Electronic Supplementary Information for Dalton Transactions


**Electronic Supporting Information for**

# Computation of $^{31}$P Chemical Shifts in Lacunary Polyoxotungstates

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# Characterisation

## $^{31}$P NMR

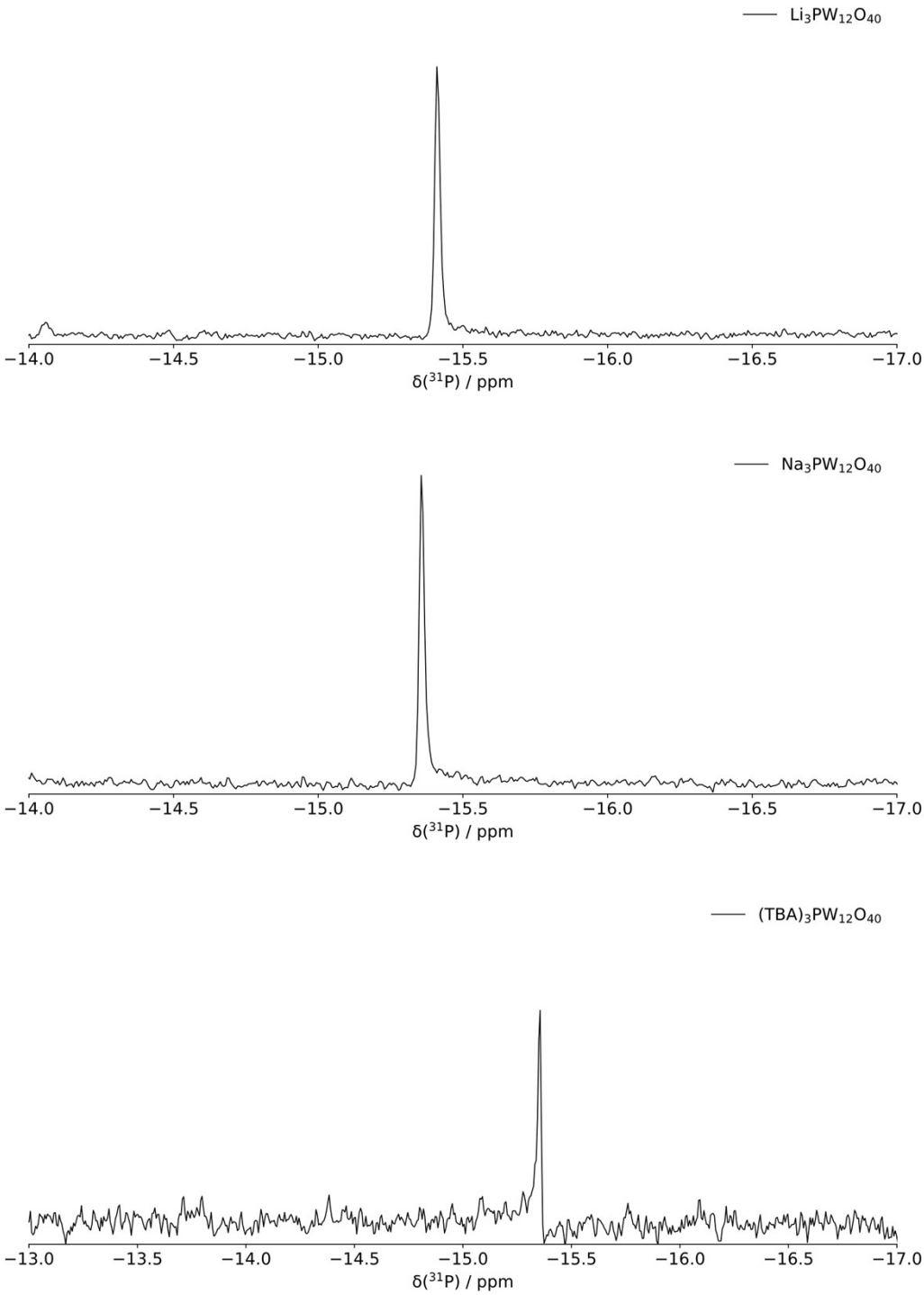


**Figure S1** $^{31}$P spectra of 50 mg Keggin, $X_3[PW_{12}O_{40}]$ (X = $Li^+$, $Na^+$) samples, recorded in $D_2O$. $TBA_3[PW_{12}O_{40}]$ salts (50 mg) were recorded in $CD_3CN$.

