Supporting Information for:

Self-Assembly and Ionic-Lattice-like Secondary Structure of a Flexible Linear Polymer of Highly Charged Inorganic Building Blocks

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**Materials and Methods**

**Materials.** All other chemicals were of analytical grade, obtained from commercial sources and used as received. Solutions were prepared with Millipore Direct-Q water.

**Instruments and procedures.** Single crystal X-ray diffraction data were collected using a Rigaku XtalLAB Synergy-S single crystal X-ray diffractometer, which includes a Hy-Pix-6000HE detector and a standard Mo Kα X-ray radiation source (λ = 0.71073 Å). EuTech pH 510 Bench-Top pH meter was used to determine the pH values of the reaction solutions. Optical (UV-Vis) spectra were recorded using an HP 8452A spectrophotometer equipped with a diode-array detector (190-1100 nm range). Electrospray ionization mass spectra (ESI-MS) were recorded from an LTQ Orbitrap XL instrument (Thermo Scientific, with an accuracy of 0.1 amu) with a nano spray ion source. Bruker Advance 400 MHz spectrometer was used to record 31P NMR, H3PO4 (0 ppm) as the reference. DLS data (obtained at Ben-Gurion University) were collected at 25 °C on an ALV-CGS-8F instrument (ALV-GmbH, Germany) at 90 deg (unless otherwise indicated), and the CONTIN method was used to obtain hydrodynamic radii (Rh). DLS and static light scattering (SLS) measurements (obtained at South China University of Technology) were performed using a BI-200SM Research Goniometer System from Brookhaven Instruments using a 633 nm He-Ne laser. Infrared (FTIR) spectra were acquired from KBr pellets using a Nicolet Impact 410 spectrophotometer. Leica, EM GP, an automated vitrification device was used for sampling. Inside 100% humidity chamber, 4µL of the sample was dropped on a glow discharged Cu grid (covered with a lacey-carbon film). The grid was transferred to liquid ethane (mp: 90.34 K) after it was blotted and cooled in liquid nitrogen (77.2K). FEI Tecnai 12 G2 electron microscope (acceleration voltage; 120 kV) was used to acquire cryo TEM images. Energy dispersive x-ray spectroscopy (EDX) analysis was done using a JEOL JEM- 2100F TEM operating at 200 kV equipped with a JED2300T energy dispersive X-ray spectrometer. JEOL Analytical Station software (v. 3.8.0.21) was used for the EDX data analysis. Samples for dry TEM and high-resolution TEM (HR-TEM) and scanning transmission electron microscopy (STEM) were prepared by pipetting 5-10 µL of the aqueous sample solution onto Cu grids covered with thin carbon-support films and dried in air. Elemental analysis results were collected using a Thermo Scientific organic elemental analyzer (OEA) Flash-2000 with CHNSO configuration, and a Spectro Arcos ICP-OES spectrometer.

SAXS measurements with sample-to-detector distance 1.22 m and 6.40 m were performed in an Xenocs Xeuss 2.0 system with MetalJet X-ray source installed. The wavelength of MetalJet X-ray source is 1.34 Å. SAXS measurements with sample-to-detector distance 0.12 m were performed in a Rigaku HomeLab system with microfocus rotating anode X-ray source installed. The wavelength of X-ray source is 1.54 Å. All the sample solutions were placed in quartz capillaries when performing SAXS measurements. For each of the sample measurements, SAXS measurements of corresponding solvents were also carried out for background reduction. SAXS curves with different sample-to-detector distances are jointed to give a full q range. The SAXS curve in the low q range was analyzed by model fitting using software SasView. A theoretical SAXS curve of keggin-type POMs (at the larger a range) was calculated from single crystal structural data using the software Crysol.

**Synthesis of K$_8$Nb$_6$O$_{19}$.** The synthesis of the K$^+$ salt of this Lindqvist ion was adapted from the literature$^1$. Nb$_2$O$_5$ (7.5 g, 0.028 mol) was dissolved in 45 mL of 3 M aqueous KOH with stirred for few minutes, then transferred to a 120 mL Teflon-lined, sealed stainless-steel vessel, and hydrothermally treated at 230 °C for 2 h. After cooling to room temperature, the solution was filtered, resulting in a colorless clear solution. The potassium hexaniobate was precipitated from the solution by addition of ethanol until no more precipitate form. The precipitate was then filtered, washed with ethanol and dried at room temperature. Yield is 60%.

**Synthesis of K$_5$PNb$_2$Mo$_{10}$O$_{40}$·10H$_2$O (K$_5$1).** The synthesis of the monomeric di-niobate substituted Keggin molybdate is a one-pot, self-assembly process. K$_5$Nb$_2$O$_{19}$ (3.393 g, 15×10$^{-3}$ mol Nb) was dissolved in 190 mL H$_2$O along with 10 mL 30% H$_2$O$_2$ in a 500-mL flask. Na$_2$HPO$_4$·7H$_2$O (1.34 g, 5×10$^{-3}$ mol) and Na$_2$MoO$_4$·2H$_2$O (10.896 g, 45×10$^{-3}$ mol) were dissolved in 78 mL 1M HCl, then the mixture solution added quickly to the solution of K$_5$Nb$_2$O$_{19}$. Then 20 mL 1 M HCl was added to the solution. The final pH of the solution was 1.8. The solution was
refluxed at 100 °C for two hours (color changed from orange to bright yellow, and a white precipitate appeared). The pH was adjusted to 3.0 by a slow titration with a concentrated solution of NaHCO₃. The precipitate was removed by filtration, and the volume of the filtrate was reduced to about 40 mL using a rotary-evaporator (if any additional precipitate appeared during this step, it was subsequently filtered off). The solution was then saturated with KCl (about 5 g) at room temperature. Any excess precipitate was immediately filtered off and the solution was heated gently to 30 - 40 °C to ensure complete dissolution of the KCl. The solution was transferred to the refrigerator (4 °C). After three hours, any excess KCl that might have precipitated again was filtered off. Yellow needle-like crystals appeared within a few hours and were harvested after four days. Yield: 42.7%. The product K₅PNb₂Mo₁₀O₄₀·₁₀H₂O (K₅I) was characterized by ³¹P-NMR, ICP and FTIR. Anal. Calcd (%): K, 8.92; P, 1.41; Nb, 8.48; Mo, 43.78. Found (%): K, 8.84; P, 1.47; Nb, 8.44; Mo, 43.99.

