

## Electronic Supporting Information

### Highly soluble iron- and nickel-substituted decaniobates with tetramethylammonium countercations

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#### Synthesis

##### Synthesis of $\text{TMA}_6[\text{H}_2\text{Fe}^{\text{III}}\text{Nb}_9\text{O}_{28}]^{6-}\cdot 14\text{H}_2\text{O}$ (**1**):

Niobic acid ( $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , also known as hydrous niobium oxide (20% w/w water); 5 g, 30 mmol Nb) was mixed with  $\text{TMAOH} \cdot 5\text{H}_2\text{O}$  (4 g, 22 mmol) and  $\text{K}_2\text{FeO}_4$  (0.66 g, 3.3 mmol). The solid mixture was reacted in a PTFE-lined autoclave at 100°C for 2 days. The brown solution obtained after reaction was washed with isopropanol three times in a plastic centrifuge tube (50 mL capacity) until brown sticky product was isolated. The product was then extracted with ethanol. Nearly colorless but slightly yellow prismatic crystals grew over several months in the viscous brown oil which formed after evaporation of the ethanol. The crystals were washed with ethanol on a glass frit. Yield: 3.0 g (44 % based on Nb). Elemental analysis calcd (%) for  $\text{C}_{24}\text{H}_{102}\text{N}_6\text{FeNb}_9\text{O}_{42}$ : C 14.13, H 5.04, N 4.12, Fe 2.74, Nb 41.02; found: C 14.33, H 4.98, N 3.92, Fe 2.56, Nb 38.25.

##### Synthesis of $\text{TMA}_6[\text{H}_3\text{Ni}^{\text{II}}\text{Nb}_9\text{O}_{28}]^{6-}\cdot 17\text{H}_2\text{O}$ (**2**):

niobic acid (5 g, 80% w/w, 30 mmol Nb) was mixed with  $\text{TMAOH} \cdot 5\text{H}_2\text{O}$  (6 g, 33 mmol) and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.8 g, 3.4 mmol). The solid mixture was reacted in a PTFE-lined autoclave at 120°C for 4 days. The resulting light green solution was washed with isopropanol three times followed by washing with ethanol in a plastic centrifuge tube (50 mL capacity). The remaining nearly colorless but slightly green product was recrystallized from methanol. After the slow evaporation of the solvent, the crystalline product was washed with aliquots of methanol on a glass frit to get the analytically pure product. Yield: 2.9 g (42 % based on Nb). Elemental analysis calcd (%) for  $\text{C}_{24}\text{H}_{109}\text{N}_6\text{NiNb}_9\text{O}_{45}$ : C 13.74, H 5.24, N 4.01, Ni 2.80, Nb 39.88; found: C 14.81, H 4.94, N 3.88, Ni 2.89, Nb 40.56.

#### Analytical Details

ESI-MS spectrometry was carried out using an Agilent G1958b single quadrupole spectrometer using a cone voltage of -20 V and an injection rate of 30  $\mu\text{L}/\text{min}$  with a syringe pump for direct source injection. Infrared spectra were collected on a Bruker Tensor 27 FT-IR spectrometer with a KBr pellet dispersed with sample. A Varian Cary 300 UV-visible spectrometer was used to obtain the UV-Vis absorption spectra. The starting solution - 2 mL of 0.1 M of TMACl solution - contained 5 mM or 0.027 mM concentration of sample. 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. Potentiometric titrations were carried out using Metrohm 718 STAT Titrino auto-titrator. The compounds were dissolved in 0.1M TMACl solution and degassed by bubbling argon before titration. The temperature was maintained at 20°C during the titration using a circulating water bath. 0.1M TMAOH/0.1M TMACl solution was used for base titration and a 0.1M HCl/0.1M TMACl solution was used for acid backtitration. Elemental analyses were performed by Galbraith Laboratories Inc. (Knoxville, TN).

