Electronic Supporting Information

Synthesis

5 g of hydrous niobium oxide was mixed with 0.48 g of $KMnO_4$ and 8.5 g of tetramethylammonium (TMA) hydroxide solution (25%) in a 23 mL capacity PTFE-lined autoclave. The mixture was reacted at 110 °C for 3 days. The resulting dark brown solution was washed with isopropanol in a plastic centrifuge tube several times until the product became sticky. The product was extracted with ethanol. Dark brown-colored viscous oily product was obtained after evaporation of ethanol. Golden-yellow crystals grew in the viscous mixture after a few months. The crystals were separated by carefully washing the product with ethanol on a sintered glass frit. Yield=3.5 g (47%). Elemental analysis calcd for $C_{32}H_{142}N_8MnNb_{10}O_{54}$ C 15.44, H 5.75, N 4.50, Mn 2.21, Nb 37.36; found C 14.21, H 5.38, N 3.79, Mn 2.17, Nb 36.40.

Analytical Details

Electrospray mass spectrometry (ESI-MS) was carried out using an Agilent G1956b 1100 series LC/MSD single quadrupole mass spectrometer with ESI/APCI source using a cone voltage of -20 V and at an injection rate of 0.1 mL/min with a syringe pump for direct source injection. The ESI-MS titration experiments were performed with 0.2 mM and 2 mM sample concentration solution. For 0.2 mM solution, the solutions with different pH were prepared separately and the solution was directly injected to ESI-MS using syringe pump. For 2 mM solution, 2 mL of solution was titrated with 2.75 M TMAOH solution or 1 M HCl solution to minimize volume change. Aliquots of 20 µL of solution in different pH were diluted with 0.4 mL of water and injected for ESI-MS. Each spectrum in the figures is averaged signal during the data acquisition for 1 min. A Varian Cary 300 UV-visible spectrometer was used to obtain the UV-Vis absorption spectra. Three sets of 2 mL starting solutions were 0.02 mM, 0.2 mM and 2 mM concentration sample solution with 0.1 M of TMACl as background salt. Background correction was applied by a blank 0.1 M TMACl solution. Dilute TMAOH or HCl solutions were used to adjust the pH to a basic or acidic direction, respectively. Infrared spectra were collected on a Bruker Tensor 27 FT-IR spectrometer with a KBr pellet dispersed with sample. Elemental analyses were performed by Galbraith Laboratories Inc. (Knoxville, TN).

X-Ray crystallography

Golden-yellow colored single crystal of **1** was attached on a glass fiber with Paratone oil and mounted on a goniometer. A Bruker APEX II single crystal X-ray diffractometer equipped with monochromated Mo Kα radiation ($\lambda = 0.71073$Å) and a CCD detector was used for data collection. Cold nitrogen stream from liquid nitrogen was flown on the mounted crystal during the data collection to fix the crystal and to maintain the data collection temperature at 86 K. After data collection, data reduction was performed by using SAINT software.[1] Multi-scan absorption correction was applied with SADABS program.[2] The crystal structure was solved with SHELXS software[3] by using direct method, which found manganese, niobium and some oxygen atom locations. Subsequent refinement cycles using SHELXL program found other atoms in the structure. Hydrogen atoms on the TMA group were refined using the riding model. Some of the methyl hydrogen atoms were not included in the refinement due to the disordered methyl groups of TMA.

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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.

