Supporting Information

Experimental Section

In a PTFE-lined autoclave reactor (23 mL), 3 g of hydrous niobium oxide, 8 mL of TMAOH solution (2.75 M) and 1.3 g of phosphoric acid (85 %) was added. The solution pH was 9.5, and the mixture was reacted at 140 ºC overnight. The resultant clear solution (pH=9.0) was washed with isopropanol several times in a plastic centrifuge tube and extracted with ethanol. The sticky product after evaporation crystallized after a few months. The crystalline material was washed with small amount of ethanol on a frit. Yield=5.2 g (92 %). Elemental analysis Found: C 15.22, H 5.97, N 4.47, P 5.36, Nb 29.9. Calcd for $C_{36}H_{167}N_9Nb_9O_{69}P_5$: C 15.33, H 5.97, N 4.47, P 5.49, Nb 29.64.

Instrumental Details

Electrospray mass spectrometry (ESI-MS) was performed with Agilent 1100 LC/MSD G1956b model equipped with single quadrupole at cone voltage of 20 V. The sample solution was directly injected into the spray chamber with a syringe pump at a speed of 0.1 mL/min. The ESI-MS spectra are averaged signals collected for 1 min. For series of ESI-MS dependent on pH, the pH of 6 mM solution of Nb_9P_5 was adjusted by using 2.75 M TMAOH solution or 1 M HCl solution to minimize volume change. For time-dependent ESI-MS study of reaction of Nb_9P_5 and H_2O_2, a 7 mM solution of Nb_9P_5 was prepared and 2 equivalents of H_2O_2 were added. Portions (10 µL) of solutions at each time were diluted with 0.5 mL of water for injection to ESI-MS. The ^{31}P solution and solid-state NMR spectra were obtained from UC Davis NMR facility. The spectra were referenced to 85% phosphoric acid. Elemental analyses were done in Galbraith laboratory (Knoxville, TN). Raman spectra were collected by using Renishaw RM1000 research laser Raman microscope equipped with Argon 514 nm laser. FT-IR data were obtained by using Bruker Tensor 27 instrument, with the sample dispersed in KBr pellet. TGA analysis was conducted by using Netzsch STA 449 system under static air with samples in Pt crucible. Powder X-ray diffraction data was collected by using Scintag XDS2000 XRD.

X-ray crystallography

The crystallographic data were collected by using APEX II diffractometer equipped with monochromatic Mo Kα radiation (λ = 0.71073 Å). The diffraction data were reduced by SAINT software[1] and absorption correction were applied with SADABS software. [2] The crystal structures were solved with direct methods by using SHELXTL package[3] and refined with SHELXL 2013 program. The methyl H atoms in TMA ions were refined with a Riding model. Crystallization waters were found on the electron density map during the final refinement stages.
Crystal data: $TMA_9[H_3Nb_9P_5O_{41}]\cdot 28H_2O$ (CCDC 1062824). $C_{36}H_{108}N_9Nb_9O_{69}P_5$, M=2767.83, Monoclinic, a=27.347(2), b=15.4386(12), c=24.5428(19) Å, β=91.742(1)°, U=10357.0(14) Å^3, T=93(2) K, space group $P2_1/c$ (no.14), Z = 4, 23883 reflections measured, 18801 unique (R_{int} = 0.0417) which were used in all calculations. The final $wR(F^2)$ was 0.1496 (all data).

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[1] Bruker (**2007**). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
[2] Bruker (**2001**). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
[3] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.

