Electronic Supporting Information

Structure, stability and photocatalytic H_2 production by Cr-, Mn-, Fe-, Co-, and Ni-substituted decaniobate clusters

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Analytical Details

ESI-MS spectrometry was carried out using an Agilent G1956b 1100 series LC/MSD single-quadrupole mass spectrometer 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 2 mM sample concentration solution. 2 mL of the solution was titrated with 2.75 M TMAOH solution or TMAOH·5H_2O for basic direction and 1 M HCl solution for acidic direction to minimize volume change. Aliquots of 20 µL solution in different pH were diluted with 1 mL of water and injected directly to ESI-MS for analysis. 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. 2 mL of starting solutions were 2 mM concentration sample solution with 0.1 M of TMACl as background salt. Background correction was applied with 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. Elemental analyses were performed by Galbraith Laboratories Inc. (Knoxville, TN). Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) were performed with Phillips CM12 unit with Oxford EDS attachment.

X-ray Crystallography

Selected single crystal was covered with Paratone oil and attached on a glass fiber or a plastic loop, which was mounted on a goniometer. The crystal was placed in a cold N_2 stream from liquid nitrogen during data collection. Bruker SMART 1000 diffractometer or Bruker Apex II diffractometer equipped with monochromated Mo Kα (λ = 0.71073 Å) radiation were used for data collection. Data reduction was performed with SAINT software.[1] Absorption correction was applied with SADABS program.[2] The crystal structure was solved with SHELXS program[3] by using direct method, and most of metal atom site and some ligand atom sites were found. Subsequent refinement cycles by using SHELXL program was conducted to find remaining atoms and crystallization water molecules from the electron density map. Some of the crystallization water molecules were refined with partial occupancy model. Hydrogen atoms on tetramethylammonium groups were refined with riding model.

Magnetic Measurements

The samples were placed in a gelatin capsule and fixed in the middle of a plastic straw for magnetic measurement by using Quantum Design MPMSXL7 Superconducting Quantum Interference Device (SQUID). The samples were zero-field cooled to 5 K and the magnetization was measured by warming to 300 K in an applied field of 0.01 T (100 Oe). Diamagnetic corrections were applied to the measured molar magnetic susceptibilities by using Pascal's constants.[4]

Photocatalytic H_2 Evolution

Irradiation tests were performed from solution of either 50 mg or 0.2 g of samples in 50 mL of 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^{-2} with 400 nm filter at the flask surface as measured by an International Light IL1400BL photometer equipped with a GaAsP detector for 280 to 660 nm sensitivity range). 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.

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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.
[4] Bain, G. A.; Berry, J. F. J. Chem. Educ. 2008, 85, 532.

Table S1 Bond-valence sum of the substituted transition metals clusters: CrNb$_9$, MnNb$_9$ and CoNb$_9$

	Cr_O length (Å)	bond valence
Cr2_O2	1.898	.625
Cr2_O6	1.909	.607
Cr2_O13	1.995	.481
Cr2_O7	2.043	.422
Cr2_O14	2.093	.369
Cr2_O23	2.103	.359
		∑=2.863

	Cr_O length (Å)	bond valence
Cr9_O21	1.843	.725
Cr9_O27	1.846	.719
Cr9_O20	2.007	.465
Cr9_O22	2.036	.43
Cr9_O23	2.187	.286
Cr9_O14	2.198	.278
		∑=2.903

* bond valence=exp((1.724 - Cr_O length)/0.37)

	Mn_O length (Å)	bond valence
Mn2_O2	1.843	.799
Mn2_O2	1.843	.799
Mn2_O7	2.125	.373
Mn2_O8	2.127	.371
Mn2_O6	2.134	.364
Mn2_O6	2.134	.364
		∑=3.070

* bond valence=exp((1.760 - Mn_O length)/0.37)

	Co_O length (Å)	bond valence
Co2_O6	2.042	.388
Co2_O2	2.054	.376
Co2_O7	2.131	.305
Co2_O13	2.134	.303
Co2_O14	2.165	.278
Co2_O23	2.183	.265
		∑=1.915

* bond valence=exp((1.692 - Co_O length)/0.37)