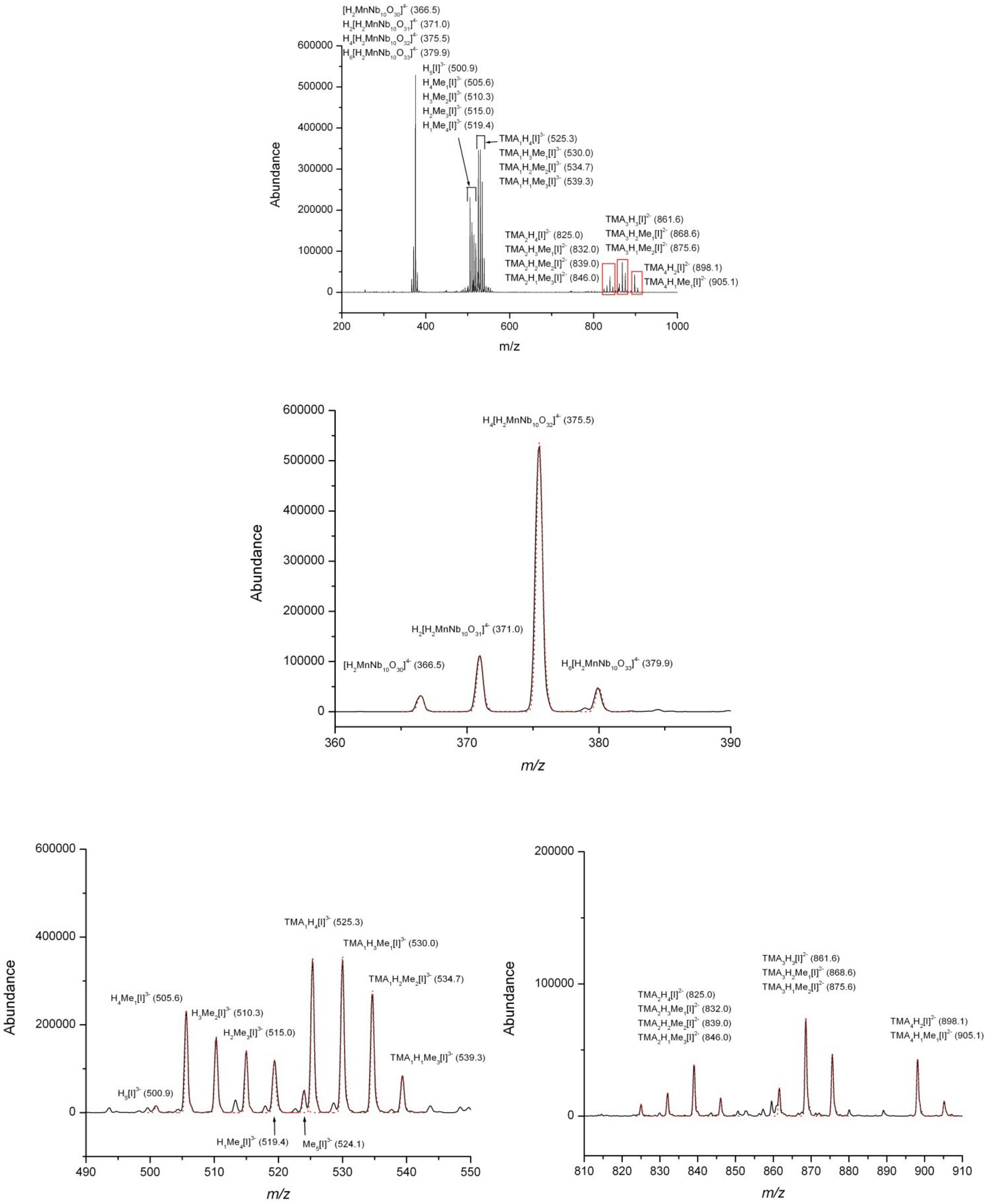
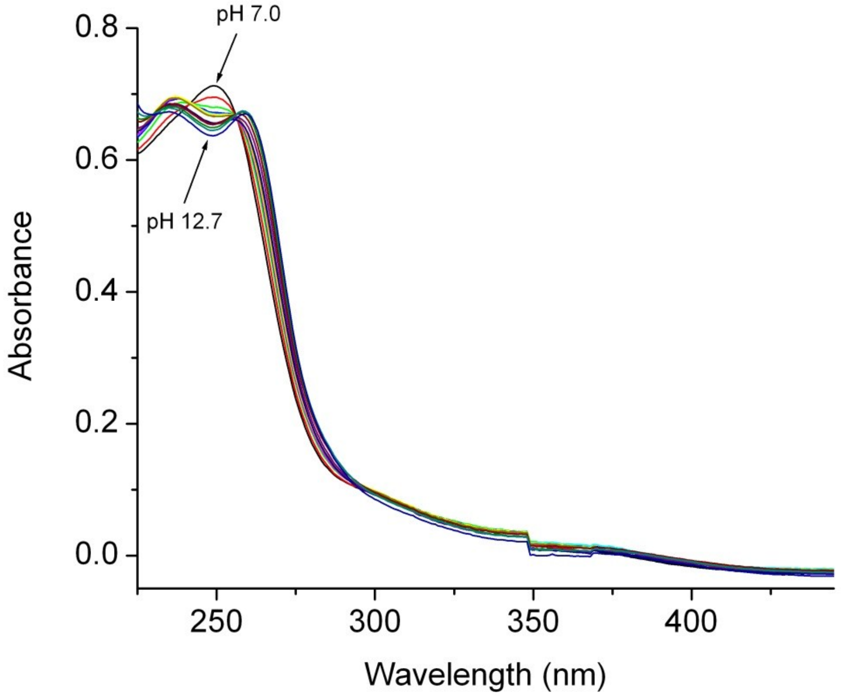


Figure S1 ESI-MS spectra of **1** with peak assignment. Calculated peaks (red dots) are overlaid with original spectra (black lines) for comparison.