Synthesis of [(CH₃(CH₂)₅)₄N]₅PNb₂Mo₁₀O₄₀ (THA₅₁). In order to replace all the alkali metal cations with organic cations, a two-phase system was used, introducing K₅I in an aqueous phase and a stoichiometric amount of organic cations in an organic phase. K₅PNb₂Mo₁₀O₄₀ (0.2264 g, 1 × 10⁻⁴ mol) was dissolved in 1 mL H₂O in a 4 mL vial. Tetrahexylammonium bromide [CH₃(CH₂)₅]₄NBr (THABr) (0.2173 g, 5 × 10⁻⁴ mol) were dissolved in dichloromethane and added to the aqueous solution of the K₅I, forming two separate phases. The mixture was vigorously stirred using a magnetic stirring bar. After 5 minutes, the organic phase was separated on a separatory funnel and dried completely using a rotary evaporator at 40 °C to ensure complete dryness. The product was a waxy, yellow solid; yield: 99%. The product [(CH₃(CH₂)₅)₄N]₅PNb₂Mo₁₀O₄₀ (THA₅₁) was characterized by ³¹P-NMR, FTIR, ESI-MS, element analysis, and single X-ray diffraction. Anal. Calcd (%): C, 40.15; H, 7.30; N, 1.95; P, 0.86; Nb, 5.17; Mo, 26.73. Found (%): C, 41.33; H, 7.72; N, 1.99; P, 0.68; Nb, 5.87; Mo, 25.56.

Crystallization of (THA₄H₁) for single crystal X-ray diffraction. THA₅₁ (0.1 g) was dissolved in 1 mL THF solution. The solution was placed in the refrigerator at 4 °C. X-ray quality crystals formed over several months.

Synthesis of [(CH₃(CH₂)₅)₄N]₅PNb₂Mo₁₀O₄₂ (THA₅₃). To prepare the di-peroxo ligated analog of the monomeric THA₅₁, glacial acetic acid (9 µL, 1.6 × 10⁻⁴ mol) was added to a 2 mL acetonitrile solution of THA₅₁ (14.4 mg, 4 × 10⁻⁶ mol, 2 mM THA₅₁). After adding 30 µL 30% H₂O₂ (2.9 × 10⁻⁴ mol), the solution was stirred vigorously for a few minutes. The mixture was transferred into a quartz cuvette and sealed with a Teflon cap, following by UV-Vis spectroscopy. The reaction was fast and takes about 3-4 hours to reach completion, indicated by a color change from yellow to orange. The solvent and glacial acetic acid were removed by rotary evaporation, after which, the product [(CH₃(CH₂)₅)₄N]₅PNb₂Mo₁₀O₄₂ (THA₅₃) was obtained as an orange powder in high yield (83.3%), as determined by ³¹P-NMR, FTIR and ESI-MS.

Polymerization. The polymerization of [(CH₃(CH₂)₅)₄N]₅PNb₂Mo₁₀O₄₀ (THA₅₁) was carried out with different concentrations of reactants and other conditions. A typical polymerization reaction was as follows. THA₅₁ (14.4 mg, 4×10⁻⁶ mol) was dissolved in 1.5 mL MeCN and 0.5 mL CD₃CN (or in some cases, 2 mL MeCN). In all cases, the concentration of THA₅₁ was 2 mM. After adding 10 µL 30% H₂O₂ (9.77 × 10⁻⁵ mol) to the POM solution at room temperature, the solution was stirred vigorously for a few minutes, and then transferred into a quartz cuvette sealed with a Teflon cap, and following by UV-Vis spectroscopy. The reaction requires 3-4 days to reach completion. The final product was characterized by ³¹P-NMR, FTIR and DLS, SAXS, and cryo-TEM.

The polymerization of THA₅₁ under 1 atm CO₂ (g) was carried out with typical polymerization conditions in a gas-tight quartz cuvette. After adding H₂O₂, the cuvette was purged with CO₂ gas for 20 min. The reaction required approximately 3-4 days to reach completion. The final product was characterized by DLS and dry-TEM.

The polymerization of THA₅₁ under 1 atm Ar (g) was carried out with typical polymerization conditions in a Schlenk flask. After adding H₂O₂, the solution was frozen in liquid N₂ and the air removed using a pump, then refilled with pure Ar gas. The freeze-pump-thaw cycles were carried out six times. No polymer was observed after five days.

NMR Kinetic study of the polymerization process. Sequential ³¹P NMR spectra were obtained during the polymerization process, here carried out in an NMR tube. THA₅₁ (7.2 mg, 2×10⁻⁶ mol) was dissolved in 0.375 mL
MeCN and 0.125 mL CD$_3$CN, after which 5 µL 30% H$_2$O$_2$ (4.8×10$^{-5}$ mol) was added to the POM solution at room temperature. The concentration of THA$_3$I was 4 mM. The solution was stirred vigorously for a few minutes, followed by the acquisition of $^{31}$P NMR spectra after constant time intervals.

**Depolymerization.** A typical polymerization reaction was allowed to reach completion (determined by UV-Vis spectroscopy). The solution was fully characterized (by UV-Vis, $^{31}$P NMR, DLS, and TEM). Glacial acetic acid (5 µL, 8.8×10$^{-5}$ mol) was then added to 2 mL of polymeric I (originally containing 2 mM of THA$_3$I), followed by 30 µL 30% H$_2$O$_2$ (2.9×10$^{-4}$ mol). The reaction was followed by UV-Vis, $^{31}$P NMR, DLS, ESI-MS, and cryo-TEM.

**Exchange of counter ions present in solutions of polymeric I.** (CH$_3$)$_4$NCl (TMACl) or LiClO$_4$ salt were used to exchange counter ions of polymeric I in MeCN. With addition of 11 mg TMACl (0.1 mmol) to the polymer solution, yellow precipitate was quickly produced and the solution became colorless. With centrifugation, the supernatant was removed and the precipitate was washed with MeCN. Then 2 mL water was added to dissolve the precipitate, giving a clear solution (TMA1) with pH = 4.18. The solution was characterized by $^{31}$P NMR, $^1$H NMR, DLS, dry-TEM, and EDX.

Upon addition of 11 mg LiClO$_4$ (0.1 mmol) to polymeric I (2 mM THA$_3$I) in MeCN, the solution remained clear. With evaporation, a yellow powder was obtained. After adding 2 mL water and 2 mL DCM to dissolve the powder, two clear layers were obtained. After centrifugation, the water layer (Li1) with pH = 4.43 was collected.

The solution was characterized by $^{31}$P NMR of I and polymeric I, Me$_4$NCl or LiClO$_4$ salts were added to the MeCN solution of THA$_3$I. After workup, the obtained powders were dissolved in D$_2$O and analyzed by $^{31}$P NMR spectroscopy.