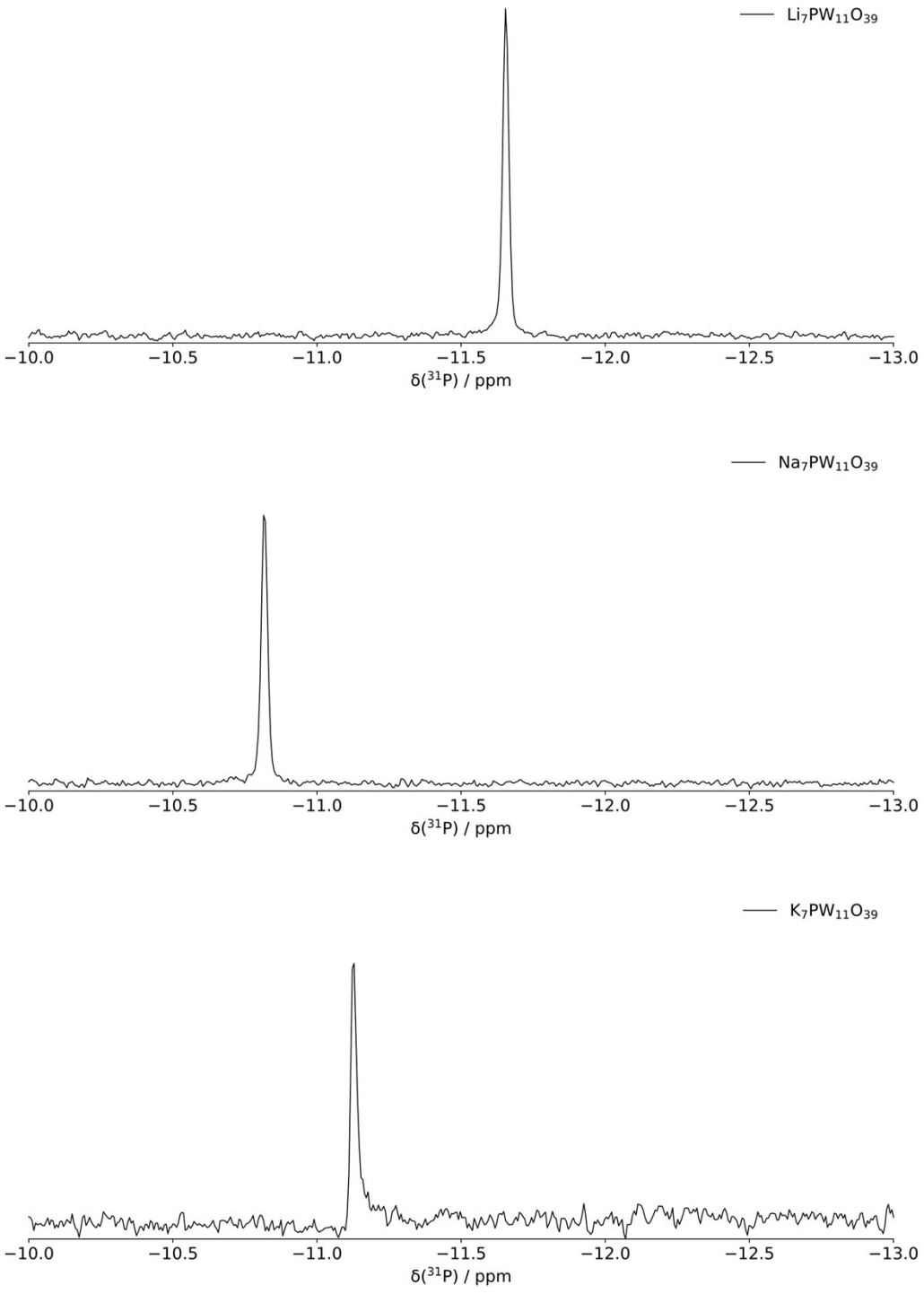


**Figure S2** $^{31}P$ spectra of 50 mg mono–lacunary Keggin, $X_7[PW_{11}O_{39}]$ ($X = Li^+, Na^+, K^+$) samples, recorded in $D_2O$.