#### X-Ray crystallography

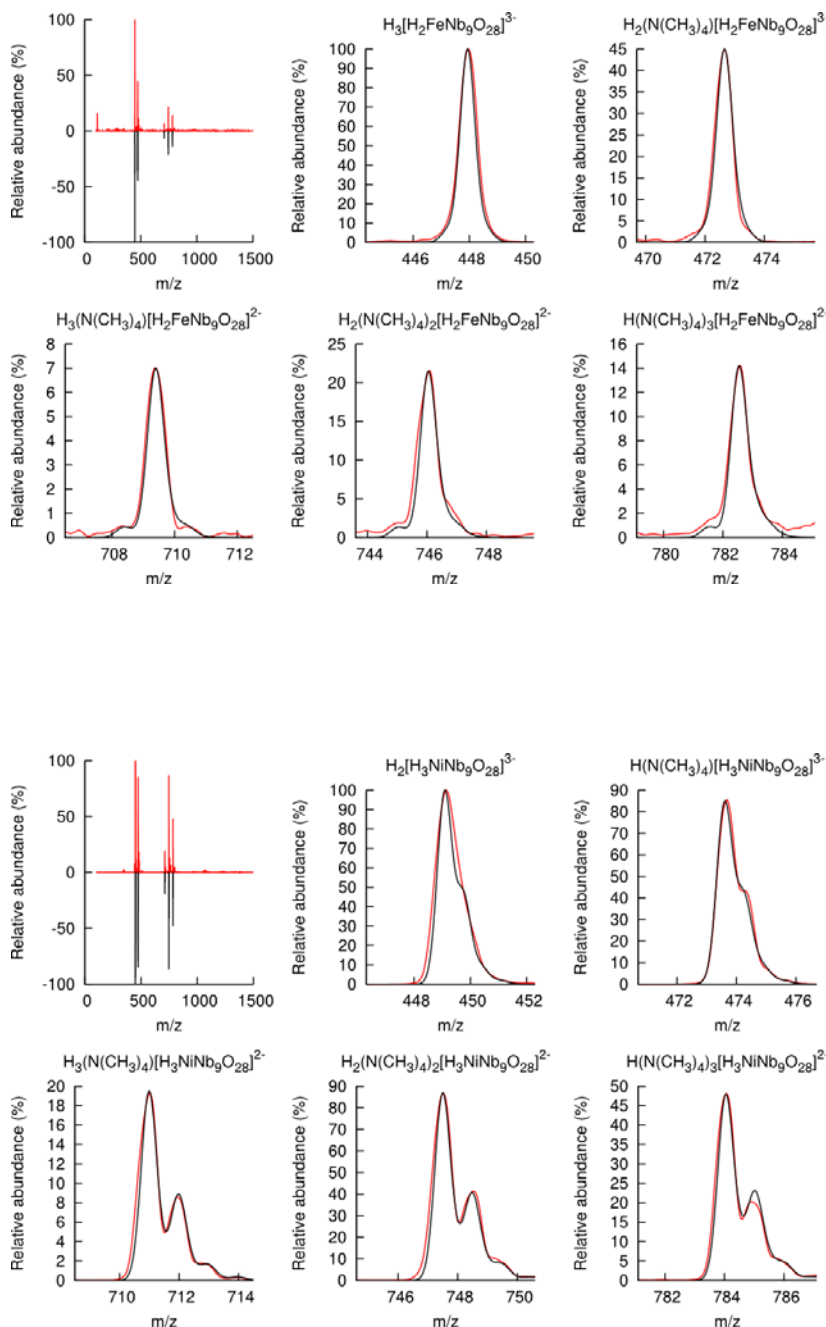
Prism-shaped single crystals of **1** and **2** were coated with Paratone oil and mounted on a glass fiber, which was attached to a goniometer. A Bruker SMART single crystal X-ray diffractometer equipped with monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ) and an area detector was used for data collection. The crystal was kept at 90K by cold nitrogen stream during the data collection. The data reduction was performed by using SAINT software.<sup>1</sup> Multi-scan absorption correction was applied with SADABS software.<sup>2</sup> The crystal structure was solved with SHELXTL software package<sup>3</sup> by using direct method, which found metal and some of oxygen, nitrogen, carbon sites. Subsequent refinement cycles found all other atoms in the structure. Hydrogen atoms on the tetramethylammonium group were refined using the riding model. Only a few hydrogen