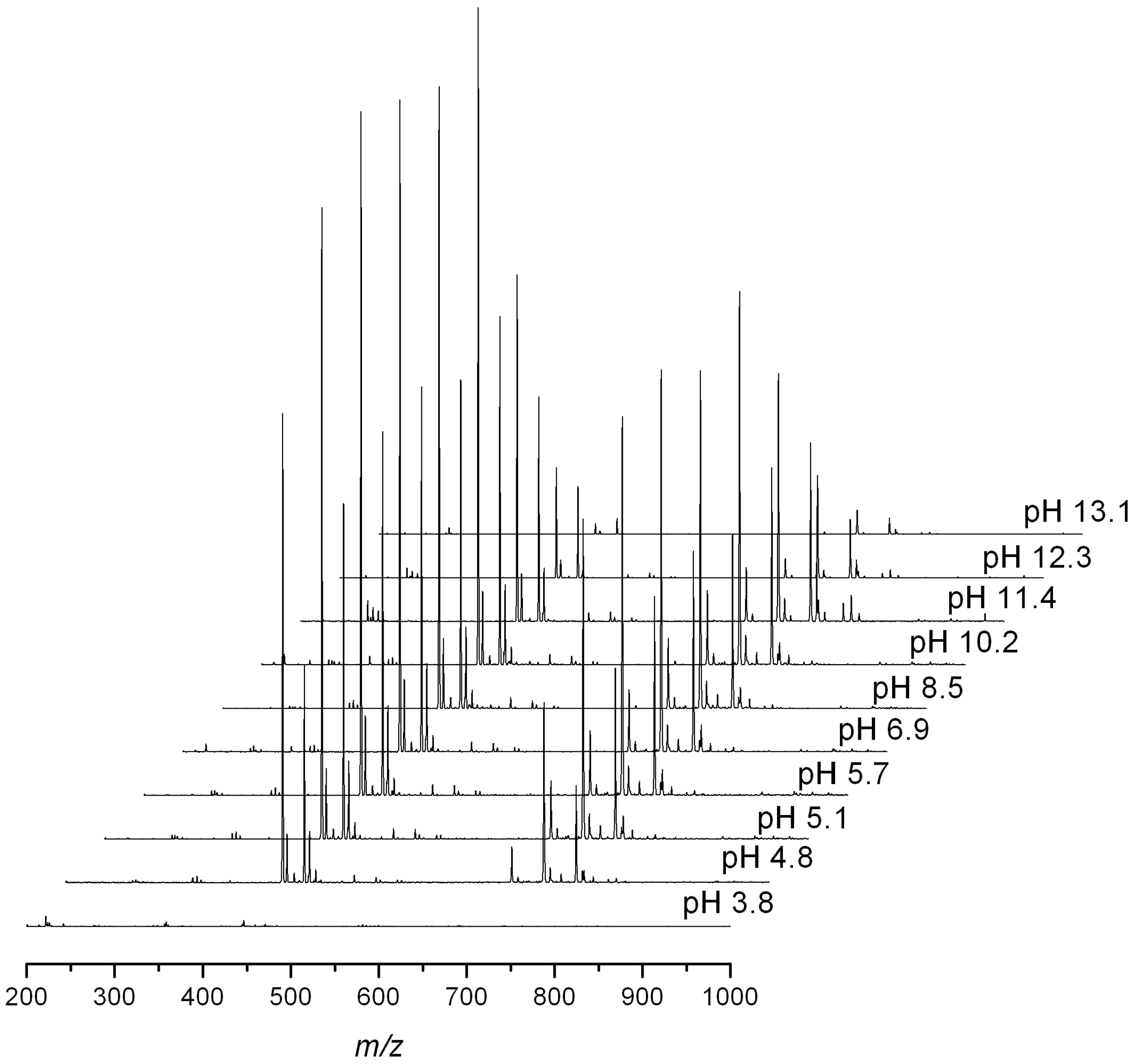


Fig. S1 ESI-MS titration of $CrNb_9$

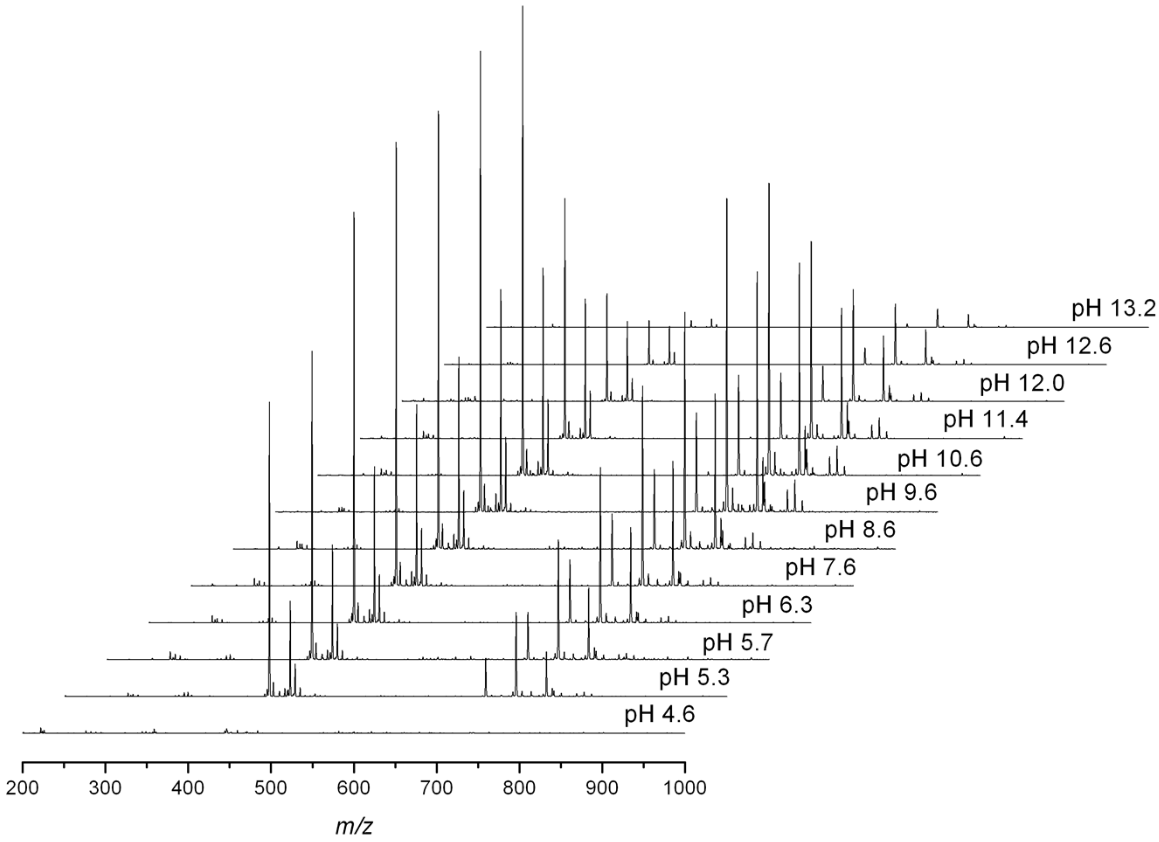