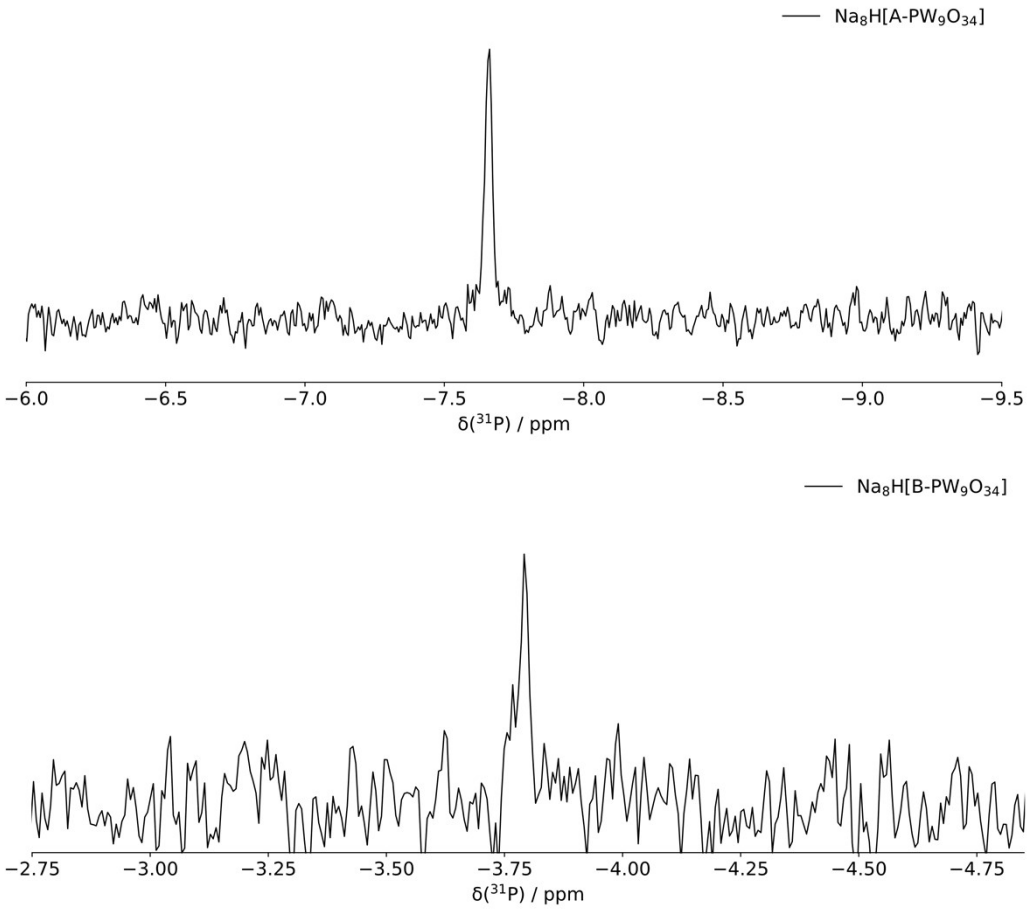


**Figure S3** $^{31}P$ spectra of 50 mg tri–lacunary Keggin samples, $Na_8H[PW_9O_{36}]$, recorded dissolved in $D_2O$.

## FT–IR Spectra

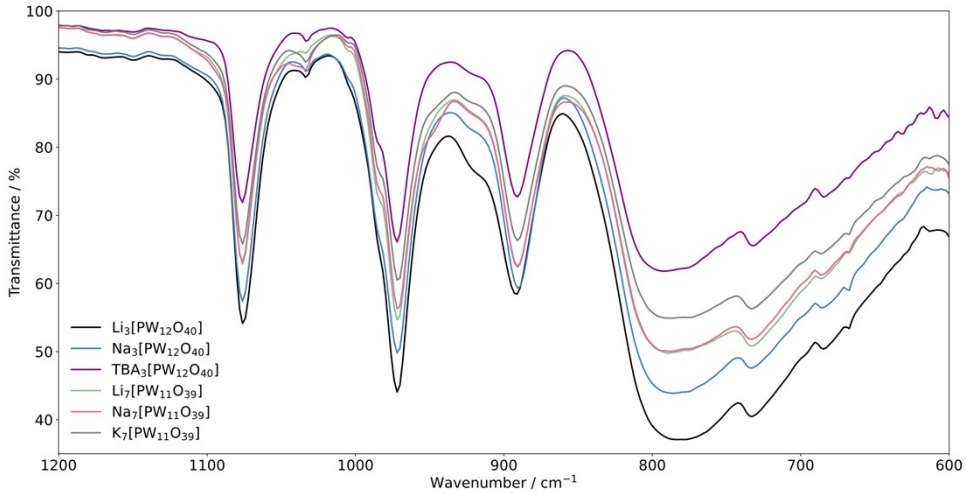


**Figure S4** IR spectra of Keggin, $X_3[PW_{12}O_{40}]$ ($X = Li^+$, $Na^+$, $TBA^+$) and mono–lacunary Keggin, $X_7[PW_{11}O_{39}]$ ($X = Li^+$, $Na^+$, $K^+$) samples.

