Supporting Information

Experimental Section

5 g of hydrous niobium oxide (80 % w/w) was mixed with 3.6 g of TMAOH·5H₂O in PTFE-lined autoclave (23 mL capacity) and hydrothermally reacted at 140 °C for 3 days. The resultant clear solution which contained mostly decaniobate was transferred to a larger beaker, and 5 mL of 30 % H₂O₂ solution was added. After the bubbles have ceased, the solution was placed in the PTFE-lined autoclave and 0.9 g of RhCl₃·3H₂O was added. The mixture was hydrothermally reacted at 80 °C for 16 h to form an orange gel. The 3.5 g of TMAOH·5H₂O was added to the reaction mixture and hydrothermally reacted at 110 °C for 3 days to obtain orange solution. The solution was washed with isopropanol a few times in a plastic centrifuge tube (50 mL) until sticky orange product remained. The product was extracted with ethanol until the ethanolic extract was nearly colorless. The remaining tan precipitate after extraction was further extracted with ethanol/methanol mixture (about 1:1), and this extract was evaporated to obtain crystalline TMA₈[H₂RhNb₉O₂₈]·14H₂O (0.45 g, 7 %). Elemental analysis Found: C 13.99, H 4.68, N 4.05, Nb 40.0, Rh 4.18. Calcd for C₂₄H₁₀₂N₆Nb₉O₄₂Rh: C 13.82, H 4.93, N 4.03, Nb 40.09, Rh 4.93. The firstly obtained orange ethanol extract was evaporated and dried in vacuo. Ethanol was added to the dried product and the mixture was mildly heated for a few hours. The precipitate formed after heating was removed by centrifuge. The orange ethanolic solution was evaporated, and the product crystallized after a few months to form crystalline TMA₈[Rh₂(OH)₄Nb₁₀O₃₀]·18H₂O (3.14 g, 40 %). The product was quickly washed with small amount of ethanol on a glass frit and kept in vacuo. Elemental analysis Found: C 15.03, H 5.23, N 4.35, Nb 34.1, Rh 7.04. Calcd for C₃₂H₁₃₆N₈Nb₁₀O₅₂Rh₂: C 14.78, H 5.27, N 4.31, Nb 35.73, Rh 7.92.

Instrumental Details

Electrospray-ionization 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 by using a syringe pump at a speed of 0.1 mL/min. The ESI-MS spectra are averaged signals collected for 1 min. For pH dependent ESI-MS spectra, the pH of 6 mM solution of clusters was adjusted by using 2.75 M TMAOH solution or 1 M HCl solution to minimize volume change. Portions (10 μ L) of solutions at each time were diluted with 0.5 mL of water. The solutions for injection to ESI-MS were 5 μ L of solution diluted with 0.5 mL of water. Elemental analyses were done in Galbraith laboratory (Knoxville, TN). The FT-IR data were obtained by using Bruker Tensor 27 instrument, with the sample dispersed in KBr pellet. A Varian Cary 300 UV-visible spectrometer was used to obtain the UV-Vis absorption spectra. The H₂ evolution data were obtained from solution containing 0.2 g of samples dissolved in 50 mL of (20 vol%) aqueous methanol solution in a quartz glass flask. The flask was purged with argon and the solution mixture was irradiated with a 300 W Xenon are lamp (370 mW·cm⁻² with 400 nm filter at the flask surface). The airtight irradiation system was connected to a Varian 3800 gas chromatograph (with a 60/80 Å molecular-sieve column and thermal conductivity detector) to identify the gas and measure the amount of gas evolved.

X-ray crystallography

The crystallographic data were collected by using SMART 1000 diffractometer equipped with monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). The data were reduced by using SAINT software.¹ Absorption corrections were applied with SADABS program. ² The crystal structures were solved with direct methods by using SHELXTL package³ and refined with SHELXL 2013 program. The methyl H atoms in TMA ions were refined with a Riding model.

Crystal data: TMA₈[H₂RhNb₉O₂₈]·14H₂O (CCDC 1417431). $C_{24}H_{100}N_6Nb_{8.88}O_{42}Rh_{1.12}$, M=2084.19, Triclinic, a=11.1230(8), b=12.1932(9), c=13.3388(10) Å, $\alpha=85.961(1)$, $\beta=68.004(1)$, $\gamma=87.862(1)^{\circ}$, U=1673.1(2) Å³, T=93(2) K, space group *P-1* (no.2), Z=1, 19423 reflections measured, 7620 unique ($R_{int}=0.0231$) which were used in all calculations. The final $wR(F^2)$ was 0.0840 (all data). TMA₈[Rh₂(OH)₄Nb₁₀O₃₀]·18H₂O (CCDC 1417432). $C_{32}H_{136}N_8Nb_{10}O_{52}Rh_2$, M=2600.40, Monoclinic, a=11.0911(15), b=15.379(2), c=24.327(3) Å, $\beta=93.748(2)^{\circ}$, U=4140.6(10) Å³, T=93(2) K, space group $P2_{1/c}$ (no.14), Z=2, 44814 reflections measured, 9483 unique ($R_{int}=0.0223$) which were used in all calculations. The final $wR(F^2)$ was 0.0460 (all data).

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 of RhNb9 and Rh2Nb10



Fig. S2 Colors of the solutions reflect the type and concentration of Rh(III)-substituted niobates. The color can be affected by pH as the RhNb₉ niobates either dissociate or form from smaller fragments at pH~12.9



Fig. S4 Change of ESI-MS spectra of Cr_2Nb_{10} when the solution pH was adjusted to 12.7



Fig. S5 Change of ESI-MS spectra of TiNb9 when the solution pH was adjusted to 12.7



Fig. S6 Change of ESI-MS spectra of CrNb9 when the solution pH was adjusted to 12.6



Fig. S7 Change of ESI-MS spectra of MnNb₉ when the solution pH was adjusted to 12.8



Fig. S8 Change of ESI-MS spectra of FeNb₉ when the solution pH was adjusted to 12.7

Fig. S9 Change of ESI-MS spectra of CoNb9 when the solution pH was adjusted to 12.8

Fig. S10 Change of ESI-MS spectra of NiNb $_9$ when the solution pH was adjusted to 12.8

Fig. S11 pH dependent ESI-MS spectra of Rh₂Nb₁₀

Fig. S12 pH dependent ESI-MS spectra of RhNb9

Fig. S13 FT-IR spectra of Rh_2Nb_{10} (top) and $RhNb_9$ (bottom)

Fig. S15 ESI-MS of RhNb₉ methanol/water solution (20% v/v) before and after irradiation

Fig. S16 The UV-Vis spectra of 20 mM solutions of the RhNb₉ ion before and after irradiation.

Fig. S17 The UV-Vis spectra of 20 mM solutions of the Rh₂Nb₁₀ ion before and after irradiation.