Fig. S2 ESI-MS titration of $MnNb_9$

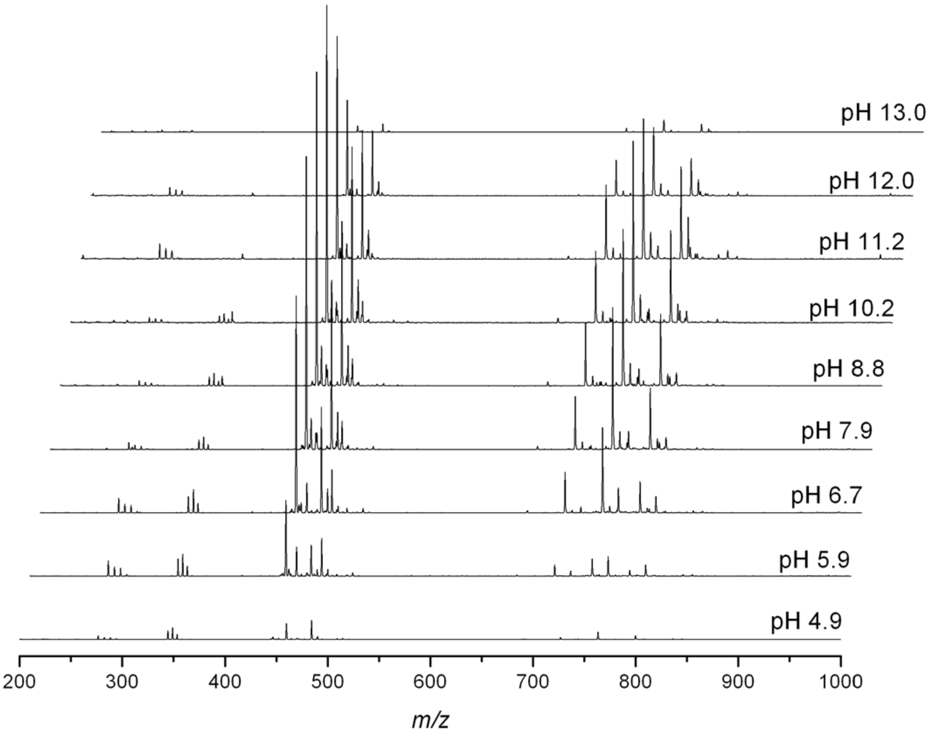


Fig. S3 ESI-MS titration of $CoNb_9$