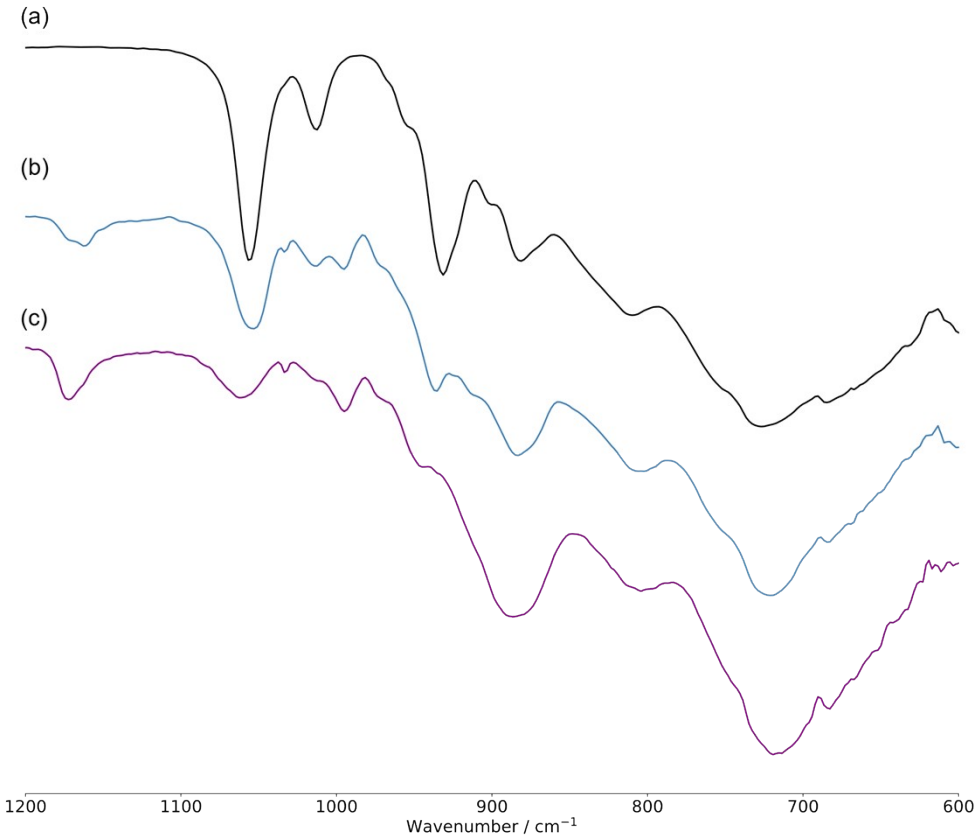


**Figure S5** IR spectra of tri–lacunary Keggin samples, $Na_8H[\Delta–PW_9O_{36}]$, freshly prepared and allowed to air–dry at room temperature, given by (a). However, if $Na_8H[\Delta–PW_9O_{36}]$ is dried at 140 °C for 1–2 h, then the spectrum shown by (b) is given. Prolonged heating (>15 h) at 140 °C produced spectra (c).

## UV–Vis Spectra

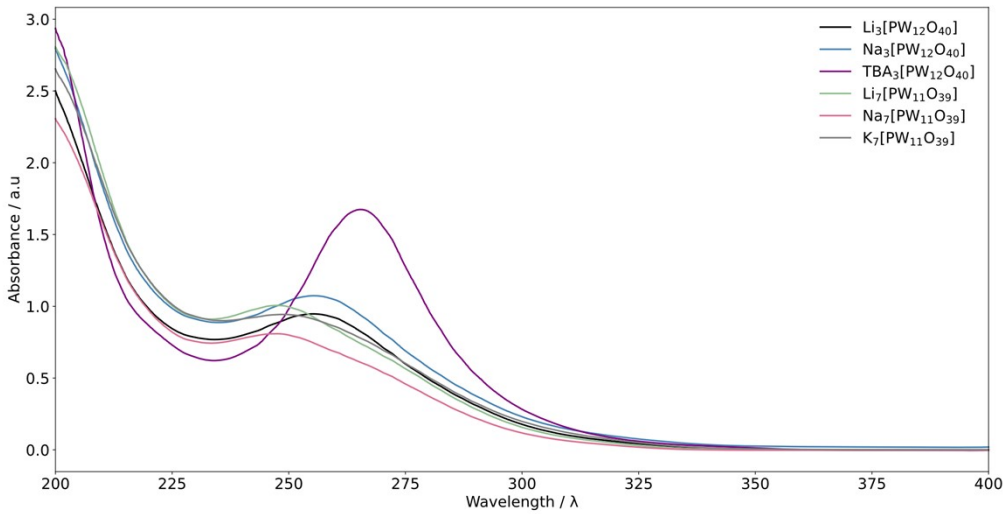


**Figure S6** UV–Vis spectra for 30 µM solutions of Keggin, $X_3[PW_{12}O_{40}]$ ($X = Li^+, Na^+$) and mono–lacunary Keggin, $X_7[PW_{11}O_{39}]$ ($X = Li^+, Na^+, K^+$) samples, recorded in aqueous solution. 30 µM solutions of $TBA_3[PW_{12}O_{40}]$ were recorded in acetonitrile.