<sup>1</sup> Bruker (2007). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

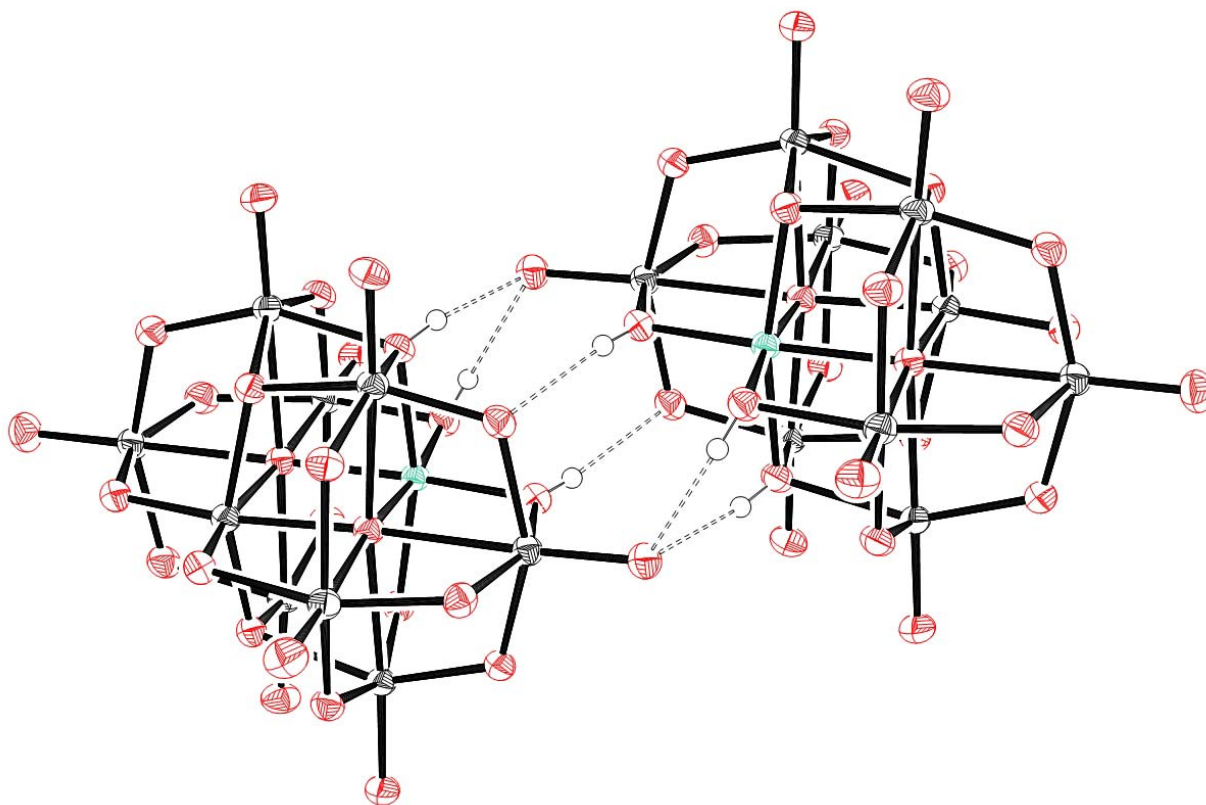
<sup>2</sup> Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

<sup>3</sup> G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.

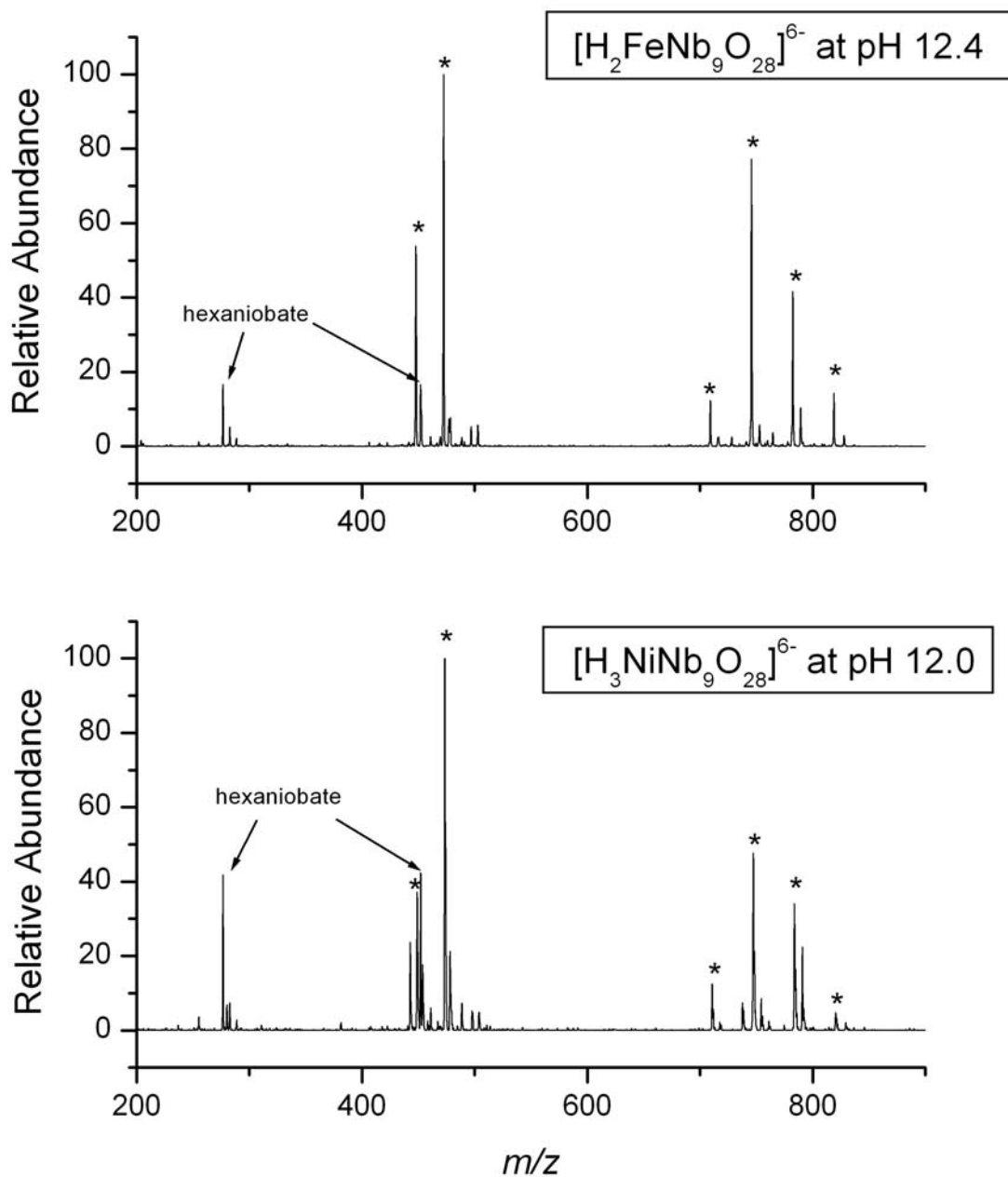
atoms on the crystallization water molecules were found in the electron density map. In the structure of **1**, two central metal sites in the cluster had lower electron density than other metal sites, and were refined with partial occupancy model of iron and niobium. Each Fe2/Nb2 and Fe9/Nb9 pair was restrained to have same atomic displacement parameters and same coordination for that purpose. During the refinement of **2**, three protons were found on the cluster during the final refinement stages. In the structure of **2**, one tetramethylammonium cation is severely disordered in two different remote sites along with crystallization water, having approximately half occupancy in each site.