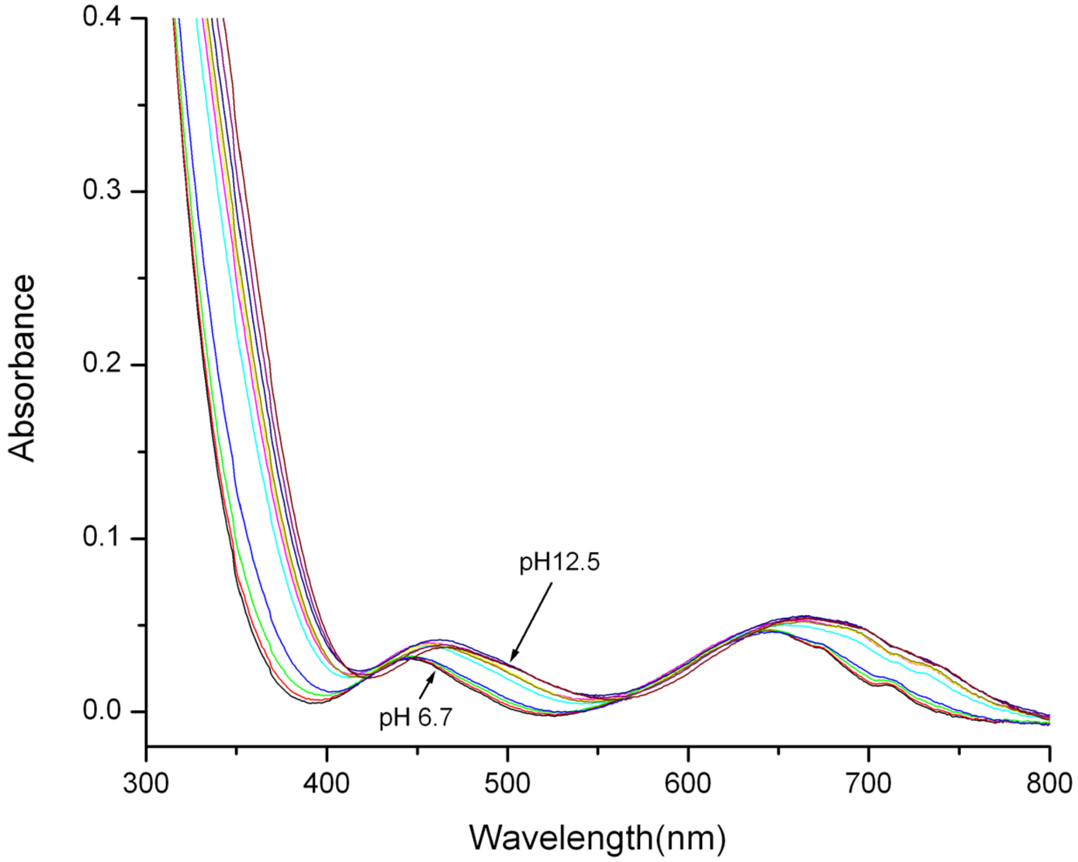


Fig. S4 UV-Vis titration of 2 mM solution of $CrNb_9$ with TMAOH solution.

