W:

³¹P-NMR (242.9 MHz, H₂O/D₂O, 20 °C): δ [ppm] = -12.9 to -14.9.

⁵¹V-NMR (157.8 MHz, H₂O/D₂O, 20 °C): δ [ppm] = -528.1, -547.3, -553.3 to -563.9.

FT-IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 1620 (w, O–H, lattice H₂O), 1061.3 (s, P–O), 964 (s, M=O_i), 884 (m, (M–O–M)_{vertex}), 724 (s, broad, (M–O–M)_{edge}).

Elemental analysis calculated for H₄[PVW₁₁O₄₀] · 15 H₂O: m/m [%] = Na: 0.00; P: 1.07; V: 3.53; W: 63.7. Found: m/m [%] = Na: < 0.10; P: 1.15; V: 3.29; W: 66.7. Data normalised to tungsten, Na/P/V/W ratio: 0.00/1.02/1.78/10.

TGA: 9.15 % weight loss upon drying, this corresponds to 15 mol lattice water per mol of the POM.

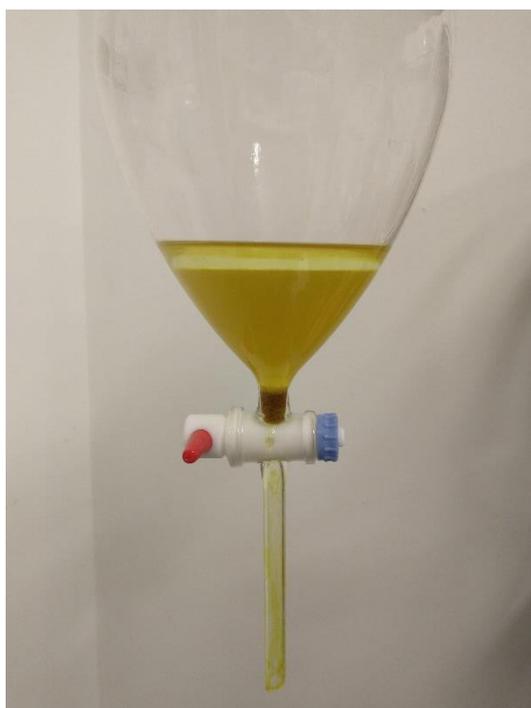


Figure S49: POM etherate method: Extraction of an acidic aqueous POM solution with diethyl ether leads, in the case of low V(V) substituted phosphotungstates, to the formation of a third, etheric POM phase with a higher density than the aqueous phase, from which the POM can be isolated as the corresponding heteropolyacid. Phase above: Diethyl ether, middle: aqueous, acidic POM phase, bottom: oily POM ether phase.

2.9 Crystallography

Both crystals were obtained by slow evaporation of water from an aqueous solution under reduced pressure in a desiccator.

The crystallographic data were solved and refined using Olex2^[5] (ShelX^[6-9]), Shelxtl^[10] and PLATON.^[11] Residual electron density was attributed to hydration water and was refined with a solvent mask (aka SQUEEZE).^[12] The observed disorder of the PO₄ tetrahedron was modelled by assigning a partial occupancy of 0.5 to all four oxygen atoms.

Table 4: Crystal structure data and structure refinement for NaPV₂W and NaPV₅W.

Compound	NaPV ₂ W	NaPV ₅ W
Empirical formula	O ₄₀ PV ₂ W ₁₀	O ₄₀ PV ₅ W ₇
Formula weight	2611.35	2212.62
Temperature/K	99.9(2)	99.97(12)
Crystal system	tetragonal	tetragonal
Space group	P4/mnc	P4/mnc
<i>a</i> [Å]	12.73019(18)	12.67239(15)
<i>b</i> [Å]	12.73019(18)	12.67239(15)
<i>c</i> [Å]	17.9486(4)	17.7115(4)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
Volume [Å ³]	2908.70(10)	2844.28(9)
<i>Z</i>	2	2
ρ_{calc} [g/cm ³]	2.982	2.584
μ [mm ⁻¹]	20.085	14.971
F(000)	2242.0	1936.0
Crystal size [mm ³]	0.24 × 0.22 × 0.1	0.26 × 0.24 × 0.16
Radiation	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)
2 θ range for data collection [°]	4.538 to 59.032	4.546 to 58.912
Index ranges	-17 ≤ <i>h</i> ≤ 17, -17 ≤ <i>k</i> ≤ 17, -23 ≤ <i>l</i> ≤ 24	-17 ≤ <i>h</i> ≤ 17, -17 ≤ <i>k</i> ≤ 17, -23 ≤ <i>l</i> ≤ 24
Reflections collected	117752	114121
Independent reflections	2076 [<i>R</i> _{int} = 0.0521, <i>R</i> _{sigma} = 0.0109]	2028 [<i>R</i> _{int} = 0.0586, <i>R</i> _{sigma} = 0.0109]
Data/restraints/parameters	2076/0/69	2028/0/69
Goodness-of-fit on F ²	1.064	1.032
Final <i>R</i> indexes [<i>I</i> >= 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0285, <i>wR</i> ₂ = 0.0681	<i>R</i> ₁ = 0.0264, <i>wR</i> ₂ = 0.0616
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0348, <i>wR</i> ₂ = 0.0734	<i>R</i> ₁ = 0.0298, <i>wR</i> ₂ = 0.0646
Largest diff. peak/hole [e Å ⁻³]	1.45/-1.18	3.22/-0.91
Deposition number	2240685	2240686

3 References

1. Domaille, P.J.; Watunya, G. Synthesis and tungsten-183 NMR characterization of vanadium-substituted polyoxometalates based on B-type tungstophosphate $PW_9O_{34}^{9-}$ -precursors. *Inorg. Chem.* **1986**, *25*, 1239–1242.
2. Odyakov, V.F.; Zhizhina, E.G. A novel method of the synthesis of molybdovanadophosphoric heteropoly acid solutions. *React. Kinet. Catal. Lett.* **2008**, *95*, 21–28.
3. Odyakov, V.F.; Zhizhina, E.G.; Maksimovskaya, R.I. Synthesis of molybdovanadophosphoric heteropoly acid solutions having modified composition. *Appl. Catal. A Gen.* **2008**, *342*, 126–130.
4. Odyakov, V.F.; Zhizhina, E.G. New process for preparing aqueous solutions of Mo-V-phosphoric heteropoly acids. *Russ. J. Inorg. Chem.* **2009**, *54*, 361–367.
5. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
6. SHELX. Available online: <https://www.noah-itn.eu/wp-content/uploads/2019/03/shelx-manual.pdf> (accessed on 22 February 2023).
7. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. Sec. A: Found. Crystallogr.* **2008**, *64*, 112–122.
8. User Guide to Crystal Structure Refinement with SHELXL. 2008.
9. Hübschle, C.B.; Sheldrick, G.M.; Dittrich, B. ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.
10. Available online: <https://digital-library.theiet.org/content/journals/10.1049/esn.1987.0025?fmt=text> (accessed on 22 February 2023).
11. Spek, A.L.J. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
12. Spek, A.L. PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallogr. Sec. C: Struct. Chem.* **2015**, *71*, 9–18.