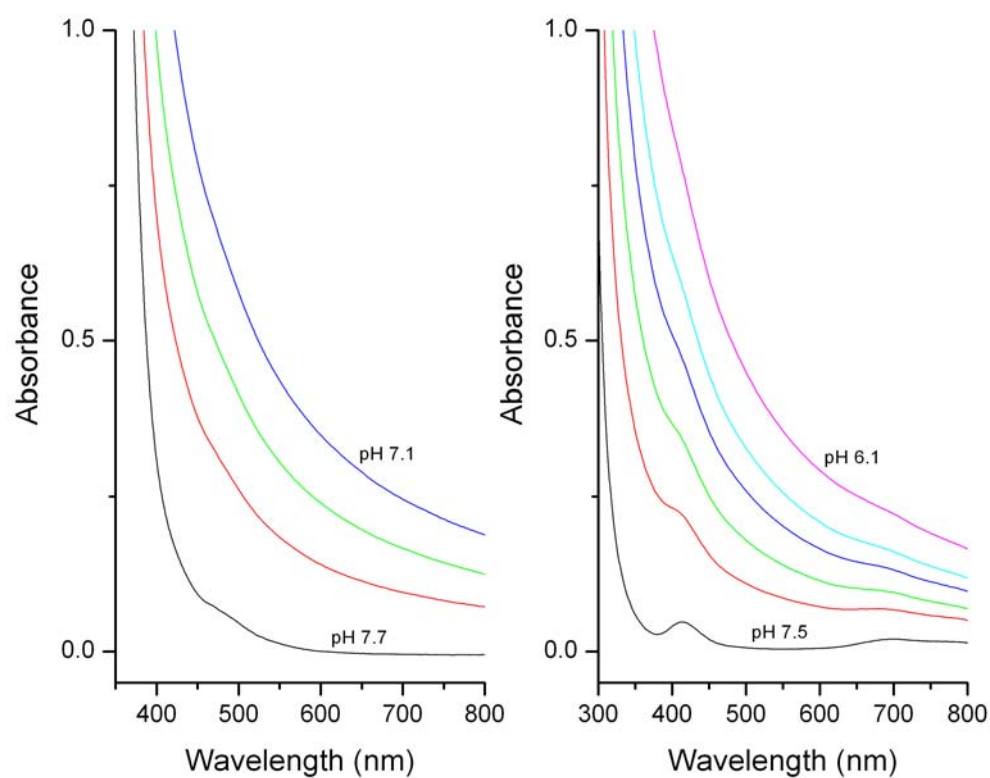
**Fig. S1** ESI-MS (red) of **1** (top) and **2** (bottom) compared with calculated spectra (black). Isotopic patterns were calculated using pyisocalc (<http://sourceforge.net/p/pyisocalc>).