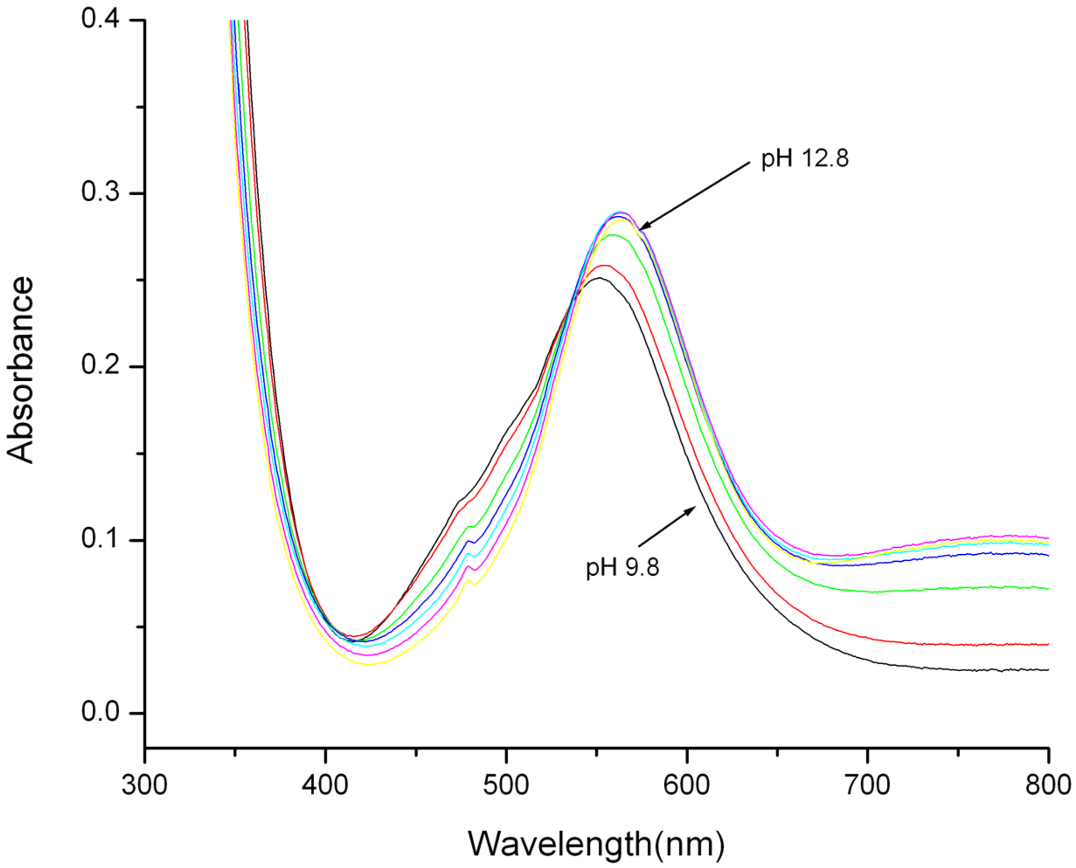


Fig. S5 UV-Vis titration of 2 mM solution of $MnNb_9$ with TMAOH solution.

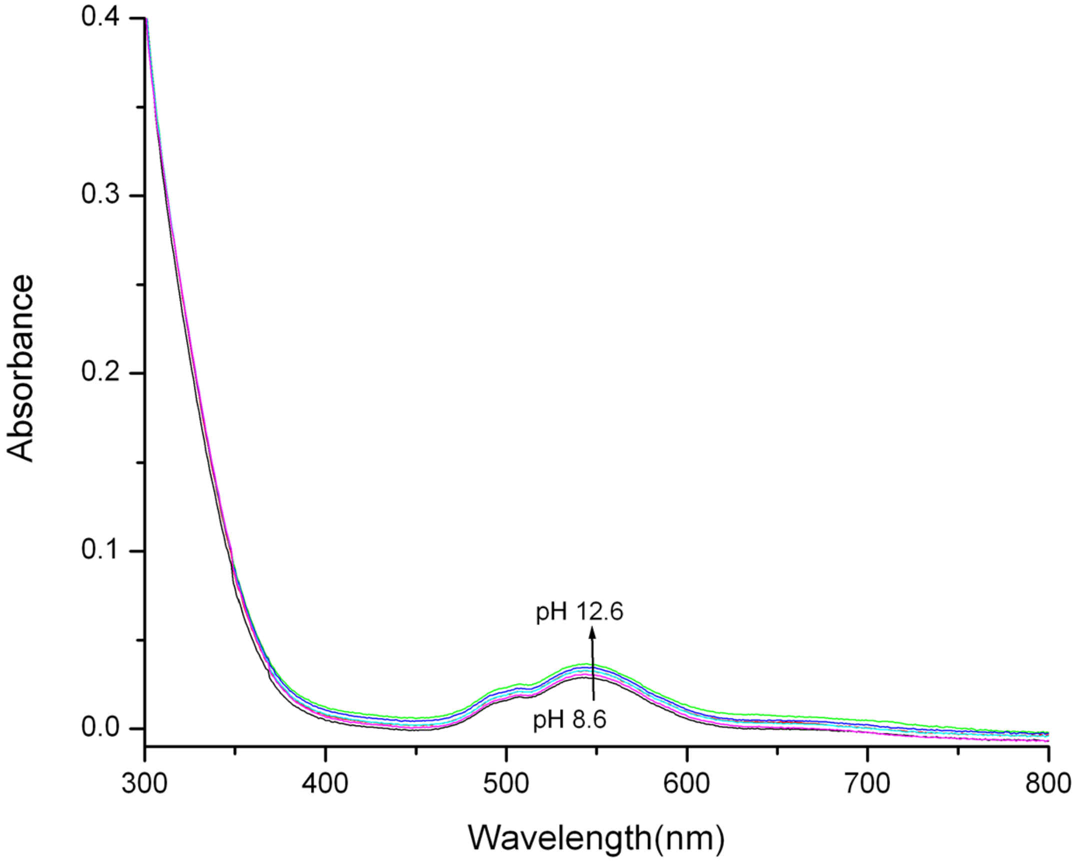


Fig. S6 UV-Vis titration of 2 mM solution of $CoNb_9$ with TMAOH solution.

