

Supplementary Material

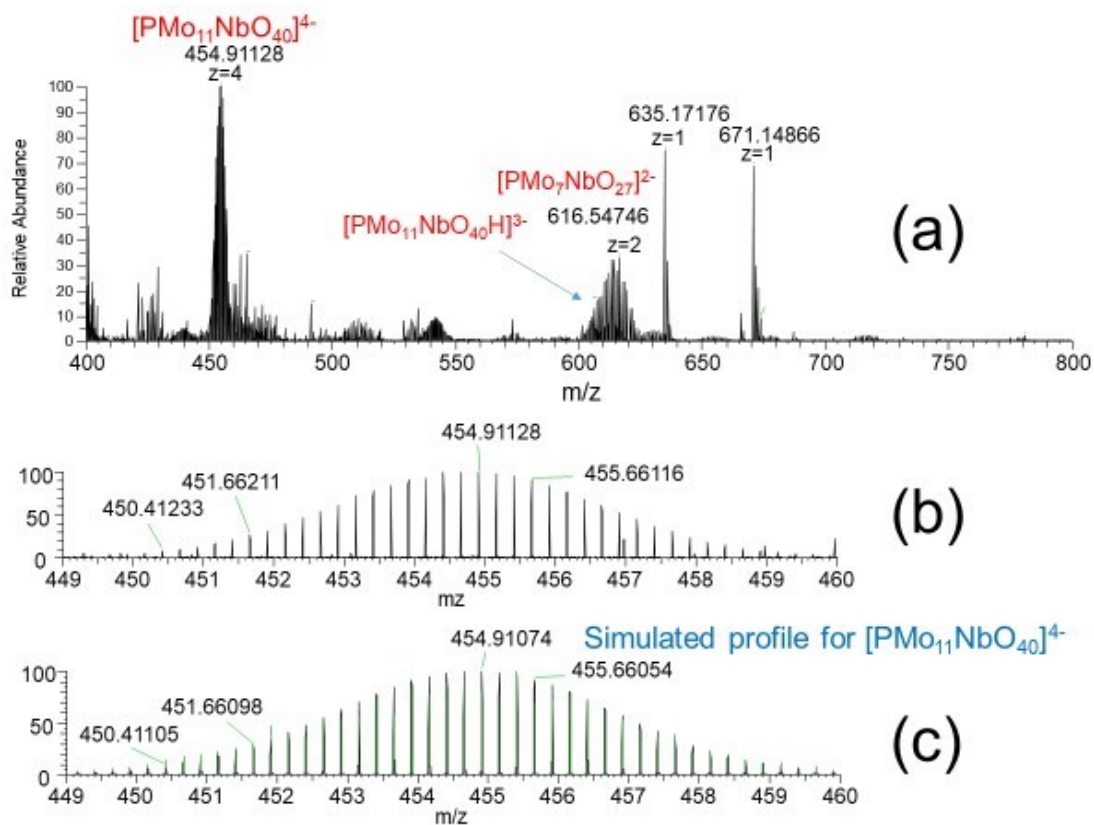


Figure S1. High-resolution ESI-MS spectra of reaction mixture of $H_3PMo_{12}O_{40}$ and $K_8Nb_6O_{19}$ (1 equivalent of Nb to $H_3PMo_{12}O_{40}$) which was heated at 85 °C for 3 h followed by centrifugation. The resulting solution was then dissolved in acetonitrile. (a) $m/z = 400$ –800. (b) Enlarged $m/z = 449$ –460, and (c) simulated profile of $[PMo_{11}NbO_{40}]^{4-}$.