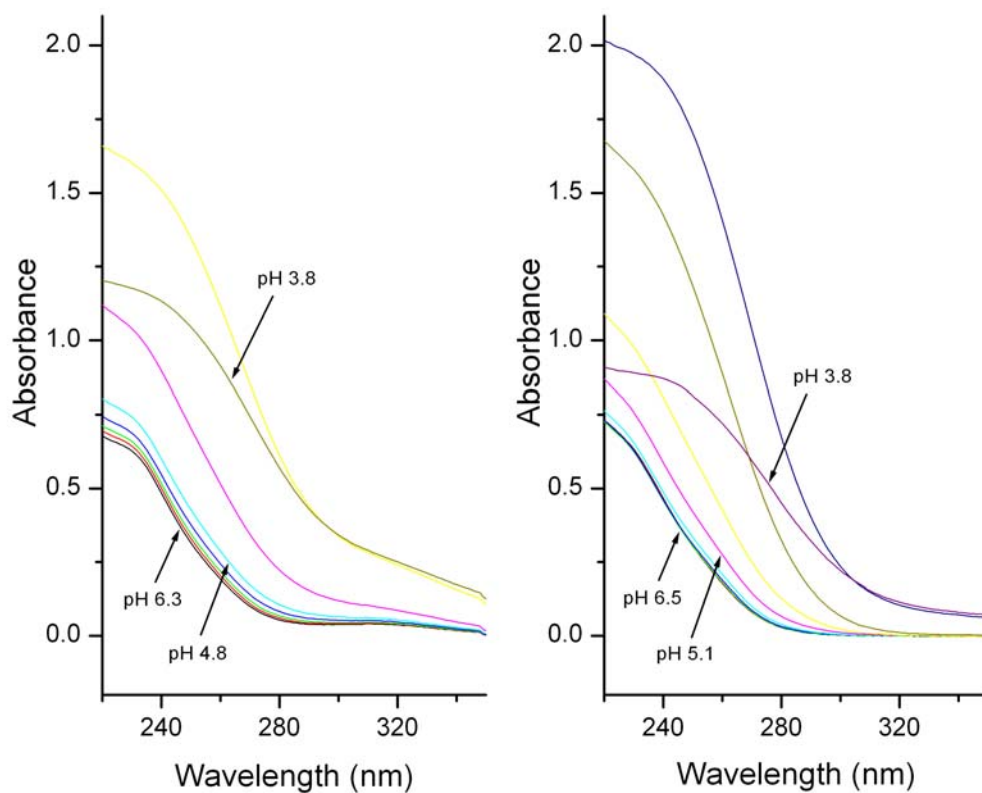
**Fig. S2** Hydrogen-bonded dimer of  $[H_3NiNb_9O_{28}]^{6-}$  in the structure of **2** (Ni:green, Nb:black, O:red, H:hollow circle) with thermal ellipsoid model. Hydrogen bonds are shown with dotted lines. Thermal ellipsoids are drawn at 50 % probability level.



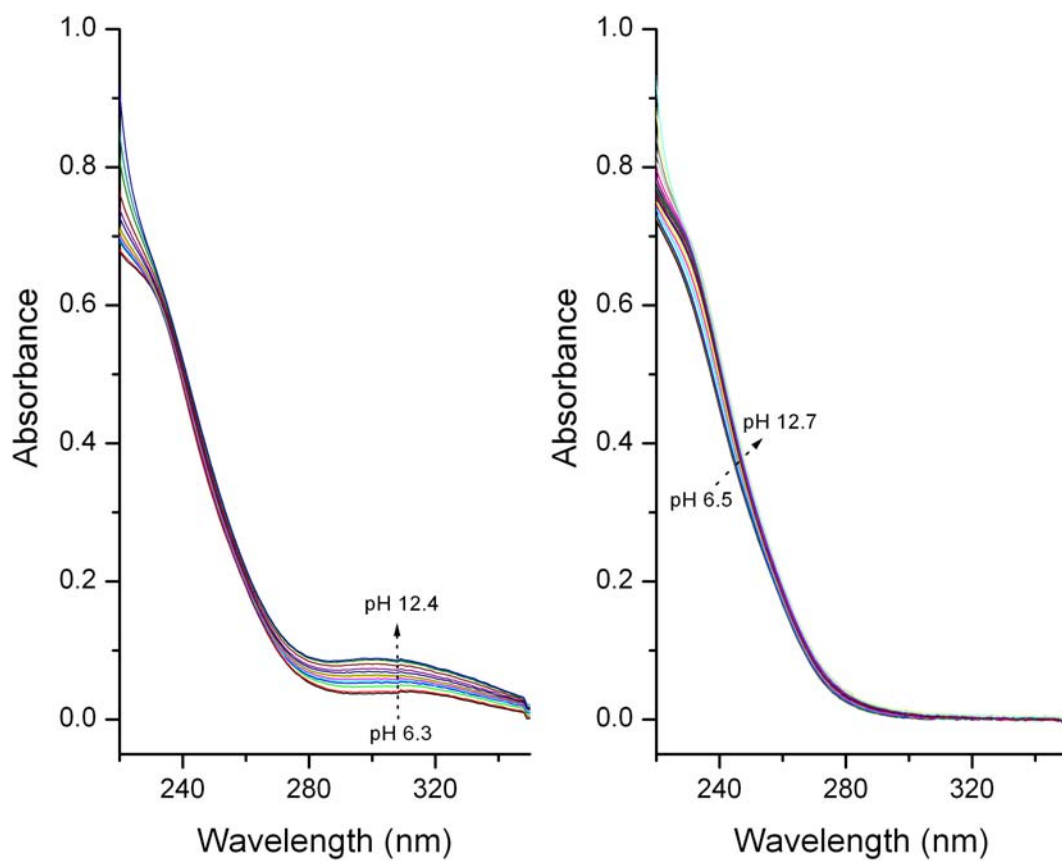
**Fig. S3** ESI-MS of the solutions of **1** (top) and **2** (bottom) titrated with TMAOH and kept for two months. Marked peaks (asterisks) correspond to the clusters. Peak assignments can be found in the main text and Fig. S1.