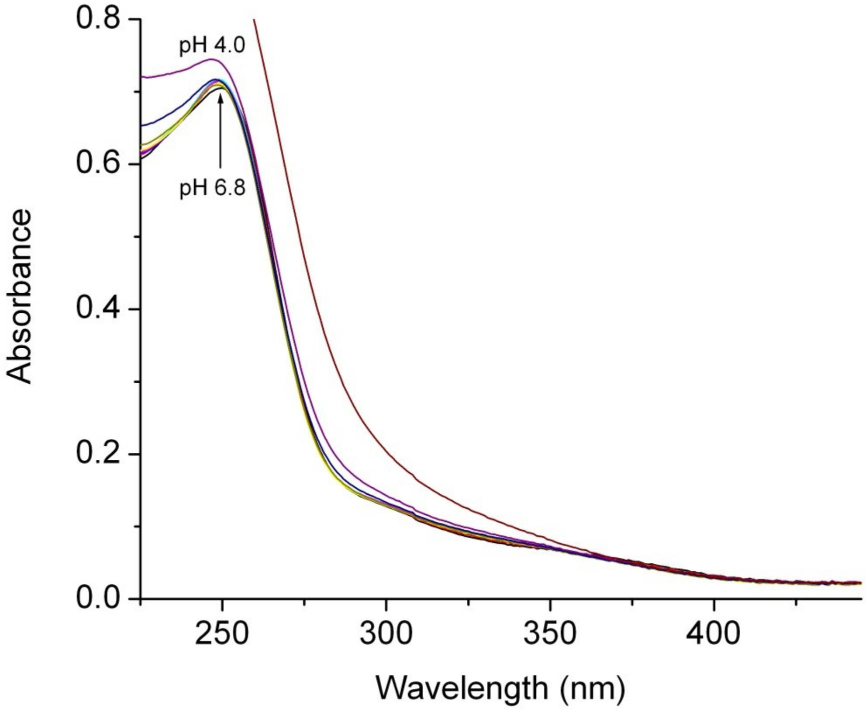
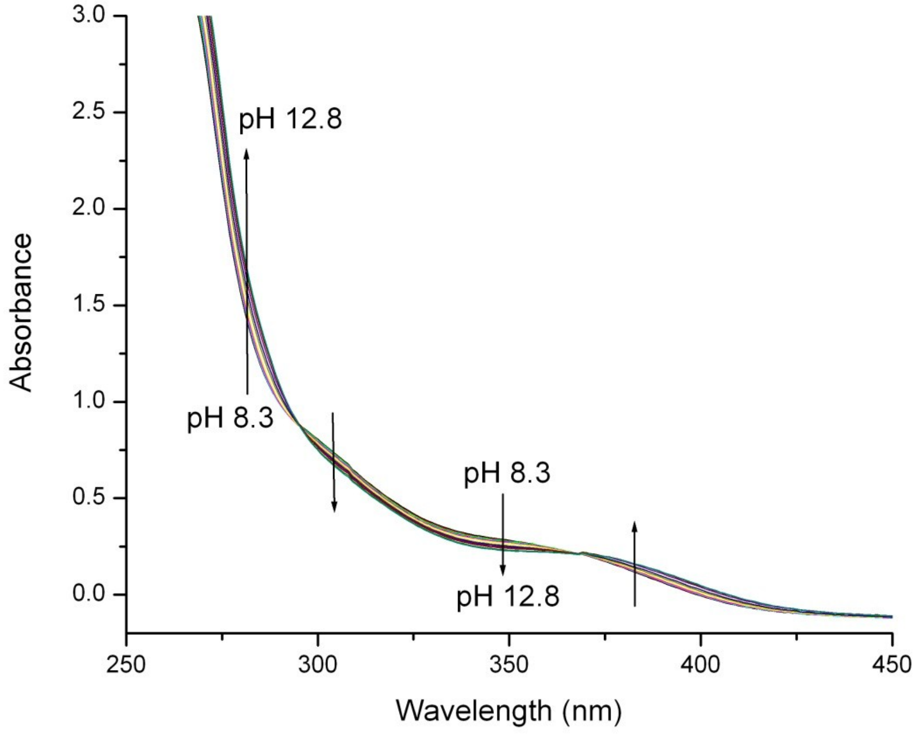


Figure S2 UV-Vis titration of a 0.02 mM solution of **1** in 0.1 M TMACl. The range (top) is from the pH reached by dissolving the crystals (~7) and then titrating to pH=12.7 with TMAOH (0.02 M to 2.75 M). A similar titration in the acid direction from pH~7 to pH=3.6 (bottom) with 0.01 M to 1.0 M HCl.