**Synthesis of a di-Nb(V) substituted Wells-Dawson (WD) anion (K$^+$ salt).** K$_8$Nb$_6$O$_{19}$ (0.0813 g, 0.33 mmol Nb) was dissolved in 10 mL of 0.5 M aqueous H$_2$O$_2$. To this stirred solution, 0.8 mL of 1.0 M aqueous HCl was added dropwise, to give a bright yellow solution, followed by addition of 0.804 g (0.17 mmol) of solid K$_{16}[\alpha_2$-P$_2$W$_{17}$O$_{61}]$·10H$_2$O.$^2$ The pH of the solution was 5.76. The solution was heated at 60 °C for two hours (the solution became a little cloudy, and the pH had changed to 6.39). KCl was then added (to 2 M KCl), giving a yellow precipitate. The precipitate was filtered and washed with water. Yield: 70.5 % (based on solid K$_{10}$P$_2$W$_{17}$O$_{61}$). The compound was characterized by FTIR and $^{31}$P-NMR. The FTIR spectrum confirmed the compound to possess the Wells-Dawson structure. In $^{31}$P NMR spectra there are four sets of signals: at -10.53 and -12.78 belonging to mono-Nb K$_7$P$_2$NbW$_{17}$O$_{62}$; at -10.74 and -12.67 belonging to the mono-Nb peroxo K$_7$P$_2$NbW$_{17}$O$_{63}$; at -9.10 and -13.21 belonging to di-Nb K$_8$P$_2$Nb$_2$W$_{16}$O$_{64}$; at -9.27 and -13.09 belonging to di-Nb peroxo K$_8$P$_2$Nb$_2$W$_{16}$O$_{64}$; the 2Nb are on the same side of the Wells-Dawson structure.$^3$

**Synthesis of a di-Nb(V) substituted Wells-Dawson (WD) anion (THA salt).** The same method was used to change K$^+$ countercations of the above mixture of Wells-Dawson anions to organic cations. The K$^+$ salt of WD derivative (0.1688 g) was dissolved in 2 mL H$_2$O in a 4 mL vial. Tetrahexylammonium bromide [CH$_3$(CH$_2$)$_5$]$_4$NBr (THABr) (0.1335 g, 3.1×10$^{-4}$ mol) was dissolved in dichloromethane and added to the aqueous solution, forming two separate phases. The mixture was vigorously stirred using a magnetic stirring bar. After 5 minutes, the organic phase was separated on a separatory funnel and dried completely using a rotary evaporator at 40 °C. The product was a waxy, yellow solid; yield: 87.5 %. The compound was characterized by FTIR, $^{31}$P-NMR, and ESI-MS. FTIR spectrum could found the compound is Wells-Dawson structure. From $^{31}$P NMR, there are four sets of peaks (the peak at -10.82 and -13.19 belong to mono-Nb THA$_7$P$_2$NbW$_{17}$O$_{62}$; the peak at -11.02 and -13.09 belonging to di-Nb peroxo THA$_8$P$_2$Nb$_2$W$_{16}$O$_{64}$; the peak at -9.54 belong to di-Nb peroxo THA$_8$P$_2$Nb$_2$W$_{16}$O$_{64}$; the 2Nb are on the same side of the Wells-Dawson structure).$^3$

**Polymerization and depolymerization.** The method of polymerization and depolymerization were the same with Keggin structure, only difference was the weight of THA salt of WD derivative (28 mg, about 2 mM). The solution was characterized by $^{31}$P NMR, DLS, cryo-TEM, and ESI-MS.
Figure S1. FTIR spectrum of K₅I (M: metal Nb or Mo; Oₖ for corner-sharing MO₆; Oₑ for edge-sharing MO₆).⁴⁻⁵

Figure S2. The ³¹P NMR spectrum of K₅I in D₂O.
Figure S3. The $^{31}$P NMR spectrum of H$_5$PV$_2$Mo$_{10}$O$_{40}$ (H$_5$2) in D$_2$O.

**Structure and relative free energies of the five isomers of [PNb$_2$Mo$_{10}$O$_{40}$]$^{5-}$.**

DFT calculations were carried out to determine the relative stability and population of the five distinct isomers of [PNb$_2$Mo$_{10}$O$_{40}$]$^{5-}$ in aqueous solution. Although this anion has not been analyzed theoretically previously, the vanadium derivative [PV$_2$Mo$_{10}$O$_{40}$]$^{5-}$ has been studied in depth by several groups.\textsuperscript{5,8} All these studies have shown that all five isomers are very close in energy, and that their relative energies depend on solvent, temperature and also might depend on the level of the calculation. A deep analysis of the electronic structure and protonation sites of vanadium molybdates anions can be found in ref 6. Our results for [PNb$_2$Mo$_{10}$O$_{40}$]$^{5-}$ show in general similar behavior. The differences between electronic energies and free energies among all isomers are very small. Hence, the relative free energy values at 25 °C were computed in a range of less than 2 kcal mol$^{-1}$ (Table S1). It is worth mentioning that we have found and characterized seven distinct minima. When we introduce the two Nb atoms in positions 1,5 and 1,8 we obtained two minima with different energies. A similar behavior was found for positions 1,6 and 1,7, as shown in Table S1. This is reminiscent of the alternating short and long bond length distortions observed within the ring structures, M$_n$O$_n$, of certain polyoxomolybdates.\textsuperscript{9,10} In contrast to molybdates, tungstates fail to show significant ring distortions or they are significantly smaller.\textsuperscript{11} DFT calculations show that metal oxide ring distortions originate from a pseudo Jahn-Teller vibronic instability at high symmetry structures.\textsuperscript{12} Distortions in tungstates are not as common as those in molybdates because their HOMO-LUMO gaps are substantially larger. To verify the origin of the distortions observed for [PNb$_2$Mo$_{10}$O$_{40}$]$^{5-}$, we have explored if the two pair of minima in positions 1,5 and 1,8 and in positions 1,6 and 1,7 could be characterized for the analogous tungstate anions [PNb$_2$W$_{10}$O$_{40}$]$^{5-}$, however all attempts have led to a unique structure.

The isomer populations given in Figure 1 were computed considering the partial populations for the seven minima, but considering only five distinct topological isomers α-1,2, α-1,4, α-1,5, α-1,6 and α-1,11 since at room temperature the potential different NMR signals for the two structures identified for each one of isomers α-1,5 and α-1,6 cannot be differentiated. According to our calculations these two isomers are the most abundant with populations of 51% and 30%, respectively. The other three isomers exhibit a much smaller abundance, between 5% and 7%. A similar series of calculations was performed for [PV$_2$Mo$_{10}$O$_{40}$]$^{5-}$ obtaining similar results, with the main difference in the populations of isomers α-1,6 and α-1,5, which are reversed for this anion, with values of 54% and 37%, respectively. The others three isomers also present much lower abundances ranging from 2% to 4%.