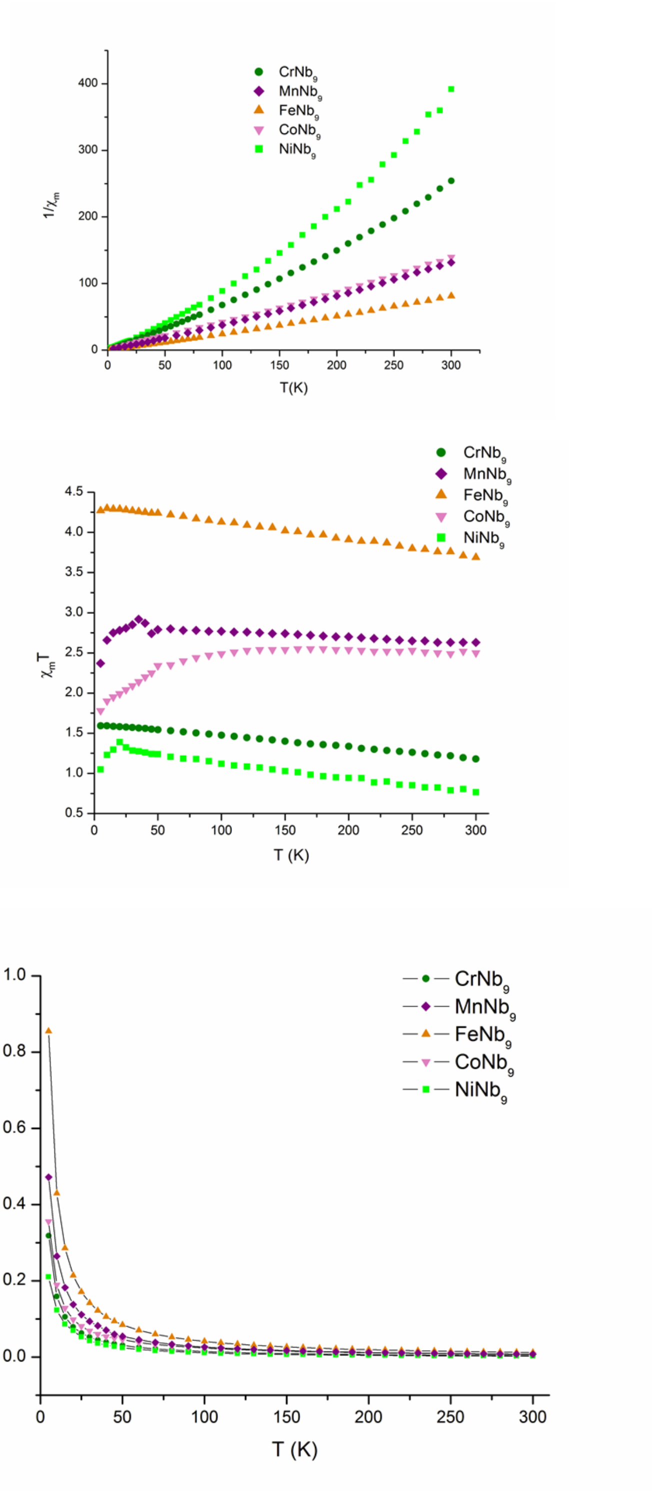


Fig. S7 χ_m^{-1} vs T (top), χ_mT vs T (middle), and χ_m vs T (bottom) plot of the TMA salts of substituted decaniobate

Table S2 Curie-Weiss constants derived by curve fitting the χ_m vs T plot with Curie-Weiss law ($\chi_m = C/(T-\theta)$). Effective magnetic moment (μ_{eff}) was calculated from $\mu_{eff} = 2.828 \times C^{1/2}$

	$CrNb_9$	$MnNb_9$	$FeNb_9$	$CoNb_9$	$NiNb_9$
C/emu K mol^{-1}	1.62(1)	2.89(2)	4.32(1)	2.13(2)	1.64(4)
θ/K	0.10(1)	1.09(6)	0.07(1)	1.03(8)	3.34(18)
μ_{eff}	3.60	4.81	5.88	4.13	3.62