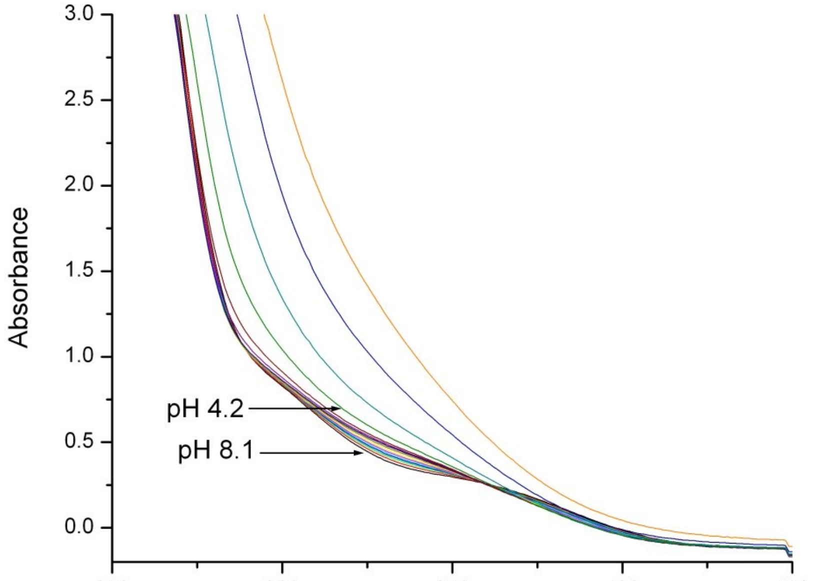
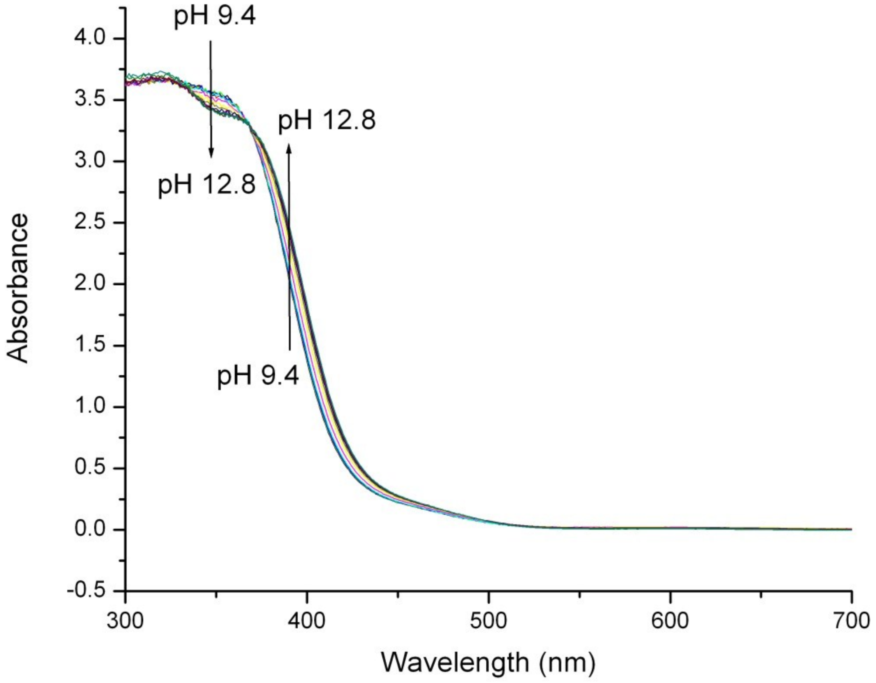


Figure S3 UV-Vis titration of 0.2 mM solution of **1** containing 0.1 M TMACl with TMAOH solution (0.02 M to 2.75 M, top) and with HCl solution (0.01 M to 1.0 M, bottom)