## ESI–MS Spectra

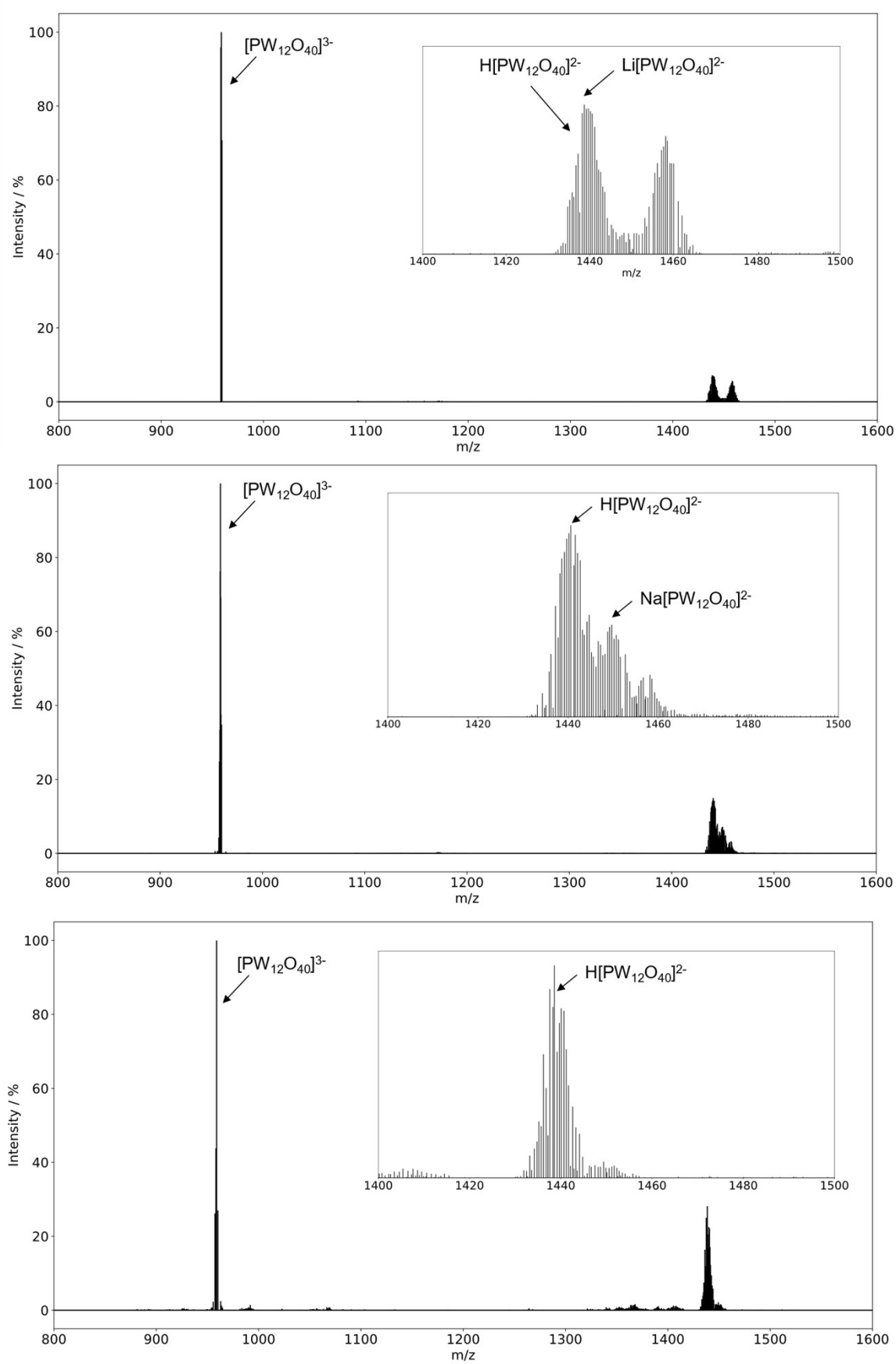


**Figure S7** ESI–MS spectra for 1000 ppm solutions of Keggin, $X_3[PW_{12}O_{40}]$ ($X = Li^+, Na^+$) clusters recorded in aqueous solution (top, middle) and $TBA_3[PW_{12}O_{40}]$ recorded acetonitrile (bottom).