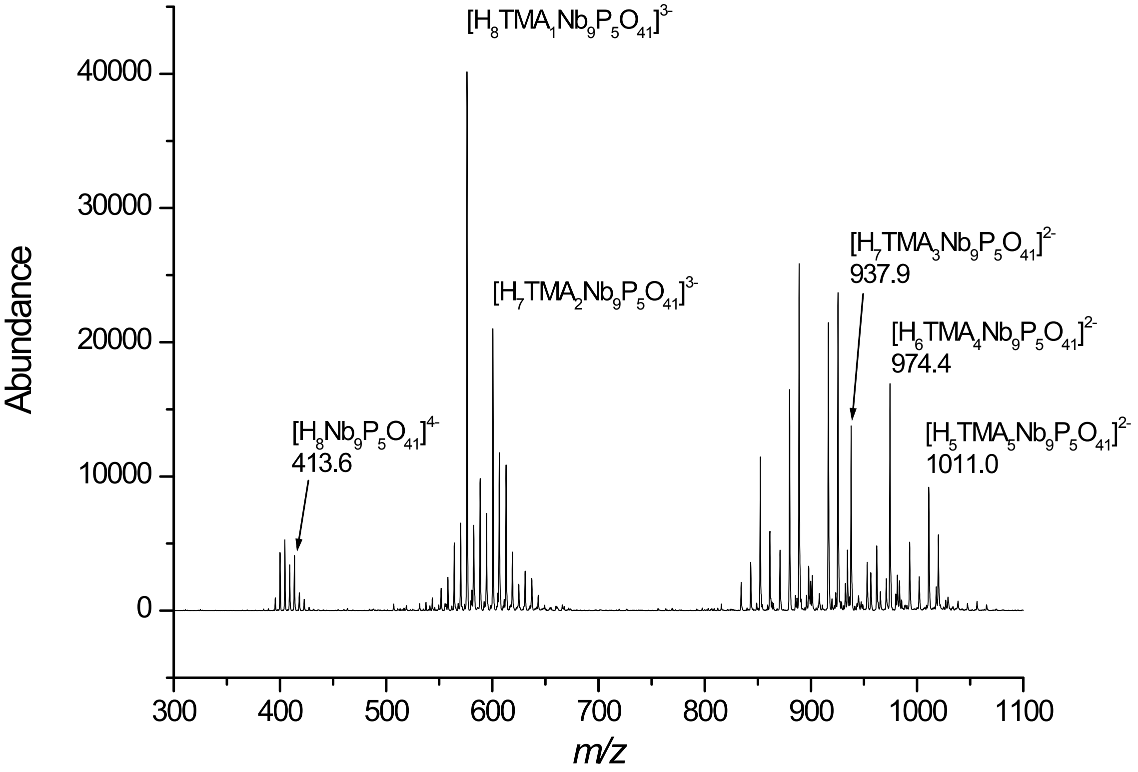

Fig. S1 ESI-MS spectrum of the Nb_9P_5 dissolved into water

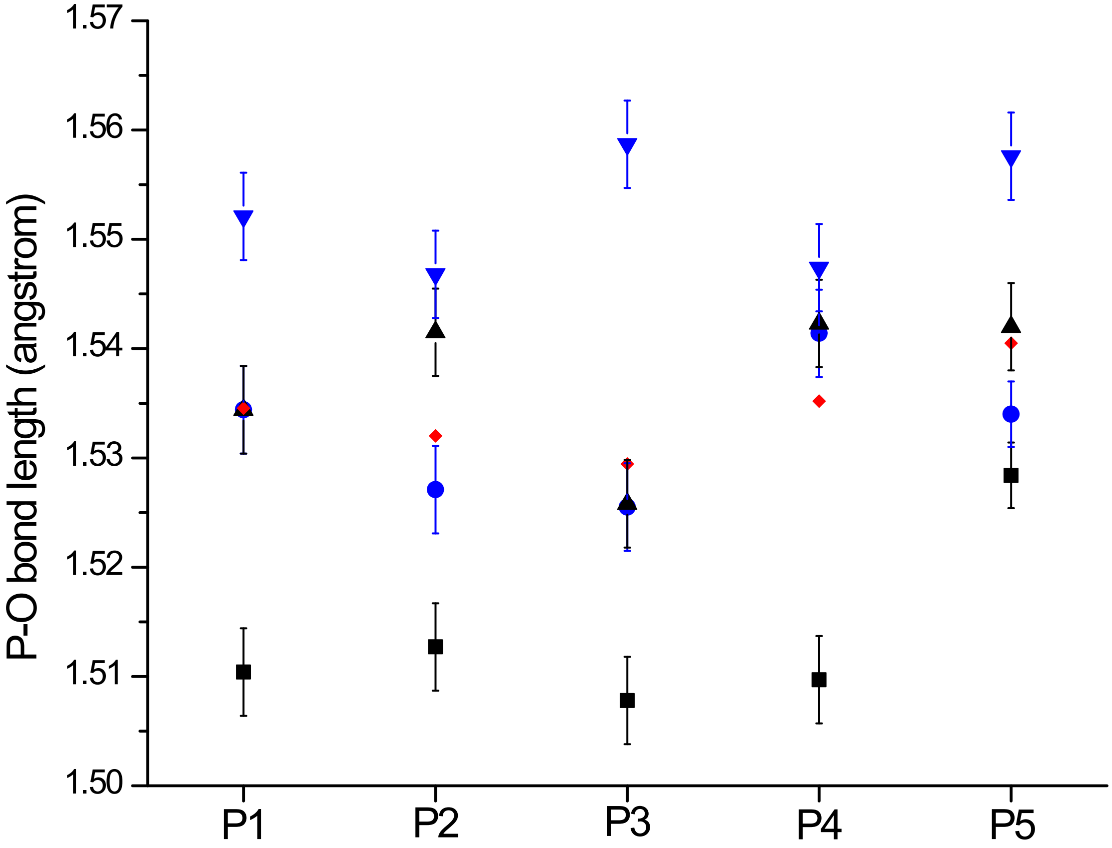

Fig. S2 Plot of P-O bond lengths for each PO_4 group in Nb_9P_5 with error bars from crystallographic data. Averaged P-O length for each PO_4 groups are shown with red dots

