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 TMA\textsubscript{4}Rh\textsubscript{2}Nb\textsubscript{9}O\textsubscript{38} \cdot 18H\textsubscript{2}O (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 C\textsubscript{32}H\textsubscript{10}N\textsubscript{8}Nb\textsubscript{10}O\textsubscript{32}Rh:\textsubscript{2} 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 solution was washed with isopropanol a few times in a plastic centrifuge tube (50 mL) until sticky orange product remained. 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 34.1, Rh 7.04. Calcd for C\textsubscript{32}H\textsubscript{10}N\textsubscript{8}Nb\textsubscript{10}O\textsubscript{32}Rh:\textsubscript{2} 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 µL) of solutions at each time were diluted with 0.5 mL of water. The solutions for injection to ESI-MS were 5 µL 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 H\textsubscript{2} 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 arc lamp (370 mW·cm\textsuperscript{-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 Kα radiation (λ = 0.71073 Å). The data were reduced by using SAINT software.\textsuperscript{1} Absorption corrections were applied with SADABS program.\textsuperscript{2} The crystal structures were solved with direct methods by using SHELXTL package\textsuperscript{3} and refined with SHELXL 2013 program. The methyl H atoms in TMA ions were refined with a Riding model.

Crystal data: TMA\textsubscript{4}[H\textsubscript{2}RhNb\textsubscript{9}O\textsubscript{38}] \cdot 14H\textsubscript{2}O (CCDC 1417431). C\textsubscript{32}H\textsubscript{10}N\textsubscript{8}Nb\textsubscript{10}O\textsubscript{32}Rh\textsubscript{12}, M\textsubscript{r} = 2084.19, Triclinic, a = 11.1230(8), b = 12.1932(9), c = 13.3388(10) Å, α = 85.961(1), β = 68.004(1), γ = 87.862(1)°, U = 1673.1(2) Å\textsuperscript{3}, T = 93(2) K, space group P-1 (no.2), Z = 1, 19423 reflections measured, 7620 unique (R\textsubscript{int} = 0.0231) which were used in all calculations. The final wR(F\textsuperscript{2}) was 0.0840 (all data). TMA\textsubscript{4}[Rh\textsubscript{2}(OH)\textsubscript{2}Nb\textsubscript{10}O\textsubscript{38}] \cdot 18H\textsubscript{2}O (CCDC 1417432). C\textsubscript{32}H\textsubscript{10}N\textsubscript{8}Nb\textsubscript{10}O\textsubscript{32}Rh\textsubscript{2}, M\textsubscript{r} = 2600.40, Monoclinic, a = 11.0911(15), b = 15.379(2), c = 24.327(3) Å, β = 93.748(2)°, U = 4140.60(10) Å\textsuperscript{3}, T = 93(2) K, space group P2\textsubscript{1}/c (no.14), Z = 2, 44814 reflections measured, 9483 unique (R\textsubscript{int} = 0.0223) which were used in all calculations. The final wR(F\textsuperscript{2}) was 0.0460 (all data).

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Fig. S1 ESI-MS of RhNb$_9$ and Rh$_2$Nb$_{10}$
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 RhNb$_9$ niobates either dissociate or form from smaller fragments at pH~12.9
Fig. S3 Change of ESI-MS spectra of Rh$_2$Nb$_{10}$ when the solution pH was adjusted to 12.9.

Fig. S4 Change of ESI-MS spectra of Cr$_2$Nb$_{10}$ 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 MnNb$_9$ when the solution pH was adjusted to 12.8.

**Fig. S8** Change of ESI-MS spectra of FeNb$_9$ when the solution pH was adjusted to 12.7.
**Fig. S9** Change of ESI-MS spectra of CoNb$_9$ 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 Rh$_2$Nb$_{10}$
Fig. S12 pH dependent ESI-MS spectra of RhNb₃
Fig. S13 FT-IR spectra of Rh$_2$Nb$_{10}$ (top) and RhNb$_9$ (bottom)
**Fig. S14** ESI-MS of Rh$_2$Nb$_{10}$ methanol/water solution (20% v/v) before and after irradiation

**Fig. S15** ESI-MS of RhNb$_9$ methanol/water solution (20% v/v) before and after irradiation
**Fig. S16** The UV-Vis spectra of 20 mM solutions of the RhNb$_9$ ion before and after irradiation.

**Fig. S17** The UV-Vis spectra of 20 mM solutions of the Rh$_2$Nb$_{10}$ ion before and after irradiation.