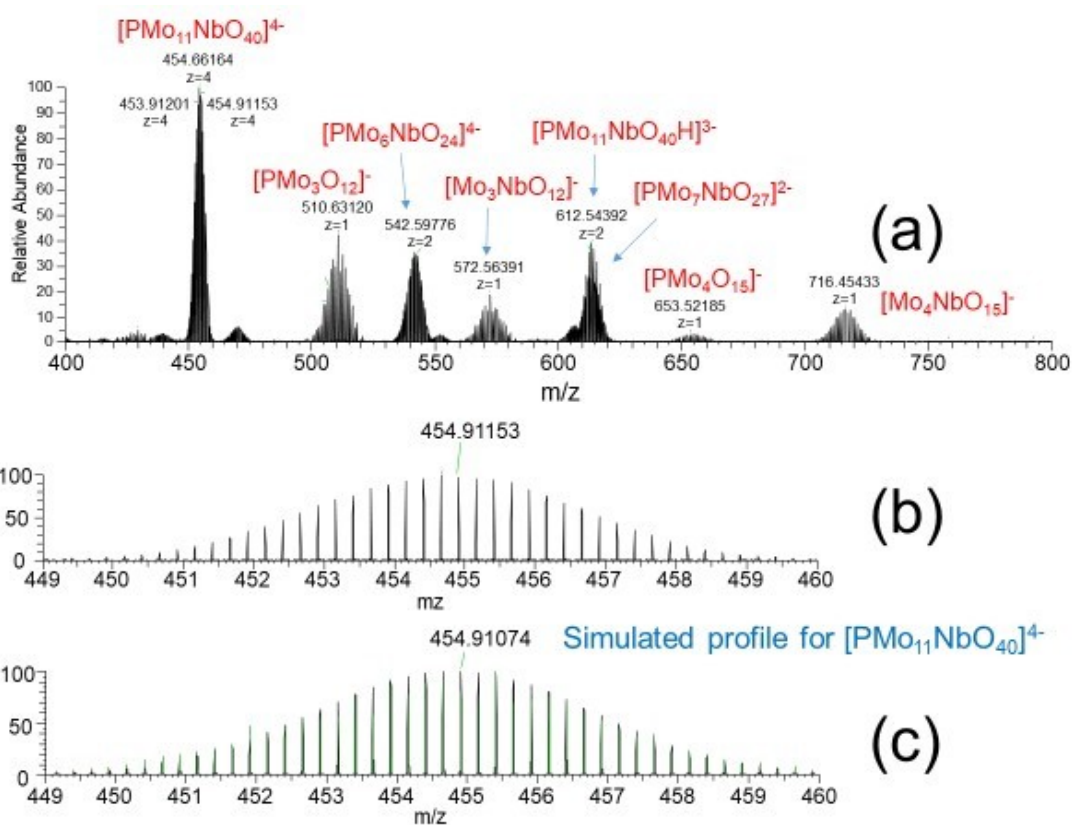


Figure S2. High-resolution ESI-MS spectra of the solid obtained by freeze-drying a solution of $\text{H}_3\text{KPMo}_{11}\text{NbO}_{40}$ dissolved in acetonitrile. (a) $m/z = 400\text{--}800$. (b) Enlarged $m/z = 449\text{--}460$, and (c) simulated profile of $[\text{PMo}_{11}\text{NbO}_{40}]^{4-}$.

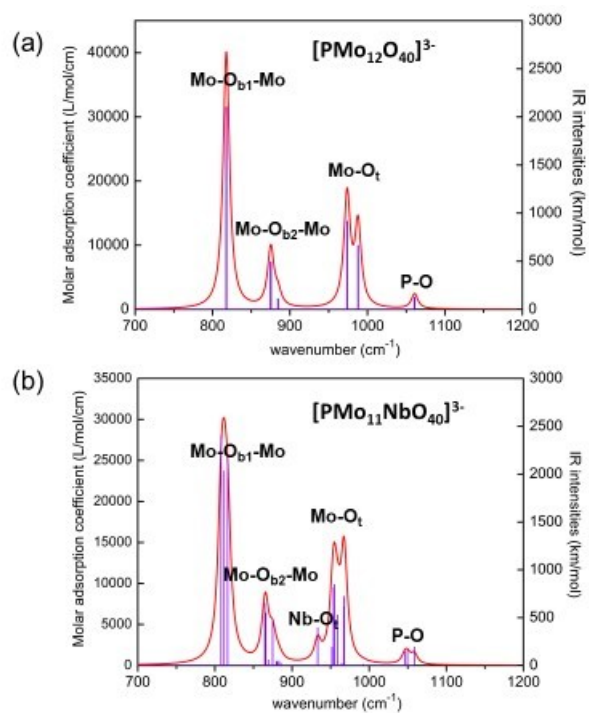


Figure S3. Simulated IR spectra of (a) [PMo₁₂O₄₀]³⁻ and (b) [PMo₁₁NbO₄₀]³⁻ at the B3LYP/6+31+G(d, p)/SDD level.