All the calculations were performed using Gaussian 09 code with the B3LYP functional under the tight convergence criteria and the ultrafine grid. LANL2DZ pseudopotential was used for V, Nb, Mo, and W atoms, and the 6-31g(d,p) basis set was used for other atoms.
Table S1. Electronic Energies and Free Energies Computed for Anions \([\text{PM}_2\text{Mo}_{10}\text{O}_{40}]^{5-}\) with \(M = V\) (2) and Nb (1). \(^a\)

|          | \(\alpha\)-1,4 | \(\alpha\)-1,2 | \(\alpha\)-1,5 | \(\alpha\)-1,5\(^b\)) | \(\alpha\)-1,6 | \(\alpha\)-1,6\(^c\)) | \(\alpha\)-1,11 |
|----------|----------------|----------------|---------------|---------------------|---------------|---------------------|--------------|
| \(M=Nb\) | \(\Delta E_{\text{elec}}\) | 0.99 | 1.13 | 0.00 | 0.89 | 0.83 | 0.97 | 1.30 |
|          | \(\Delta G\)   | 1.33 | 1.52 | 0.44 | 0.00 | 084 | 1.00 | 1.02 |
|          | \(d_{\text{Nb-Nb}}\) | 3.51 | 3.77 | 5.34 | 5.06 | 6.31 | 6.32 | 7.28 |
| \(M=V\)  | \(E_{\text{elec}}\)  | 1.23 | 1.03 | 0.00 | 0.30 | 0.43 | 0.32 | 0.91 |
|          | \(\Delta G\)   | 1.59 | 1.74 | 0.00 | 0.75 | 0.17 | 0.99 | 1.46 |
|          | \(d_{\text{V-V}}\) | 3.27 | 3.55 | 4.79 | 5.29 | 6.16 | 6.10 | 7.05 |

\(a\) Energies and free energies at 25 °C are given in kcal·mol\(^{-1}\) and distances in Å; \(b\) Structure obtained starting from Nb and V dispositions in sites 1,8; \(c\) Structure obtained starting from Nb and V dispositions in sites 1,7.

Figure S4. FTIR spectrum of THA₃I (M: metal Nb or Mo; O₆ for corner-sharing MO₆; O₆ for edge-sharing MO₆). \(^4\)\(^-\)\(^5\)
Figure S5. The $^{31}$P NMR spectrum of THA$_5$I in CD$_3$CN.

Figure S6. Positive-mode ESI-MS of THA$_5$I in MeCN solution.
Crystallographic data: Single-crystal X-ray structure of one isomer of 1.

A yellow crystal with the shape of a rectangular prism (0.22 x 0.18 x 0.17 mm³) of [N(C₆H₁₃)₄]₄H[PNb₂Mo₁₀O₄₀]·2C₄H₈O was mounted on a CrystalCap™ ALS HT cryo-loop mount for data collection at 100K on a Rigaku XtalLAB Synergy-S single crystal x-ray diffractometer, which includes a Hy-Pix-6000HE detector and a standard Mo Kα x-ray radiation source (λ = 0.71073 Å). Unit cell dimensions, space group assignment, data reduction and finalization were done by using the CrysAlis PRO software package¹³ (ver. 39.49, released 2018). A total of 152862 reflections were collected, of which 24228 were used after merging by SHELXL¹⁴ according to the crystal class and based on Friedel pair equivalency for structure solution. Analytical numeric absorption correction was done using a multifaceted crystal model¹⁵ and empirical absorption correction was done using spherical harmonics¹⁶. The structure was solved in the monoclinic P2₁ space group (no. 4) by SHELXT¹⁷ via intrinsic phasing and refined by SHELXL using a full-matrix least-squares technique as an inversion twin (Flack parameter = 0.49), graphics were done by the Olex2 software package¹⁸.

Figure S7. ORTEP diagram showing the atom labeling scheme of the anion, [PNb₂Mo₁₀O₄₀]⁵⁻. Thermal ellipsoids are drawn at the 40% probability level.

The final refinement cycle included the atomic coordinates and anisotropic thermal parameters of all atoms (not including hydrogen atoms), which converged toward R₁ = 0.0621, wR₂ = 0.1541 and S = 1.020. All non-hydrogen atoms were located except a single terminal carbon atom of the tetrahexylammonium (THA) cation. The location of the two niobium atoms was found using bond length of the O-M bonds (O = PO₄³⁻ oxygens, M = Mo, Nb metal centers), differences in electron density of the refined structure and bond valence sum method,¹⁹ one atom was located precisely while the other was split due to disorder between two locations with partial occupancies, the anionic part of the structure is shown in Figure S7, polyhedral representation is shown in Figure S8. A summary of crystal data is given in Table S2.
Figure S8. Polyhedral representation of the anion $[\text{PNb}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$. Pink octahedra depict a niobium site, both precise and shared. Blue octahedra depict a molybdenum site. Orange tetrahedron shows the location of the phosphate group. Labeling is based on the ORTEP representation, showing the two shared sites of niobium and molybdenum.

The crystalline lattice of $[\text{N}(\text{C}_6\text{H}_{13})_4]_4\text{H}[\text{PNb}_2\text{Mo}_{10}\text{O}_{40}]\cdot2\text{C}_4\text{H}_8\text{O}$ shows discrete $[\text{PNb}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ anions, THA (four per unit) and two co-crystallized tetrahydrofuran (THF) molecules. The lack of a single tetrahexylammonium cation can be attributed to charge balance by a proton being present from the crystallization process, as protonated structures, including POMs, in organic solvents have been previously reported. Also, the bond valence sum calculations support the presence of a proton which is disordered over at least four terminal oxygen atoms (see Table S5). The crystallization process involves the addition of THA to an aqueous acidic solution (pH = 3) of the anion, precipitation of $[\text{N}(\text{C}_6\text{H}_{13})_4]_5[\text{PNb}_2\text{Mo}_{10}\text{O}_{40}]$ from solution and re-dissolve in THF in order to obtain single crystals suitable for diffraction. The niobium sites were located by considerable differences in the bond distances for the 12 metal sites, the crystalline radius of hexacoordinate Mo(VI) being 0.05 Å shorter compared to hexacoordinate Nb(V), resulting in considerable shorter bond length for Mo and O found in the central phosphate group, ca. 2.47 Å for Mo-O bonds compared to ca. 2.51 Å for Nb-O bond lengths, which corresponds well to the difference of their respective Shannon radii. This observed difference was coupled with a lower electron density around the Nb sites that was accounted for from the electron density map ($F_o$) of the refined structure (Figure S9). Finally, bond valence sum method shows that the precisely located Nb atom has 5.127 valence units (v.u.) corresponding to a charge of +5, while the two partially occupied Nb/Mo sites have v.u. in the range of 5.449-5.576, corresponding to a charge of ca. +5.4-5.6, which is the result of the partial occupancy of the atomic site with both Nb(V) and Mo(VI) throughout the crystalline lattice, a comprehensive table is located in Table S5.
**Table S2.** Crystal Data and Structure Refinement Details of [N(C₆H₁₃)₄]₄H[PNb₂Mo₁₀O₄₀]·2C₄H₈O