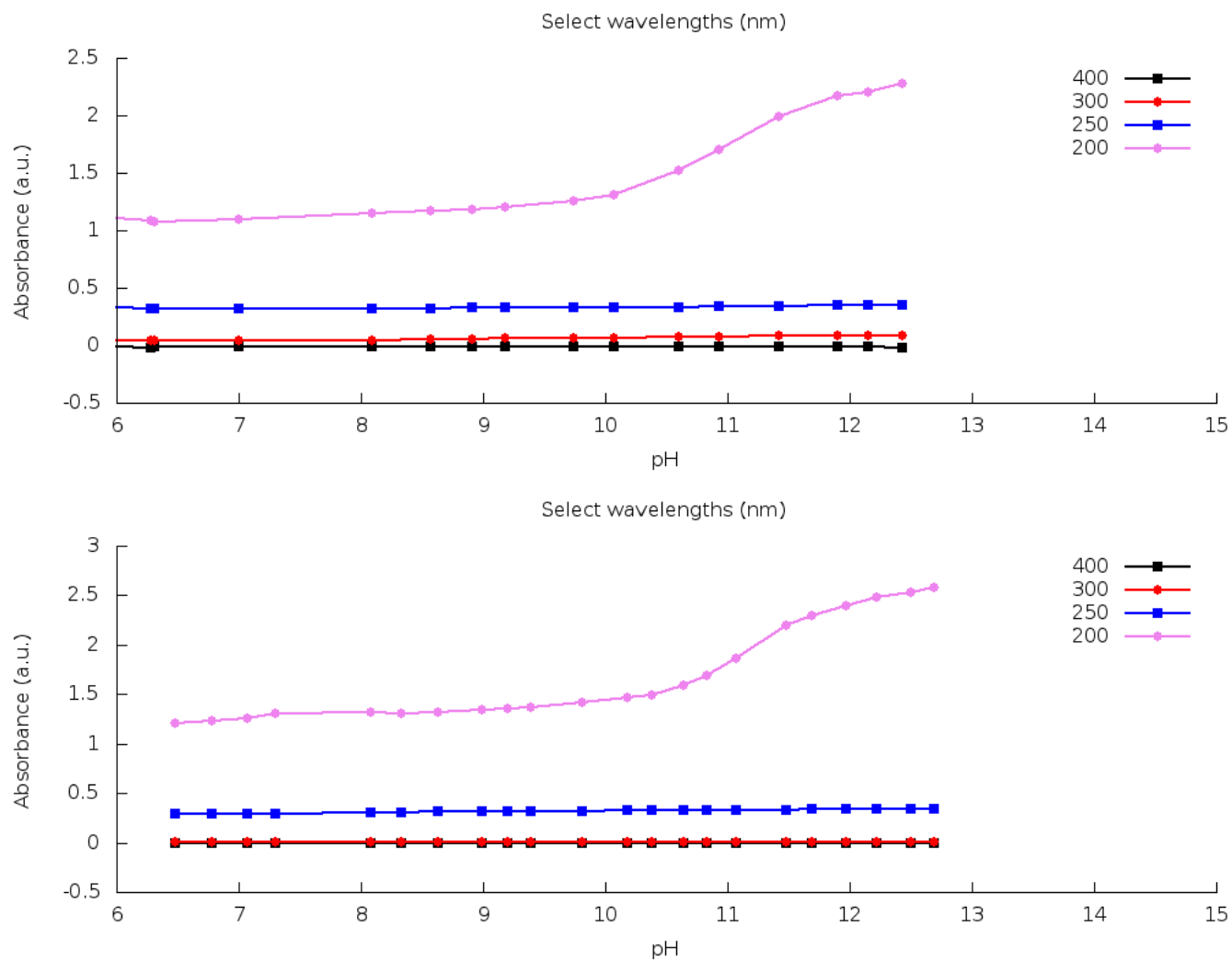
**Fig. S4** UV-Vis spectra of 5 mM solutions of **1** (left) and **2** (right) during the titration with HCl solution. The increase of absorbance across the entire spectrum is due to the colloid formation by each addition of acid.