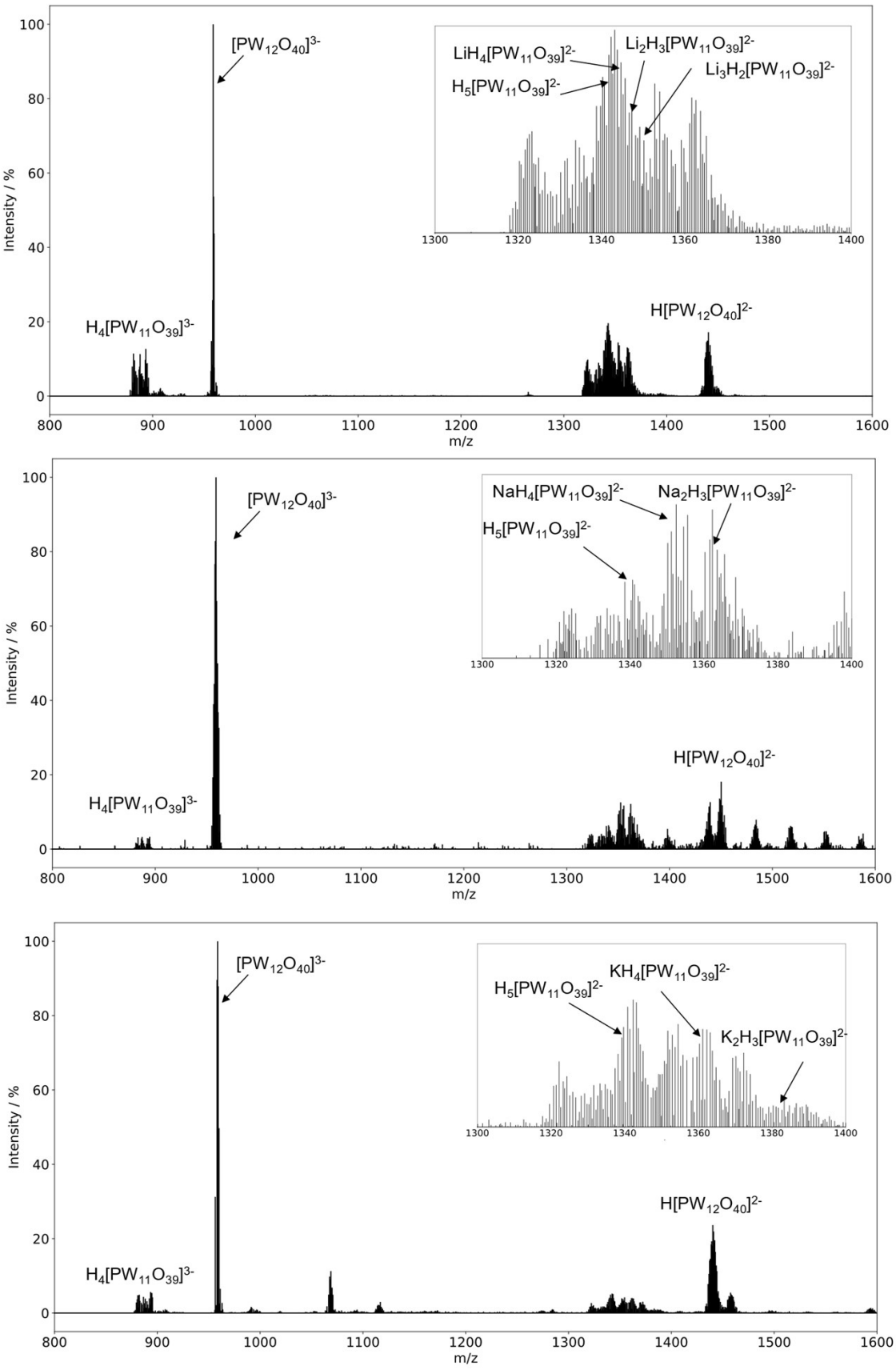


**Figure S8** ESI–MS spectra for 1000 ppm solutions of mono–lacunary Keggin, $X_7[PW_{11}O_{39}]$ ($X = Li^+$, $Na^+$, $K^+$) clusters, recorded in aqueous solution.