| Crystal Data |
|-------------|
| **Chemical Formula** | C₁₀₃H₂₁₄N₄O₄₂PNb₂Mo₁₀ |
|  **M_r (g·mol⁻¹)** | 3349.90 |
|  **Crystal system, space group** | Monoclinic, P2₁ |
|  **Temperature** | 100 |
|  **Radiation type, λ (Å)** | Mo Kα, 0.71073 |
|  **a, b, c (Å)** | 14.4887 (2), 22.9828 (2), 21.1268 (2) |
|  **β (°)** | 103.175 (1) |
|  **V (Å³)** | 6849.86 (13) |
|  **μ (mm⁻¹)** | 1.128 |
|  **Z** | 2 |
|  **ρ_calcd (g·cm⁻³)** | 1.624 |

| Data collection |
|----------------|
|  **Diffractometer** | Rigaku Oxford Diffraction XtaLAB Synergy, Dualflex, HyPix |
|  **Absorption correction** | Analytical, CrystAlis PRO 1.171.39.46¹³. Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J. S. Reid¹⁵. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm¹⁶. |
|  **T_min, T_max** | 0.089, 0.176 |
|  **No. of measured, independent and observed [I > 2σ(I)] reflections** | 152862, 24228, 22389 |
|  **R_{int}** | 0.039 |
|  **(sin θ/λ)_{max} (Å⁻¹)** | 0.596 |

| Refinement |
|-------------|
|  **R[F^2 > 2σ(F^2)], wR(F^2), S** | 0.0621, 0.1543, 1.029 |
|  **No. of reflections** | 24202 |
|  **No. of parameters** | 936 |
|  **H-atom treatment** | H-atom parameters constrained |
|  **Δρ_{max}, Δρ_{min} (e·Å⁻³)** | 1.60, -1.42 |
|  **Absolute structure** | Refined as an inversion twin |
|  **Absolute structure parameter** | 0.49 (8) |
|  | w = 1/[σ²(F_o^2) + (0.0607P)² + 51.6614P] where P = (F_o^2 + 2F_c^2)/3 |

Hydrogen atoms were placed at calculated positions (C-H = 0.98-0.99 Å) and refined in riding mode, with U_{iso}(H) = 1.2U_{eq}(C) for CH₂ groups and 1.5U_{eq}(C) for CH₃ groups.
Table S3. Selected Bond Lengths (Å) for [N(C₆H₁₃)₄]₄H[PNb₂Mo₁₀O₄₀]·2C₄H₈O.