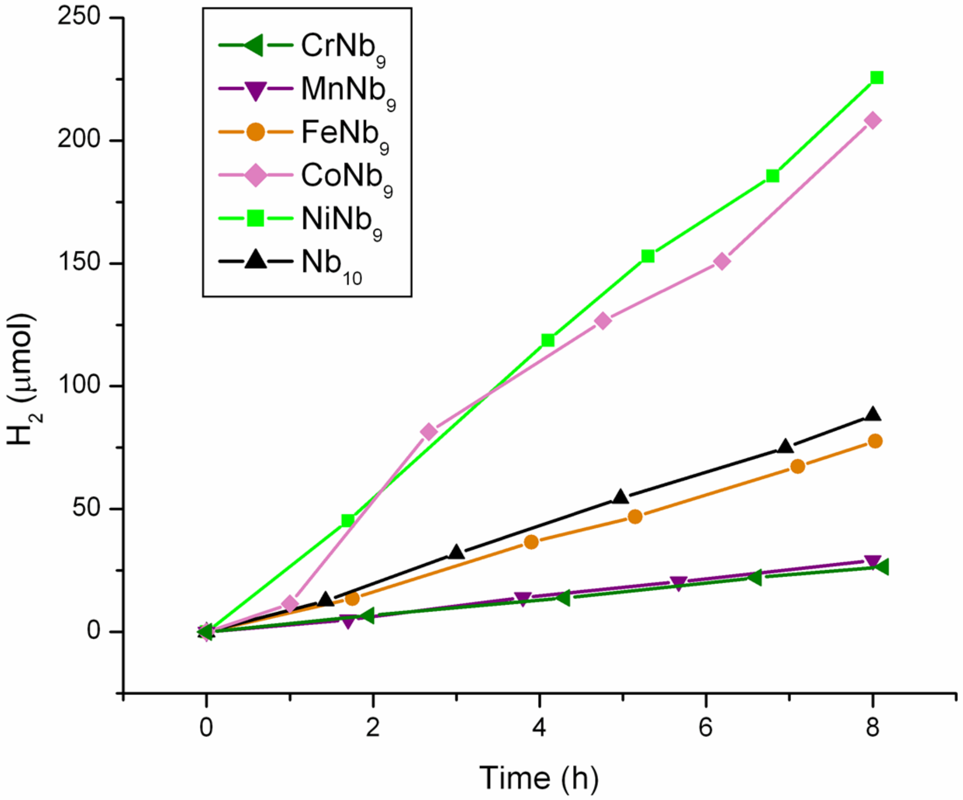


Fig. S8 H_2 evolution from Xe-lamp irradiation of 50 mg of TM-substituted decaniobate in 50mL MeOH/H_2O solution (20% v/v).

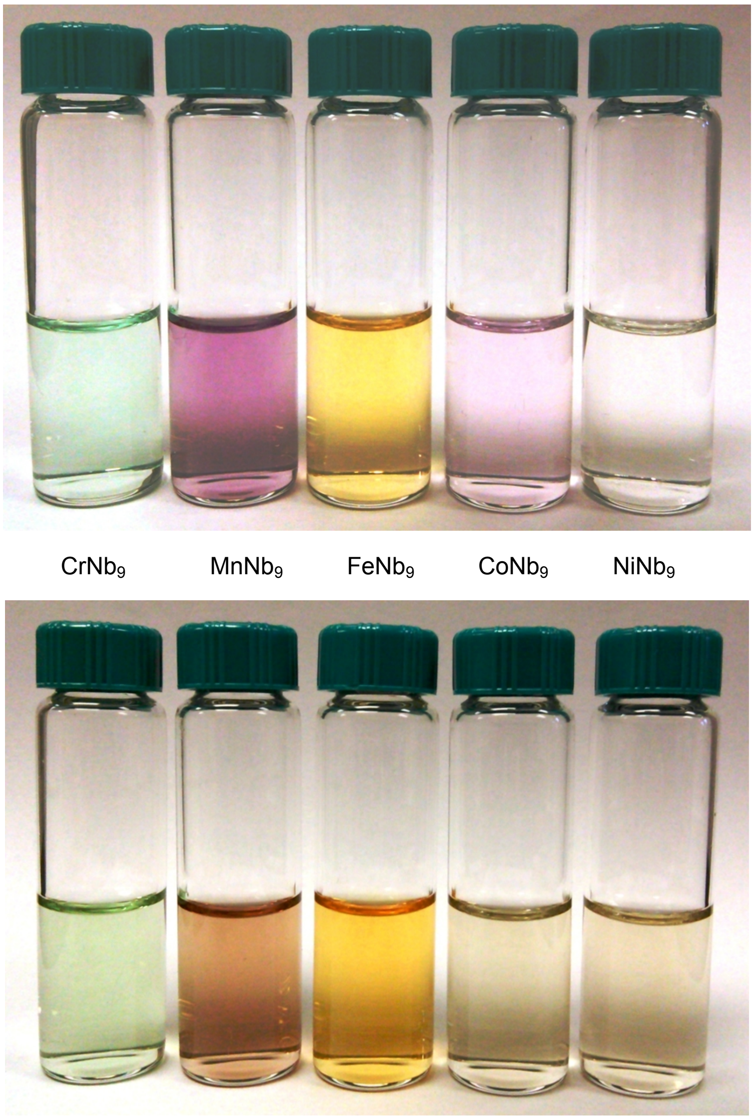


Fig. S9 Solution color before (top) and after (bottom) Xe-lamp irradiation from $CrNb_9$ (far left) to $NiNb_9$ (far right). Each solutions are portions from 0.2 g of samples in 50 mL MeOH/water (20% v/v) solution.