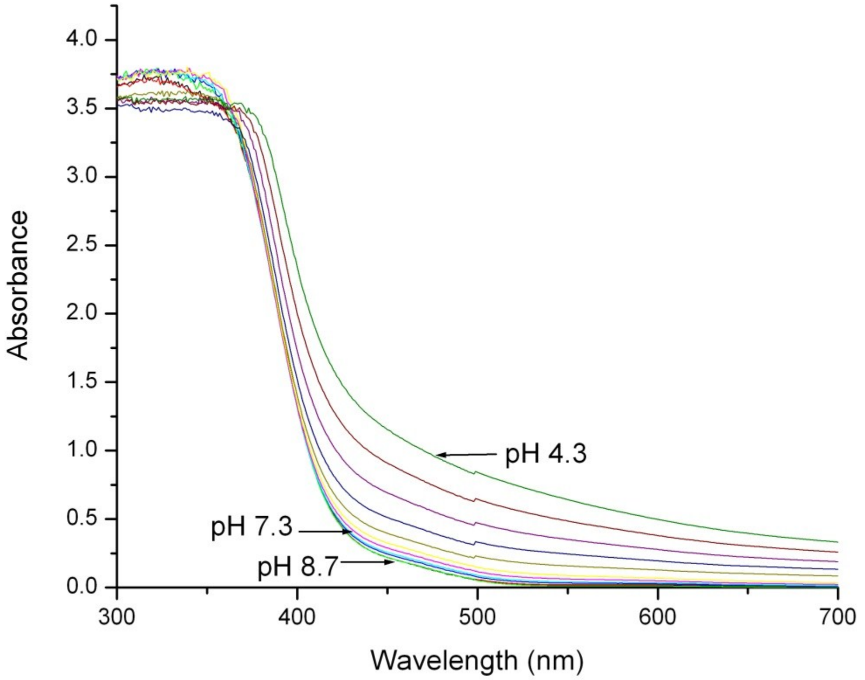


Figure S4 UV-Vis titration of 2 mM solution of **1** containing 0.1 M TMACl with TMAOH solution (0.02 M to 2.75 M, top) and with HCl solution (0.01 M to 1.0 M, bottom)