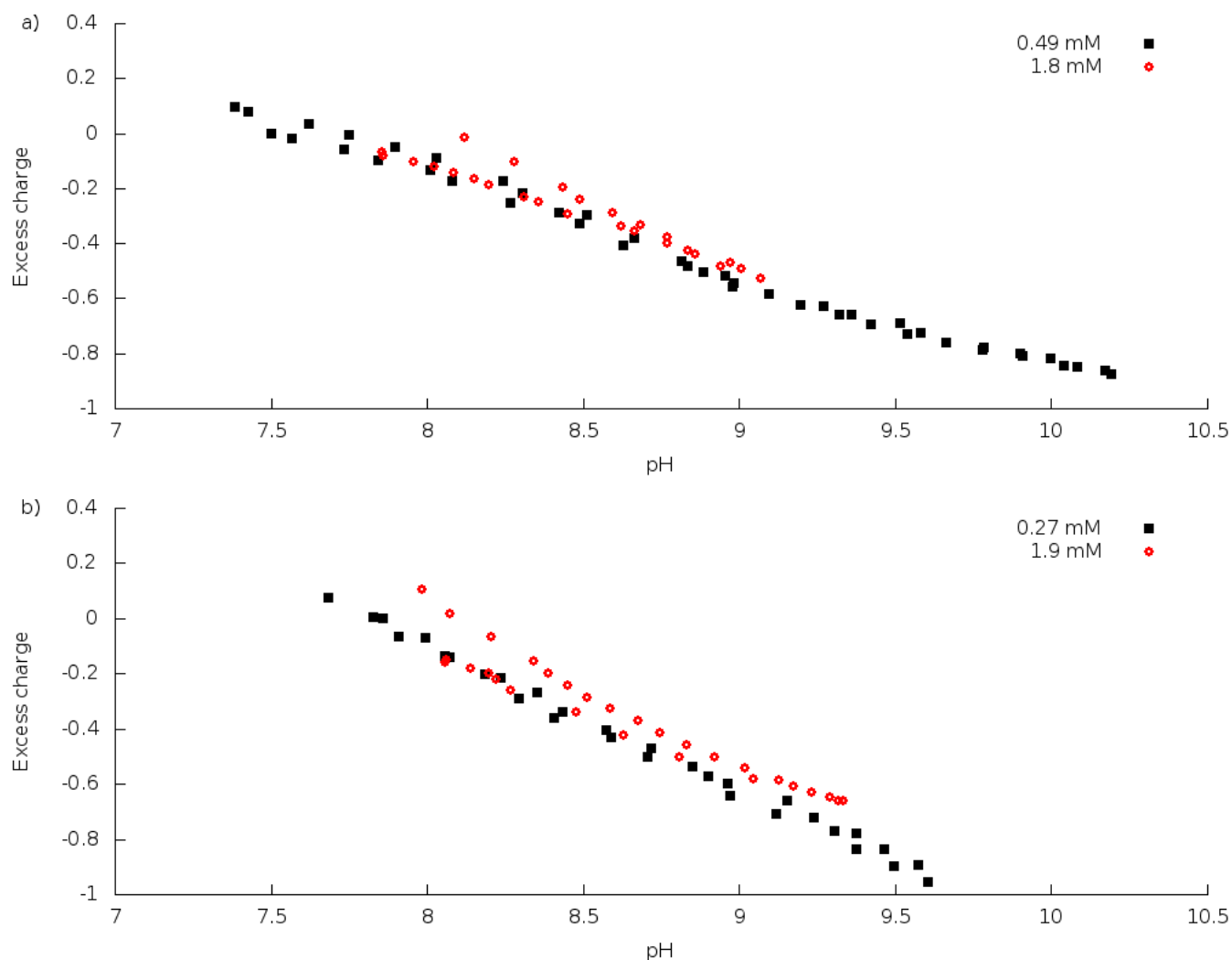
**Fig. S5** UV-Vis spectra of 0.027mM solutions of **1** (left) and **2** (right) during the titration with HCl solution. Colloid formation is detected by Tyndall effect below pH ~5 for both compounds. Thus the spectra at pH=3.8 were in the presence of condensed compound.



**Fig. S6** UV-Vis spectra of 0.027mM solutions of **1** (left) and **2** (right) during the titration with TMAOH solution.