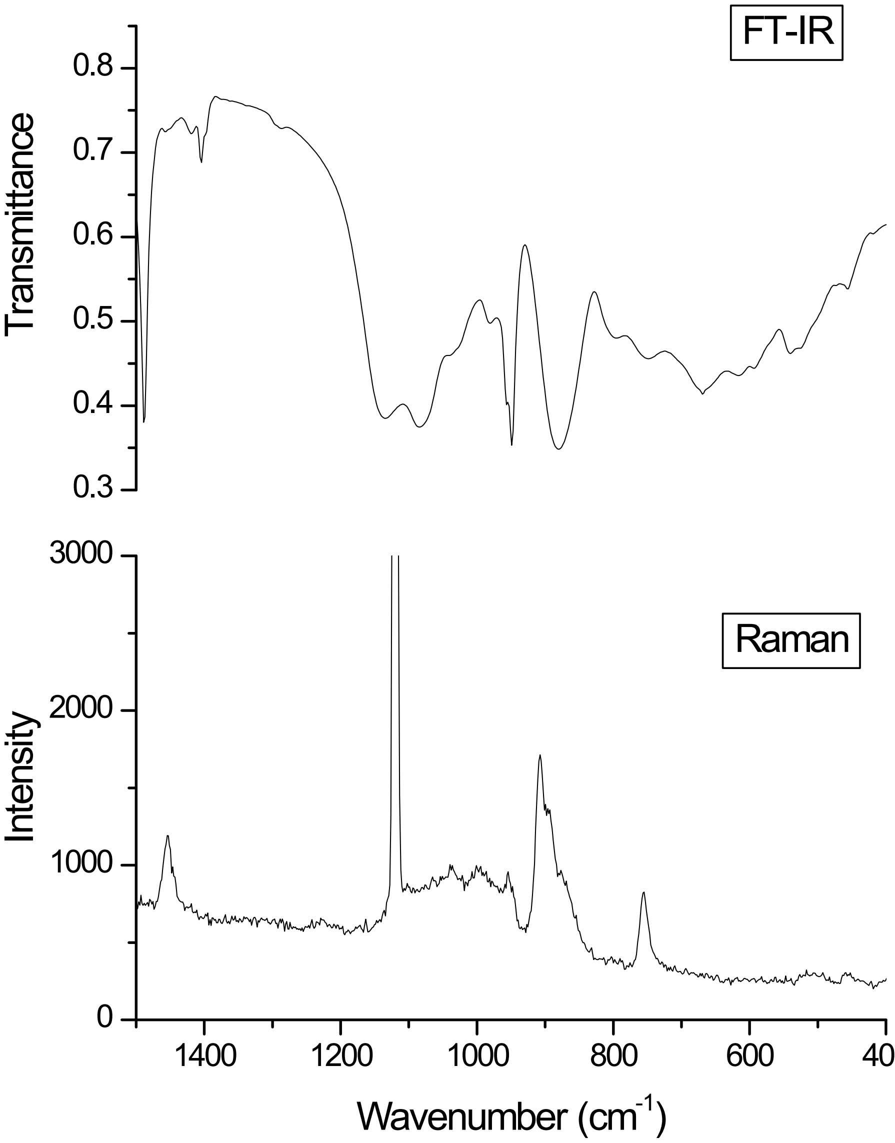

Fig. S3 FT-IR and Raman spectra of the Nb_9P_5. In the Raman spectra, the large peak at 1120 cm^{-1} originates from the aluminium foil substrate.