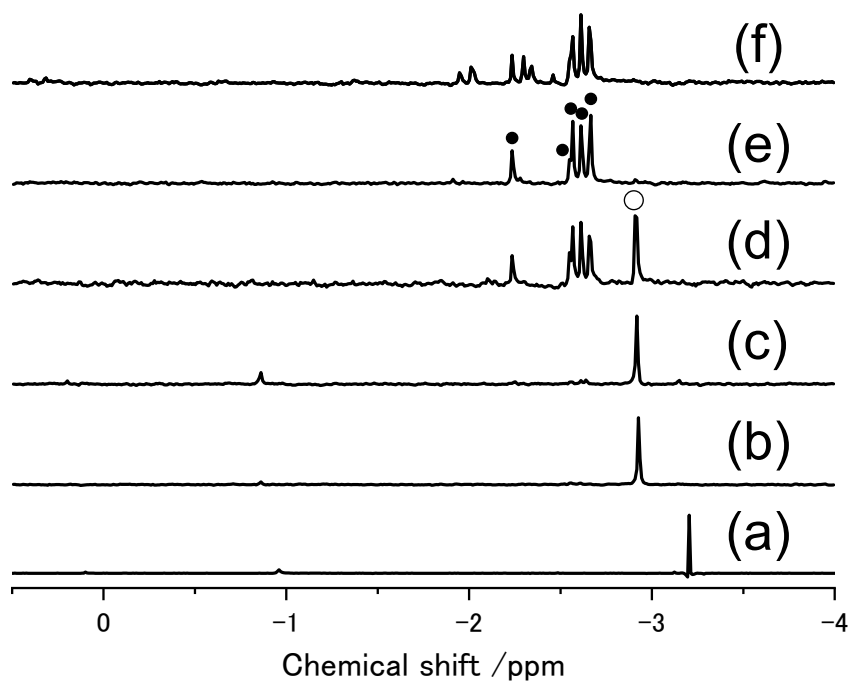


Figure S4. ^{31}P NMR spectra of (a) $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (0.15 M) and the solid obtained after freeze-drying the reaction mixture of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (0.15 M) with (b) 1, (c) 2, (d) 3, (e) 4, and (f) 5 equiv of Nb ($\text{K}_8\text{Nb}_6\text{O}_{19}$) in H_2O . The reaction mixture was heated at $85\text{ }^\circ\text{C}$ for 3 h, and the precipitate was removed by centrifugation. The open circles and five closed circles indicate peaks assignable to $[\text{PMo}_{11}\text{NbO}_{40}]^{4-}$ and $[\text{PMo}_{10}\text{Nb}_2\text{O}_{40}]^{6-}$, respectively. The solid ($\sim 30\text{ mg}$) was dissolved in D_2O ($\sim 1\text{ mL}$).