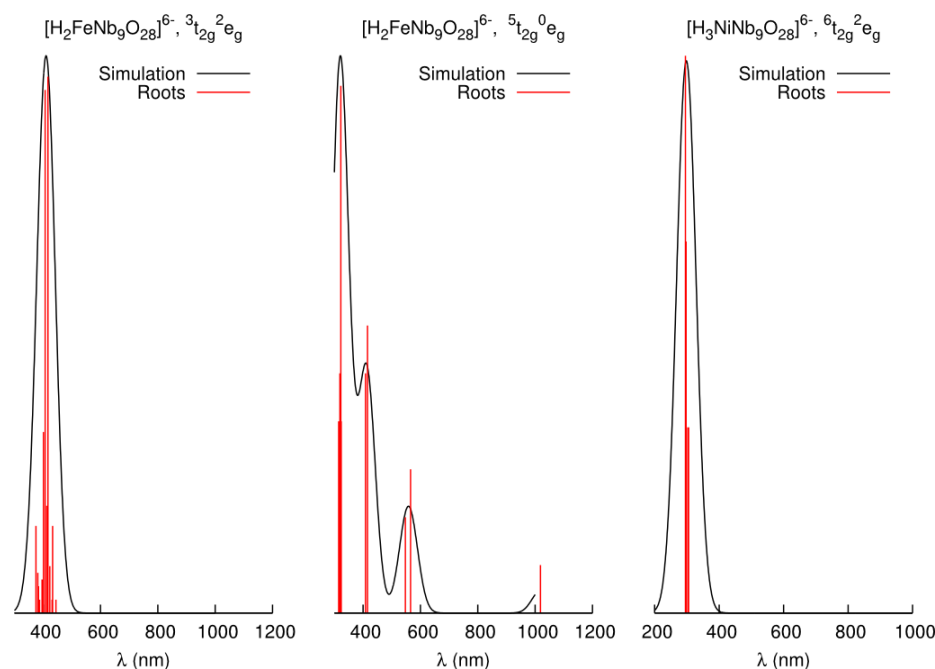


**Fig. S7** Plot of pH-dependent absorbance values at different wavelengths from the UV-Vis titration data of 0.027 mM solution of **1** (top) and **2** (bottom).



**Fig. S8** Plot of excess charge ('z') of **1** (a) and **2** (b) as a function of pH at different concentrations.<sup>4</sup> The titrations have been adjusted to use a common reference point. The steadily decreasing charge with pH may indicate partial deprotonation of the molecule.

<sup>4</sup> Ohlin, C. A., Harley, S. J., McAlpin, J. G., Hocking, R. K., Mercado, B. Q., Johnson, R. L., Villa, E. M., Fidler, M. K., Olmstead, M. M., Spiccia, L., Britt, R. D. and Casey, W. H. *Chem. Eur. J.*, 2011, 17, 4408–4417.



**Fig. S9** Calculated transitions and simulated spectra for the sextet and doublet forms of **1**, and the triplet form of **2**. The transitions were calculated using time-dependent density functional theory for structures optimised in Gaussian 09 at the b3lyp/LANL2DZ(Nb,Ni,Fe)/6-31+G\* (O,H) level of theory with implicit solvation (polarisable continuum model).

**Table S1.** Electronic transitions and energies for the sextet and doublet configurations of  $\text{H}_2[\text{FeNb}_9\text{O}_{28}]^{6-}$ , and the triplet state of  $\text{H}_3[\text{NiNb}_9\text{O}_{28}]^{6-}$ .

| Compound                                      | Multiplicity | Electronic energy (Hartree) <sup>a</sup> | Wavelengths of electronic transitions in nm (oscillator strengths in parentheses) <sup>a,b</sup>                                                                                                                                             |
|-----------------------------------------------|--------------|------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{H}_2[\text{FeNb}_9\text{O}_{28}]^{6-}$ | Doublet      | -2740.9299154                            | 1018.67 (0.0001), 565.37 (0.0003), 457.26 (0.0002), 415.18 (0.0006), 408.28 (0.0005), 323.87 (0.0004), 322.23 (0.011), 319.22 (0.0005), 316.89 (0.0001), 314.68 (.0004)                                                                      |
| $\text{H}_2[\text{FeNb}_9\text{O}_{28}]^{6-}$ | Sextet       | -2740.93793187                           | 444.82 (0.0002), 432.84 (0.0013), 430.94 (0.0002), 423.19 (0.0007), 416.62 (0.0080), 415.31 (0.0015), 413.24 (0.0016), 407.09 (0.0078), 400.72 (0.0027), 396.43 (0.0005), 387.27 (0.0002), 383.90 (0.0004), 381.39 (0.0006), 375.11 (0.0013) |
| $\text{H}_3[\text{NiNb}_9\text{O}_{28}]^{6-}$ | Triplet      | -2787.41904730                           | 305.32 (0.0001), 303.76 (0.0001), 298.33 (0.0001), 297.79 (0.0002), 296.97 (0.0001), 295.38 (0.0003)                                                                                                                                         |

<sup>a</sup>Structure optimizations and time dependent DFT were carried out using Gaussian 09 at the B3LYP/LANL2DZ (Nb,Ni,Fe)/6-31+G\*(O,H) level of theory using the unrestricted Kohn-Sham approach. <sup>b</sup>The first 18 and 16 roots were calculated for the iron species and the nickel species, respectively.