| Site 1 | Site 2 | Distance  | Site 1 | Site 2 | Distance |
|--------|--------|-----------|--------|--------|----------|
| P1     | O4     | 1.520(9)  | Mo8    | O8     | 1.977(11)|
| P1     | O1     | 1.568(9)  | Mo8    | O6     | 1.991(10) |
| P1     | O3     | 1.559(8)  | Mo8    | O5     | 1.648(13) |
| P1     | O2     | 1.518(9)  | Mo8    | O16    | 1.908(12) |
| Mo1    | O37    | 1.650(13) | Mo8    | O11    | 1.978(12) |
| Mo1    | O39    | 1.845(9)  | Mo8    | O1     | 2.459(8)  |
| Mo1    | O4     | 2.489(8)  | Mo9    | O8     | 1.998(11) |
| Mo1    | O29    | 2.066(11) | Mo9    | O9     | 1.930(13) |
| Mo1    | O30    | 1.988(11) | Mo9    | O14    | 1.760(8)  |
| Mo1    | O40    | 1.814(10) | Mo9    | O15    | 1.756(7)  |
| Mo2    | O32    | 1.779(10) | Mo9    | O1     | 2.487(8)  |
| Mo2    | O36    | 1.668(12) | Mo9    | O10    | 1.688(10) |
| Mo2    | O31    | 1.919(15) | Mo10   | O20    | 1.992(4)  |
| Mo2    | O35    | 1.754(7)  | Mo10   | O33    | 1.977(4)  |
| Mo2    | O40    | 1.928(11) | Mo10   | O22    | 1.956(4)  |
| Mo2    | O3     | 2.4614(14)| Mo10   | O21    | 1.6604(14)|
| Mo3    | O25    | 1.734(11) | Mo10   | O15    | 1.971(4)  |
| Mo3    | O24    | 1.797(13) | Mo10   | O2     | 2.504(8)  |
| Mo3    | O13    | 1.852(10) | Mo11   | O38    | 1.6503(14)|
| Mo3    | O31    | 1.923(13) | Mo11   | O39    | 1.978(4)  |
| Mo3    | O26    | 1.863(11) | Mo11   | O33    | 1.969(4)  |
| Mo3    | O3     | 2.485(9)  | Mo11   | O34    | 1.981(4)  |
| Mo4    | O27    | 1.678(10) | Mo11   | O35    | 1.965(4)  |
| Mo4    | O4     | 2.459(8)  | Mo11   | O2     | 2.505(8)  |
| Mo4    | O12    | 1.853(11) | Nb1    | O14    | 1.991(6)  |
| Mo4    | O30    | 1.961(10) | Nb1    | O32    | 2.035(6)  |
| Mo4    | O28    | 1.984(10) | Nb1    | O3     | 2.528(8)  |
| Mo4    | O26    | 1.865(10) | Nb1    | O24    | 2.028(7)  |
| Mo5    | O9     | 1.859(10) | Nb1    | O23    | 1.6698(14)|
| Mo5    | O18    | 1.870(10) | Nb2    | O33    | 1.977(4)  |
| Mo5    | O17    | 1.649(8)  | Nb3    | O39    | 1.978(4)  |
| Mo5    | O29    | 1.879(10) | Nb3    | O38    | 1.6503(14)|
| Mo6    | O16    | 1.892(13) | Nb3    | O33    | 1.969(4)  |
| Mo6    | O20    | 1.936(9)  | Nb3    | O2     | 2.505(7)  |
| Mo7    | O18    | 1.958(9)  | Nb3    | O2     | 2.505(8)  |
| Mo7    | O19    | 1.599(13) | Nb3    | O34    | 1.981(4)  |
| Mo7    | O2     | 2.452(8)  | Nb3    | O2     | 2.505(8)  |
| Site 1 | Site 2 | Site 3 | Angle  | Site 1 | Site 2 | Site 3 | Angle |
|-------|-------|-------|--------|-------|-------|-------|-------|
| O9    | Mo5   | O6    | 88.7(6)| O39   | Mo11  | O2    | 92.1(6)|
| O9    | Mo5   | O13   | 83.7(7)| O39   | Mo1   | O4    | 93.5(6)|
| O9    | Mo5   | O12   | 150.8(7)| O39  | Mo1   | O29   | 90.9(6)|
| O9    | Mo5   | O1    | 64.5(6)| O39   | Mo1   | O30   | 162.9(6)|
| O9    | Mo9   | O8    | 88.7(6)| O39   | Nb3   | O34   | 92.8(6)|
| O9    | Mo9   | O1    | 63.2(5)| O39   | Nb3   | O2    | 92.1(6)|
| P1    | O4    | Mo6   | 124.9(5)| O38  | Mo11  | O39   | 101.7(7)|
| P1    | O1    | Mo5   | 124.0(5)| O38  | Mo11  | O33   | 96.4(5)|
| P1    | O1    | Mo8   | 124.4(4)| O38  | Mo11  | O34   | 96.5(5)|
| P1    | O3    | Mo2   | 124.1(4)| O38  | Mo11  | O35   | 109.0(5)|
| P1    | O3    | Nb1   | 124.2(4)| O38  | Mo11  | O2    | 160.7(5)|
| P1    | O2    | Mo11  | 122.3(5)| O38  | Nb3   | O39   | 101.7(7)|
| P1    | O4    | Mo1   | 121.8(5)| O38  | Nb3   | O33   | 96.4(5)|
| P1    | O4    | Mo4   | 125.2(5)| O38  | Nb3   | O34   | 96.5(5)|
| P1    | O1    | Mo9   | 123.1(5)| O38  | Nb3   | O35   | 109.0(5)|
| P1    | O3    | Mo3   | 123.7(4)| O38  | Nb3   | O2    | 160.7(5)|
| P1    | O2    | Mo7   | 126.3(5)| O37  | Mo1   | O39   | 99.6(7)|
| P1    | O2    | Mo10  | 125.3(4)| O37  | Mo1   | O4    | 159.7(6)|
| P1    | O2    | Nb3   | 122.3(5)| O37  | Mo1   | O29   | 95.7(6)|
| P1    | O2    | Nb2   | 125.3(4)| O37  | Mo1   | O30   | 96.2(6)|
| O8    | Mo9   | O1    | 70.2(3)| O37   | Mo1   | O40   | 109.6(6)|
| O8    | Mo8   | O6    | 84.1(4)| O36   | Mo2   | O32   | 100.4(7)|
| O8    | Mo8   | O1    | 71.2(4)| O36   | Mo2   | O31   | 99.4(7)|
| O8    | Mo8   | O11   | 163.0(6)| O36  | Mo2   | O35   | 110.4(6)|
| O7    | Mo5   | O9    | 101.6(7)| O34  | Nb3   | 128.6(5)|
| O7    | Mo5   | O6    | 95.0(5)| O37   | O2    | Mo11  | 91.1(3)|
| O7    | Mo5   | O13   | 106.4(5)| O37  | O2    | Mo10  | 91.0(3)|
| O7    | Mo5   | O12   | 107.6(6)| O37  | O2    | Nb3   | 91.1(3)|
| O7    | Mo5   | O1    | 159.2(5)| O37  | O2    | Nb2   | 91.0(3)|
| O6    | Mo5   | O1    | 70.3(4)| O36   | O18   | Mo7   | 143.4(7)|
| O6    | Mo8   | O1    | 70.5(4)| O36   | O4    | Mo1   | 91.4(3)|
| O5    | Mo8   | O16   | 102.0(6)| O36  | O29   | Mo1   | 128.2(5)|
| O5    | Mo8   | O8    | 93.5(7)| O36   | O28   | Mo4   | 127.5(6)|
| O5    | Mo8   | O6    | 96.9(5)| Mo5   | O9    | Mo9   | 139.1(8)|
| O5    | Mo8   | O1    | 160.7(6)| Mo5  | O1    | Mo9   | 91.6(3)|
| O5    | Mo8   | O11   | 103.5(8)| Mo4  | O4    | Mo1   | 91.7(3)|
| O40   | Mo1   | O39   | 90.6(5)| Mo4   | O4    | Mo6   | 92.3(5)|
| O40   | Mo1   | O4    | 85.5(4)| Mo4   | O12   | Mo5   | 146.1(7)|
| O40   | Mo1   | O29   | 154.2(4)| Mo4  | O30   | Mo1   | 128.0(5)|
| O40   | Mo1   | O30   | 90.1(5)| Mo3   | O24   | Nb1   | 139.3(9)|
| O40   | Mo2   | O3    | 82.8(4)| Mo3   | O13   | Mo5   | 147.7(6)|
| O4    | P1    | O1    | 107.9(5)| Mo3  | O26   | Mo4   | 147.7(6)|
| O4    | P1    | O3    | 110.0(5)| Mo3  | O3    | Nb1   | 91.4(3)|
| O39   | Mo11  | O34   | 92.8(6)| Mo2  | O31   | Mo3   | 136.9(9)|
Table S5. Selected Bond Valence Sum Values for Different Atoms Located within the Anionic Part of [\(\text{N} (\text{C}_6\text{H}_{13})_4\text{H} \text{[PNb}_2\text{Mo}_{10}\text{O}_{40}] \cdot 2\text{C}_4\text{H}_8\text{O}\)].