**Table S1** Summary of observed fragments from the ionisation of Keggin, $X_3[PW_{12}O_{40}]$ (X = $Li^+$, $Na^+$) and mono–lacunary Keggin, $X_7[PW_{11}O_{39}]$ (X = $Li^+$, $Na^+$, $K^+$) clusters.

| Anion | Observed *m/z* | Theoretical *m/z* |
|---|---|---|
| $[PW_{12}O_{40}]^{3-}$ | 958.8 | 959.00 |
| $H[PW_{12}O_{40}]^{2-}$ | 1439.2 | 1439.02 |
| $Li[PW_{12}O_{40}]^{2-}$ | 1441.7 | 1441.98 |
| $Na[PW_{12}O_{40}]^{2-}$ | 1450.2 | 1450.01 |
| $H_4[PW_{11}O_{39}]^{3-}$ | 893.4 | 893.74 |
| $H_5[PW_{11}O_{39}]^{2-}$ | 1341.2 | 1341.12 |
| $Li_4H[PW_{11}O_{39}]^{2-}$ | 1343.8 | 1344.08 |
| $NaH_4[PW_{11}O_{39}]^{2-}$ | 1352.5 | 1352.11 |
| $K_4H[PW_{11}O_{39}]^{2-}$ | 1360.3 | 1360.16 |

## Density Functional Theory (DFT)

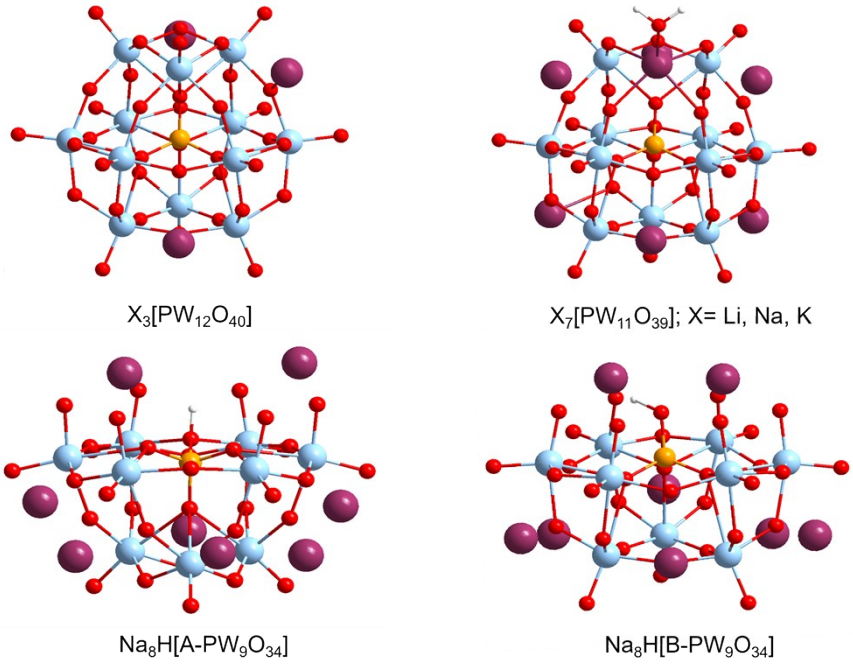


**Figure S9** Structures of Keggin, $X_3[PW_{12}O_{40}]$ (X = $Li^+$, $Na^+$), mono–lacunary, $X_7[PW_{11}O_{39}]$ (X = $Li^+$, $Na^+$, $K^+$) and tri–lacunary, $Na_8H[PW_9O_{36}]$ clusters, optimised at PBE0/TZP label of theory.