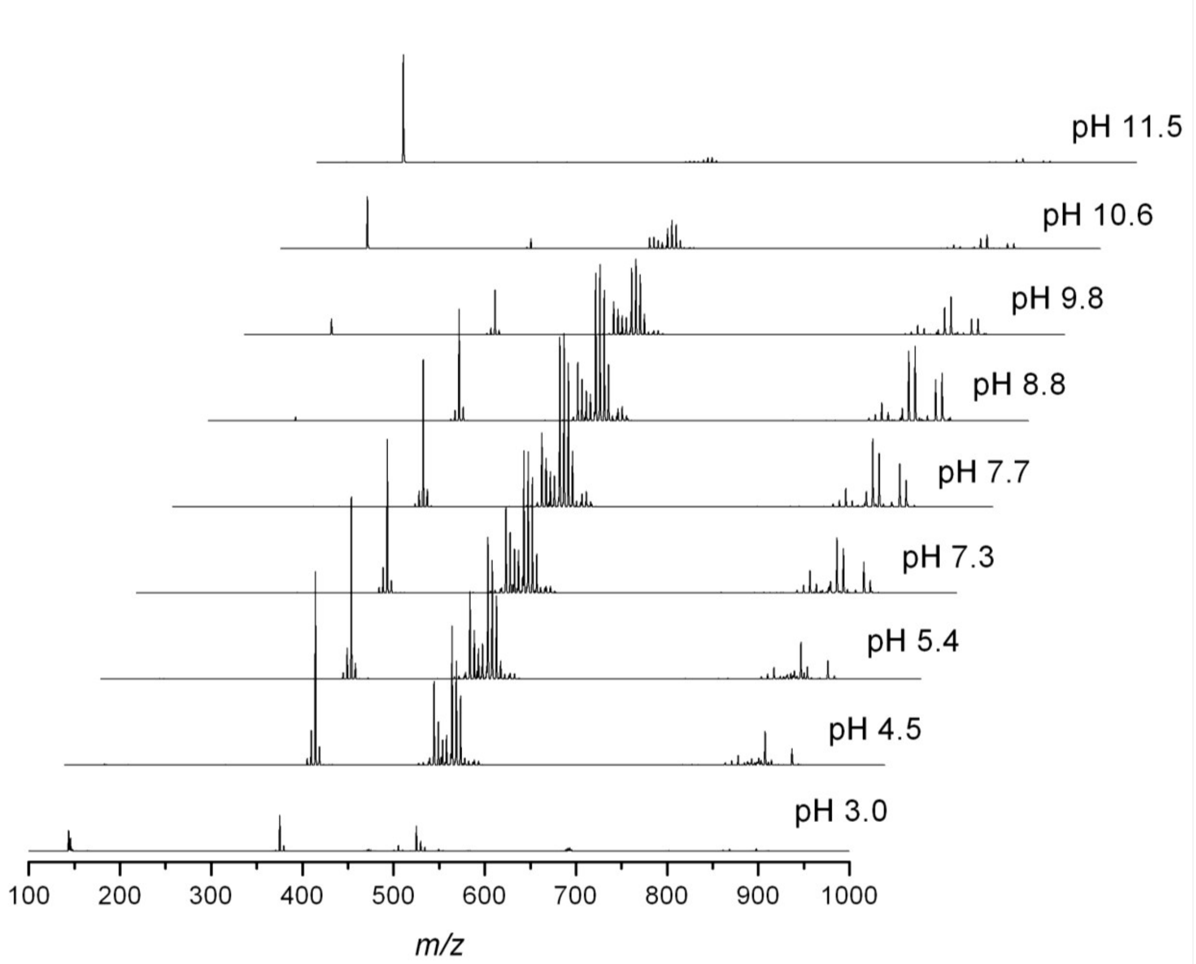


Figure S5 ESI-MS of 0.2 mM solution of **1** during titration in different pH

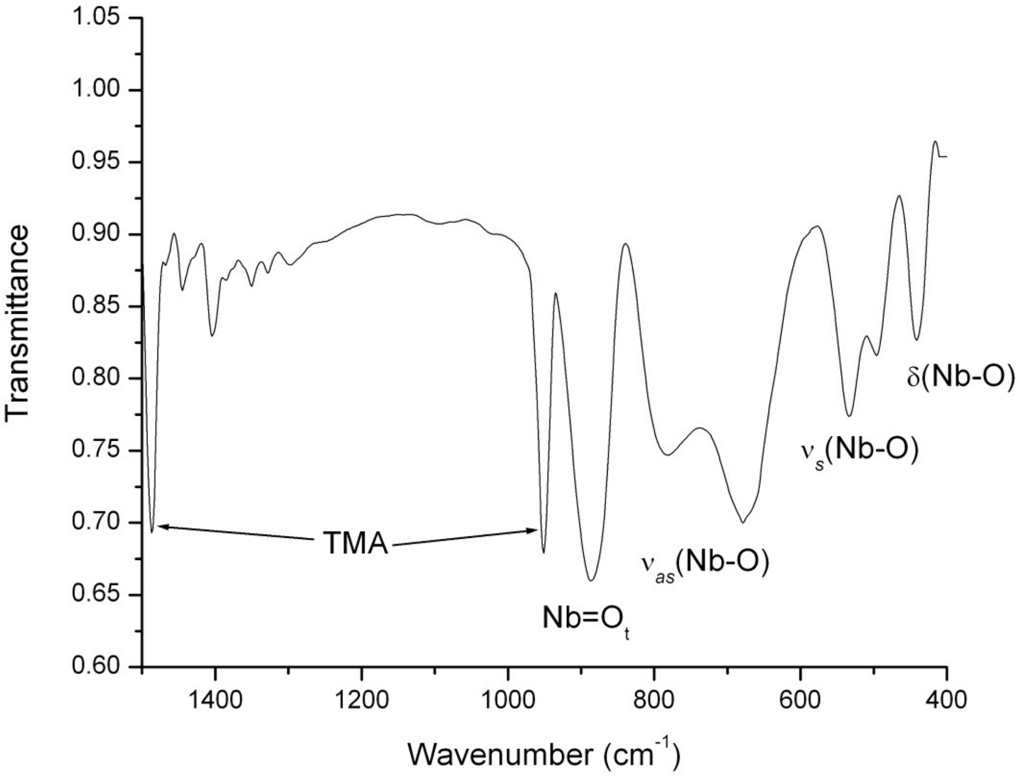


Figure S6 FT-IR spectra of 1. Nb=O$_t$ stretching mode at 885 cm^{-1}, asymmetric Nb-O stretching at 781 and 677 cm^{-1}, symmetric Nb-O stretching at 532 and 496 cm^{-1}, Nb-O bending at 442 cm^{-1}.