| Atom      | BVS value | Atom      | BVS value |
|-----------|-----------|-----------|-----------|
| Mo1       | 6.133     | Mo7       | 6.072     |
| Mo2       | 6.008     | Mo8       | 5.958     |
| Mo3       | 6.056     | Mo9       | 6.057     |
| Mo4       | 6.018     | Mo10/Nb2  | 5.449     |
| Mo5       | 5.934     | Mo11/Nb3  | 5.576     |
| Mo6       | 6.016     | Nb1       | 5.127     |

| Terminal oxo | BVS value | Phosphate group | BVS value |
|--------------|-----------|-----------------|-----------|
| O5           | 2.076     | O1              | 1.741     |
| O7           | 1.769     | O2              | 1.869     |
| O10          | 1.852     | O3              | 1.754     |
| O17          | 2.071     | O4              | 1.883     |
| O19          | 2.132     | P1              | 4.930     |
| O21          | 2.004     |                 |           |
| O23          | 1.912     | O22             | 1.923     |
| O25          | 1.789     | O28             | 1.942     |
| O27          | 1.905     | O30             | 2.045     |
| O36          | 1.533     | O33             | 2.100     |
| O37          | 2.065     | O39             | 1.979     |
| O38          | 2.063     | O40             | 2.012     |

Bond valence sum calculation were performed via the KCryost program\(^{23}\) using the parameters given by Gagne et al.\(^{19}\) for ion pairs involving oxygens. Atomic sites which contained a mix of Nb(V)/Mo(VI) atoms have v.s. values ranging from 5.449 to 5.576, corresponding to an oxidation state of ca. +5.5, as expected from the partial occupancy. Atomic sites which contain only Mo(VI) have v.s. values ranging from 5.934 to 6.133, corresponding to an oxidation state of +6, which the Nb(V) atomic site has a v.s. value of 5.127, corresponding to an oxidation state of +5. The oxo values presented in table S5 show that at least four of the terminal oxygens are likely to be partially protonated throughout the crystalline lattice (O7, O10, O25 and O36), which is in line with the assigned single protonated state of the anion, the values vary due to disorder.

Figure S9. A. 2D Contour map depicting the observed electron density \(F_o\) along a plane containing two niobium atoms, one of which (bottom left) is partially occupied. B. Addition of atomic placements corresponding to the observed electron densities. C. The full Keggin unit superimposed on the 2D contour map.
Figure S10. Sequential $^{31}$P NMR spectra of THA$_3$ in CD$_3$CN during its polymerization under ambient air. Notably, some signals originally present are entirely absent in the final, polymerized solution, consistent with dynamic replenishment of monomeric units with distal Nb(V)=O positions. This conclusion remains tentative, however, as definitive confirmation would require the (difficult) assignment of each signal to a specific positional isomer.

Figure S11. FTIR of polymeric THA$_3$ MeCN solution after drying (M: metal Nb or Mo; O$_c$ for corner-sharing MO$_6$; O$_e$ for edge-sharing MO$_6$).$^{4,5}$ The peak at 671 cm$^{-1}$ is diagnostic for the Nb-O-Nb linkage.$^{24-26}$
Figure S12. Dynamic and static light scattering (DLS and SLS) data (A and B, respectively) for MeCN solutions of polymerized 1. Unlike the DLS data in Figure 4A of the text, the scattering-intensity data in Figure S12A were partially number weighted to emphasize the more abundant medium-sized coiled polymers, giving an effective $R_h$ of ca. 23 nm, somewhat larger than in the unweighted result (Figure 4A). For these coiled polymers, Guinier fitting of the SLS data in panel B gives a radius of gyration of $R_g$ of 13.27. Notably, to obtain the Zimm plot of SLS data, it is necessary to use the intermediate-angle data, and to remove data obtained at low angles. The low-angle data mainly includes information about the largest species, while the intermediate range data are due to the $R_h = \text{ca. } 23$ nm (average) species. Using these DLS and SLS data, that both refer to the intermediate sized species, the ratio between $R_g$ and $R_h$ is 0.58, definitive for solid, compact spheres of the monomeric units. This conclusion is consistent with the fitting of the SAXS results (Figure 4B of the text), which also gave compact spheres.

Figure S13. Unweighted DLS of THA$_5$1 after polymerization in MeCN under Ar / air / CO$_2$. Due to the step-growth mechanism, the number of larger polymers is small relative to the number of monomers,
oligomers and small polymers. This is typical of step-growth polymerization. If we show the *number weighted* spectra, the scattering from the objects observed by SAXS and TEM will not appear.

**Table S6.** The Unweighted DLS (radii) of THA$_5$1 after Polymerization in MeCN Under Ar / Air / CO$_2$.

|         | Air          | CO$_2$       | Ar           |
|---------|--------------|--------------|--------------|
| **Peak 1** | 0.64 nm 4.0 % | 0.4 nm 2 %   | 0.6 nm 98%   |
| **Peak 2** | 12 nm 13.2 %  | 11.6 nm 9.6 %| 21.77 nm 2%  |
| **Peak 3** | 136 nm 82.8 %| 200 nm 88.4 %| ---          |

**Figure S14.** Dry-TEM images of THA$_5$1 after polymerization under CO$_2$ in MeCN.

**Figure S15.** ESI-MS of THA$_5$1 after polymerization under CO$_2$ in MeCN.
Figure S16. UV-Vis absorbance at 460 nm with time after addition of acetic acid and H$_2$O$_2$ to 1 in MeCN.

Figure S17. FTIR spectrum of THA$_3$ (M: metal Nb or Mo; O$_c$ for corner-sharing MO$_6$; O$_e$ for edge-sharing MO$_6$).$^{4-5}$

Figure S18. The $^{31}$P NMR spectrum of THA$_3$ compound in CD$_3$CN.
**Figure S19.** Positive-mode ESI-MS of THA$_3$3 in MeCN solution.

**Figure S20.** UV-Vis absorbance at 460 nm with time after addition of H$_2$O$_2$ to 1 in MeCN.

**Figure S21.** (A) UV-Vis absorbance at 460 nm with time after combining THA$_3$1 (1 mM) and THA$_3$3 (1 mM) in MeCN. (B) Unweighted DLS of the solution after five days. (C) The $^{31}$P NMR spectrum of the solution after five days.
Figure S22. Cryo-TEM images of THA₅ after polymerization under CO₂ in MeCN. (A-C) Clustered oligomeric chains; (D) small coiled polymers and (E-H) large coiled polymers.