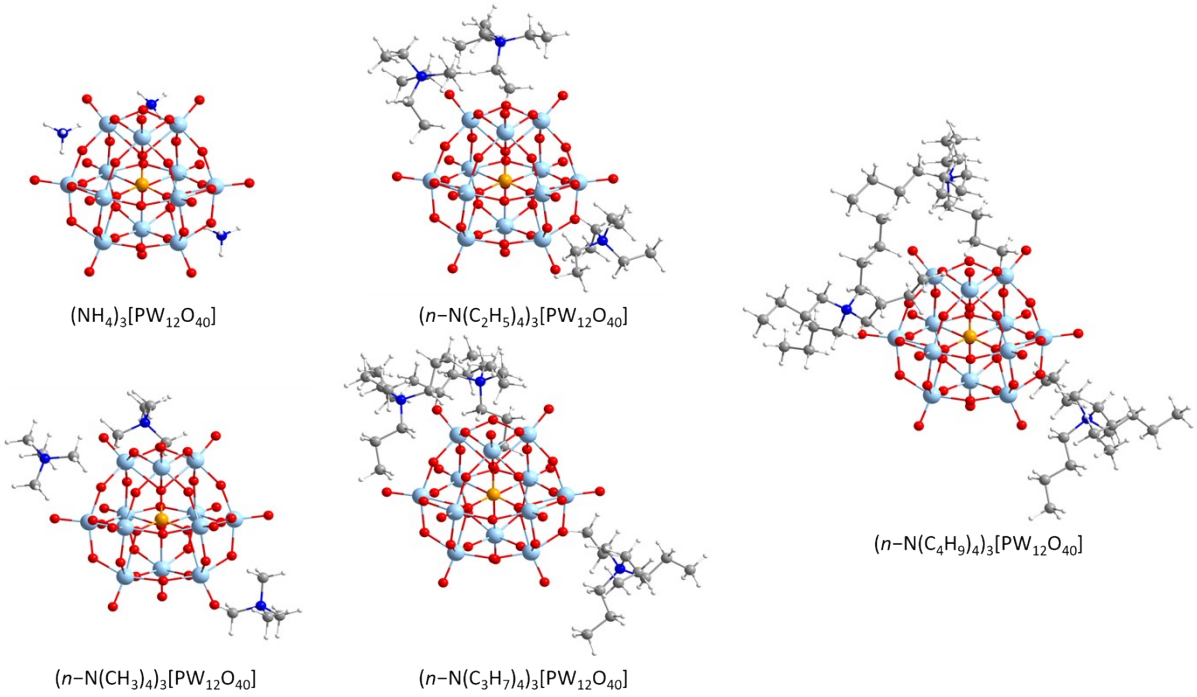


**Figure S10** Structures of $[(n\text{–}C_xH_{2x+1})_4N]_3[PW_{12}O_{40}]$; where x = 0 – 4, optimised at PBE0/TZP label of theory.

**Table S2** Computed, $\delta_{Calc}(^{31}P)$, fitted, $\delta_{Fitted}(^{31}P)$, and experimental, $\delta_{Exp}(^{31}P)$, signals for Keggin, $X_3[PW_{12}O_{40}]$ (X = $Li^+$, $Na^+$, $TBA^+$), mono–lacunary, $X_7[PW_{11}O_{39}]$ (X = $Li^+$, $Na^+$, $K^+$) and tri–lacunary, $Na_8H[PW_9O_{36}]$ clusters.

| Complex | $\delta_{Calc}$ | $\delta_{Fitted}$ |
|---|---|---|
| $Li_3[PW_{12}O_{40}]$ | –12.84 | –14.73 |
| $Na_3[PW_{12}O_{40}]$ | –13.04 | –14.87 |
| $TBA_3[PW_{12}O_{40}]$ | –12.33 | –14.62 |
| $Li_7[PW_{11}O_{39}]$ | –7.27 | –11.24 |
| $Na_7[PW_{11}O_{39}]$ | –7.35 | –11.29 |
| $K_7[PW_{11}O_{39}]$ | –8.55 | –12.04 |
| $Na_8H[A\text{–}PW_9O_{36}]$ | –5.10 | –9.87 |
| $Na_8H[B\text{–}PW_9O_{36}]$ | 6.28 | –2.72 |

**Table S2** Computed energies (PBE/TZP) for the highest occupied (HOMO), lowest unoccupied molecular orbitals (LUMO) and the corresponding energy gap for Keggin, $X_3[PW_{12}O_{40}]$ ($X = Li^+$, $Na^+$, $TBA^+$), mono–lacunary, $X_7[PW_{11}O_{39}]$ ($X = Li^+$, $Na^+$, $K^+$) and tri–lacunary, $Na_8H[PW_9O_{36}]$ clusters, reported in eV.

| Complex | HOMO | LUMO | Gap |
|---|---|---|---|
| $Li_3[PW_{12}O_{40}]$ | –7.909 | –5.466 | 2.443 |
| $Na_3[PW_{12}O_{40}]$ | –7.608 | –5.117 | 2.491 |
| $TBA_3[PW_{12}O_{40}]$ | –7.877 | –3.993 | 3.884 |
| $Li_7[PW_{11}O_{39}]$ | –7.591 | –4.766 | 2.825 |
| $Na_7[PW_{11}O_{39}]$ | –7.097 | –4.181 | 2.916 |
| $K_7[PW_{11}O_{39}]$ | –6.749 | –3.828 | 2.921 |
| $Na_8H[A–PW_9O_{36}]$ | –6.549 | –3.305 | 3.244 |
| $Na_8H[B–PW_9O_{36}]$ | –6.702 | –3.586 | 3.116 |