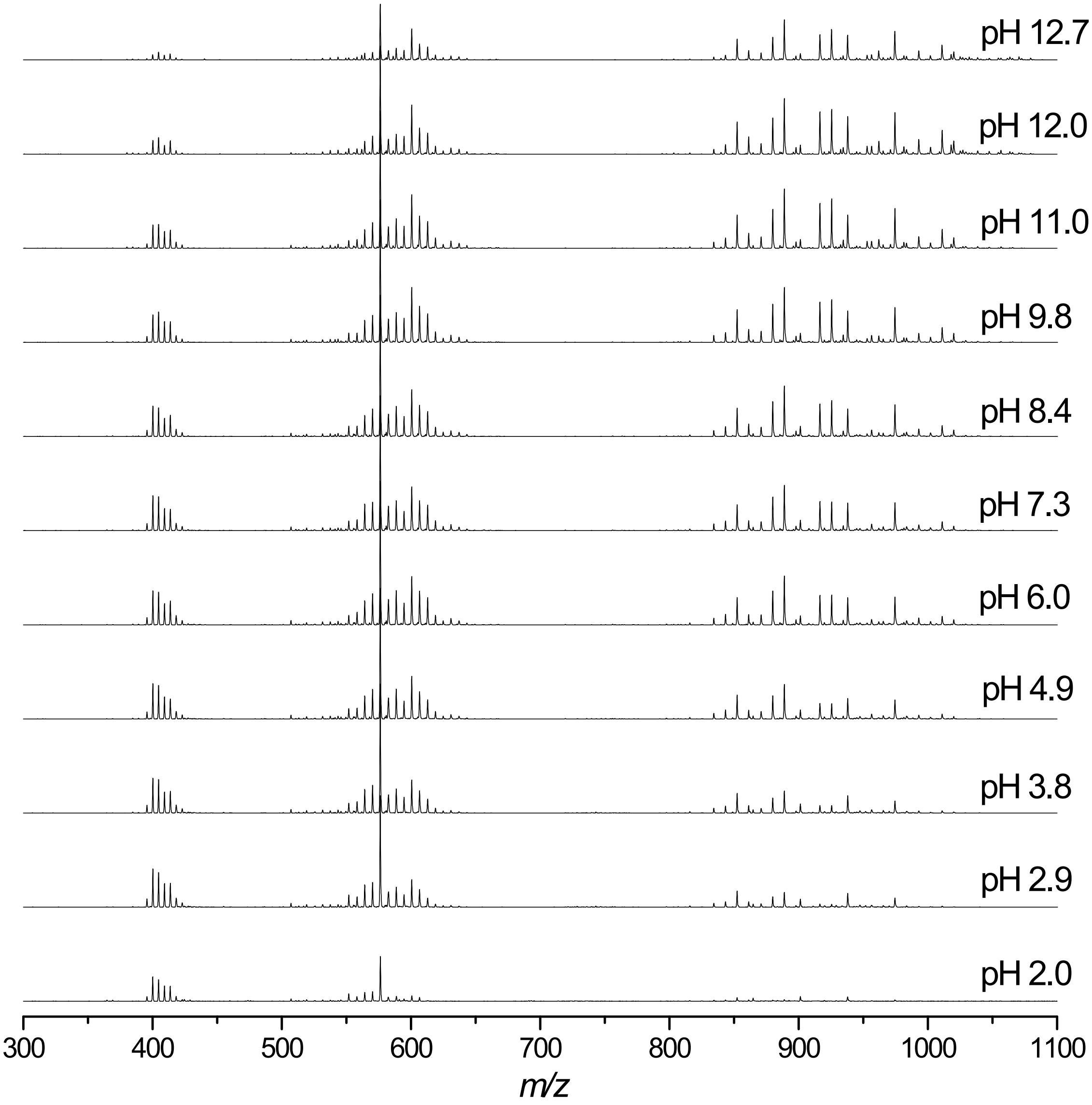

Fig. S4 The ESI-MS spectra of Nb_9P_5 solutions as a function of pH.

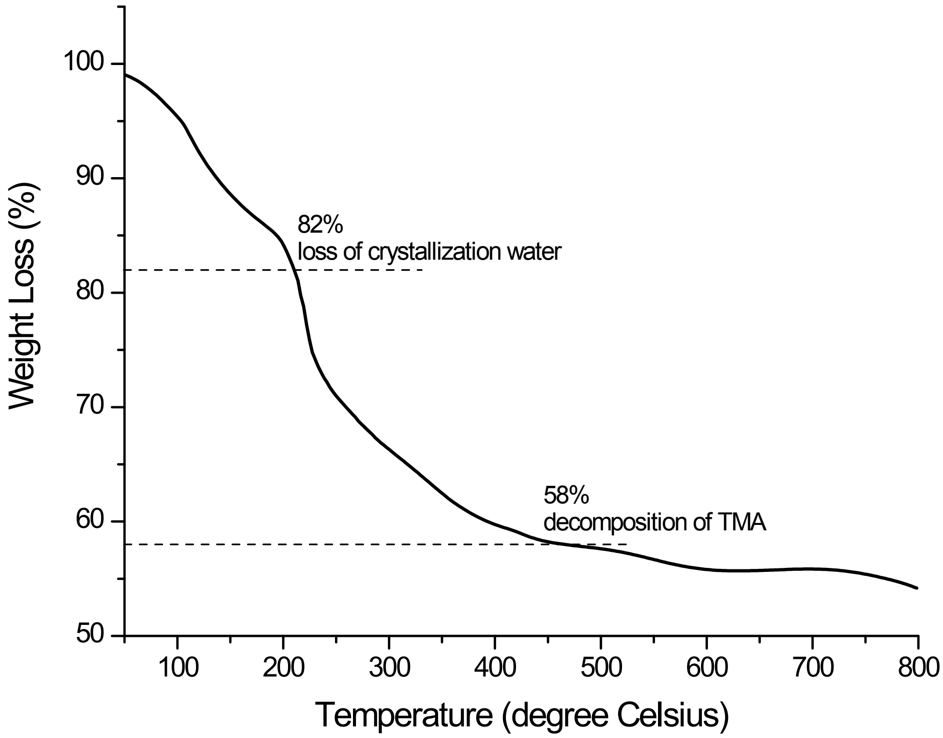

Fig. S5 The thermogravimetric analysis data of $(N(CH_3)_4)_9[H_3Nb_9P_5O_{41}]\cdot 28H_2O$. The remaining solid after TGA was amorphous as checked by using powder XRD.