Figure S23. Diameter of particles and distance between adjacent particles measured from cryo-TEM images. The diameter of the particles is 2.94 ± 0.13 nm with 95% confidence interval, and the distance between adjacent particles is 1.12 ± 0.06 nm with 95% confidence interval. Hence, the effective radius of each particle (particle and space) is 2.59 ± 0.13 nm with 95% confidence interval. These particle sizes and interparticle distances are larger than those expected for individual Keggin ions and the linkages between them. This, at least in part, is a consequence of working close to the resolution limit of cryo-TEM. Fortunately, by calculating the degree of polymerization (DP) on the basis of these larger observed monomer sizes and linkages, the DP reported in text errs on the side of being smaller than the likely actual value. This is the reason for stating that calculated value as a "minimum estimated DP".
Figure S24. (A) The $^{31}$P NMR spectrum of tetramethylammonium (TMA) exchanged polymerized THA$_5$I. (B) The $^{31}$P NMR spectrum of TMA exchanged monomeric THA$_5$I for comparison with the spectrum in A. (C) Unweighted DLS of TMA exchanged polymeric 1 after dissolution in water.

Figure S25. (A-B) Dry-TEM images and (C-H) EDX mapping of TMA-exchanged polymeric 1. (C) is the scanning transmission electron microscopy (STEM) image of the selected area for EDX mapping analysis. The homogeneous distribution of the N, O, Nb and Mo, respectively, can be seen in panels D-G. (H) EDX spectrum of (C), showing the peaks for O, N, Nb, and Mo. The elemental distribution is found as 1:5 (percent) for Nb:Mo. Two peaks arising from the Cu TEM grid are also observed.
Figure S26. (A) $^1$H NMR spectrum of the TMA exchanged, polymerized THA$_3$I in D$_2$O. (B) H NMR spectrum of TMA exchanged polymeric I after depolymerization by addition of acetic acid and H$_2$O$_2$, and extraction into CDCl$_3$. This demonstrates that the THA originally present in polymeric I had been quantitatively replaced by TMA.

Figure S27. (A) The $^{31}$P NMR spectrum of Li$^+$ exchanged polymerized THA$_3$I. (B) The $^{31}$P NMR spectrum of Li$^+$ exchanged monomeric THA$_3$I for comparison with the spectrum in A. (C) Unweighted DLS of Li$^+$ exchanged polymeric I after dissolution in water.

Figure S28. (A-B) Dry-TEM images and (C-G) EDX mapping of Li$^+$-exchanged polymeric I. (C) is the scanning transmission electron microscopy (STEM) image of the selected area for EDX mapping analysis. The homogeneous distribution of the N, O, Nb and Mo, respectively, can be seen in panels D-G. (G) EDX spectrum of (C), showing the peaks for O, N, Nb, and Mo. The elemental distribution is found as 1:5 (percent) for Nb:Mo. Two peaks arising from the Cu TEM grid are also observed.
Figure S29. (A) $^1$H NMR spectrum of the Li$^+$ exchanged, polymerized THA$_3$I in D$_2$O. (B) $^1$H NMR spectrum of Li$^+$ exchanged polymeric I after depolymerization by addition of acetic acid and H$_2$O$_2$, and extraction into CDCl$_3$. This demonstrates that the THA originally present in polymeric I had been quantitatively replaced by Li$^+$. 

Figure S30. The UV-Vis absorbance at 460 nm with time after addition of acetic acid and H$_2$O$_2$ to a MeCN solution of polymeric I. 

Figure S31. Unweighted DLS of polymeric I after depolymerization in MeCN.
Figure S32. Positive-mode ESI-MS of polymeric 1 after depolymerization in MeCN.

Figure S33. FTIR spectrum of the K⁺ salt of the WD derivative.

Figure S34. The ³¹P NMR spectrum of the K⁺ salt of the WD derivative in D₂O. From ³¹P NMR, there are four sets of signals (the peaks at -10.53 and -12.78 belong to mono-Nb K₇P₂NbW₁₇O₆₂; the peaks at -10.74 and -12.67 belong to mono-Nb peroxo K₇P₂NbW₁₇O₆₃; the peaks at -9.10 and -13.21 belong to di-Nb K₈P₂Nb₂W₁₆O₆₂; the peaks at -9.27 and -13.09 belong to di-Nb peroxo K₈P₂Nb₂W₁₆O₆₄; the 2Nb are on the same side of the Wells-Dawson structure).³
Figure S35. FTIR spectrum of the THA salt of the WD derivative.

Figure S36. The $^{31}$P NMR spectrum of the THA salt of the WD derivative in CD$_3$CN. From $^{31}$P NMR, there are four sets of signals (the peaks at -10.82 and -13.19 belong to mono-Nb THA$_7$P$_2$NbW$_{17}$O$_{62}$; the peaks at -11.02 and -13.08 belong to mono-Nb peroxy THA$_3$P$_2$Nb$_2$W$_{16}$O$_{63}$; the peaks at -9.33 and -13.57 belong to di-Nb THA$_3$P$_2$Nb$_2$W$_{16}$O$_{62}$; the peak at -9.54 belongs to di-Nb peroxy THA$_3$P$_2$Nb$_2$W$_{16}$O$_{64}$; the 2Nb are on the same side of the Wells-Dawson structure).  

Figure S37. Positive-mode ESI-MS of the THA salt of the WD derivative in MeCN solution.
Figure S38. Formation of a polyether-like inorganic polymer from a di-Nb(V) substituted Wells-Dawson anion. The monomeric unit is a bifunctional Wells-Dawson anion, $\alpha$-[P$_2$Nb$_2$W$_{16}$O$_{62}$]$^{8-}$ (red: P-centered tetrahedra; gray: W-centered polyhedra; green: Nb-centered polyhedra). Upon formation of intermolecular Nb-$\mu$-O-Nb linkages, each repeating unit possesses a 6- charge. As shown at the right, steric considerations require that each Wells-Dawson cluster be organized offset by 180° from those before and after it.

Figure S39. (A) Unweighted DLS and (B) $^{31}$P NMR spectrum of the THA salt of the WD derivatives after polymerization in MeCN. From the $^{31}$P NMR spectrum, only mono-Nb and mono-Nb peroxo derivatives could be seen.
**Figure S40.** Cryo-TEM images of the THA salt of the WD derivative in MeCN solution after polymerization. (A) monomeric units; (B) coiled oligomeric chains; (C) slightly larger coiled polymers, and (D-F) large coiled polymers. These appear less compact than those prepared from 1 (see Figure 6 of the text), which also may reflect some damage during sample preparation.

**Figure S41.** (A) Cryo-TEM images, (B) the $^{31}$P NMR spectrum and (C) Unweighted DLS of the WD derivatives in CD$_3$CN after depolymerization by reaction with excess peroxide and glacial acetic acid. From the $^{31}$P NMR spectrum, only peroxy derivative could be seen.
Figure S42. Positive-mode ESI-MS of the THA salt of the mixture of WD derivatives after depolymerization in MeCN.
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