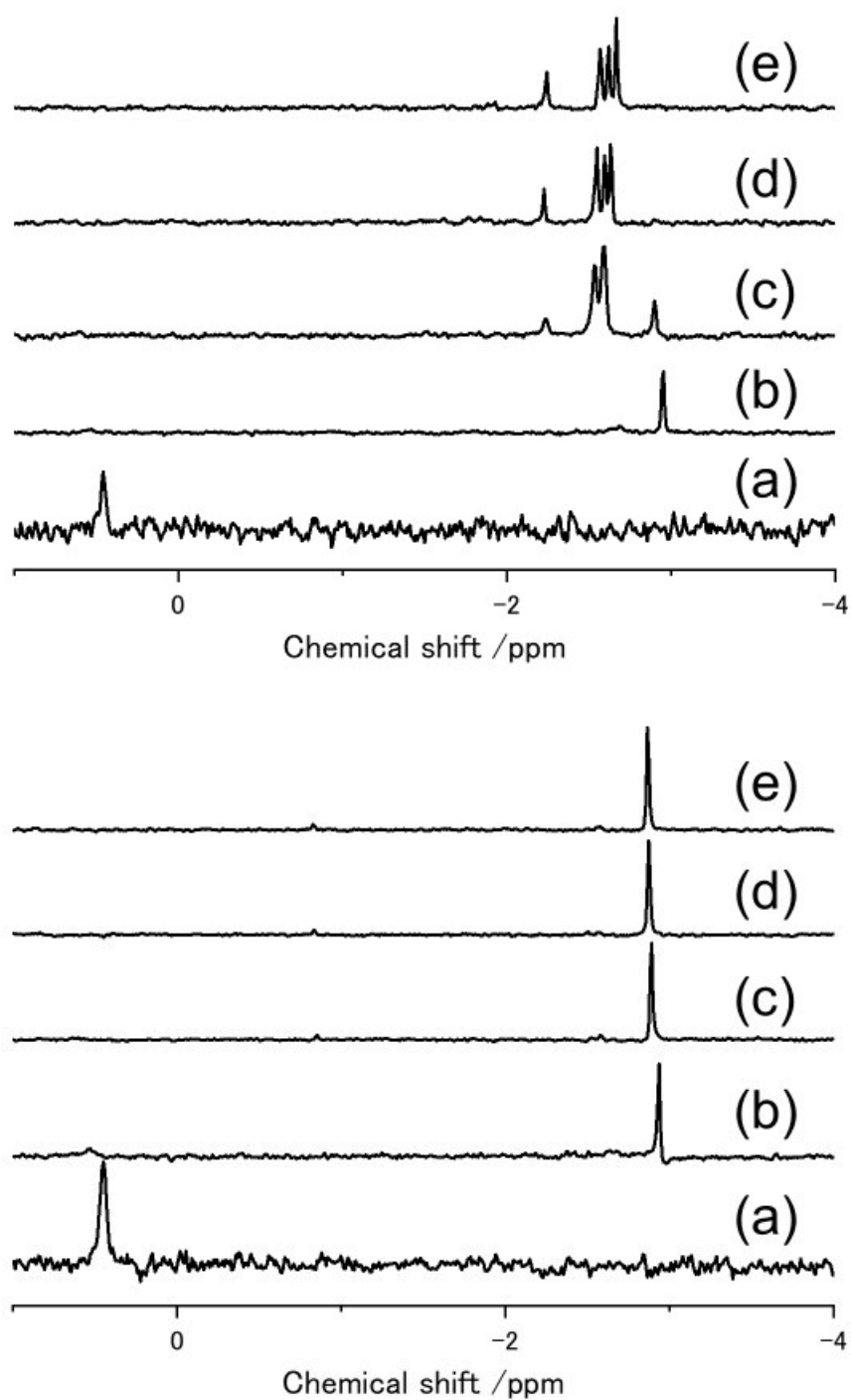


Figure S5. ^{31}P NMR spectra of (top) $\text{K}_5[\text{PMo}_{10}\text{Nb}_2\text{O}_{40}]$ and (bottom) $\text{H}_3\text{K}[\text{PMo}_{11}\text{NbO}_{40}]$ in (a) 6 M HCl, (b) 1.2 M HCl, (c) 0.24 M HCl, (d) 0.048 M HCl, and (e) 0.0096 M HCl aqueous solution.

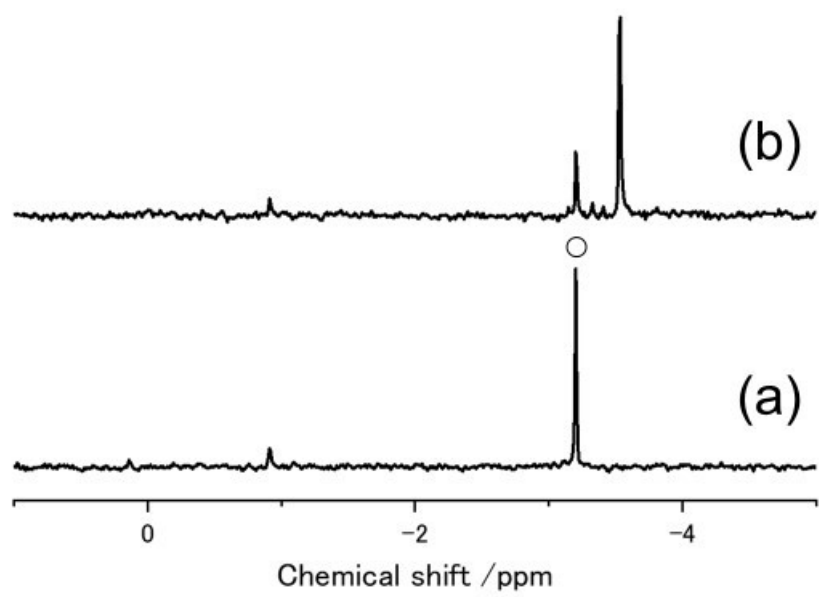


Figure S6. ^{31}P NMR spectra of (a) $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ and (b) $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$. Solid (~ 30 mg) was dissolved with D_2O (~ 1 mL).