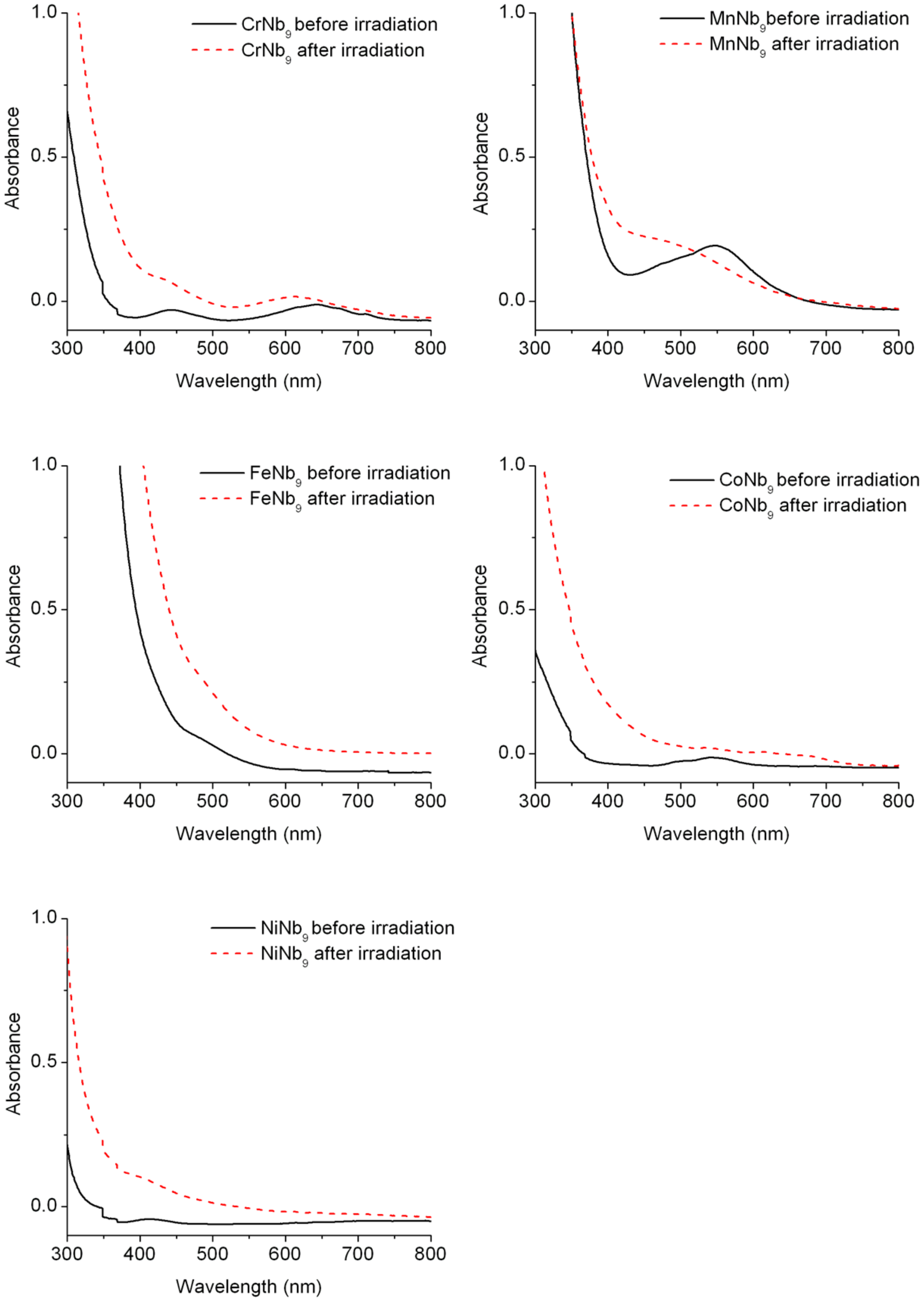


Fig. S10 UV-Vis spectra of the solutions before and after irradiation. Each solutions are portions from 0.2 g of samples in 50 mL MeOH/water (20% v/v) solution.

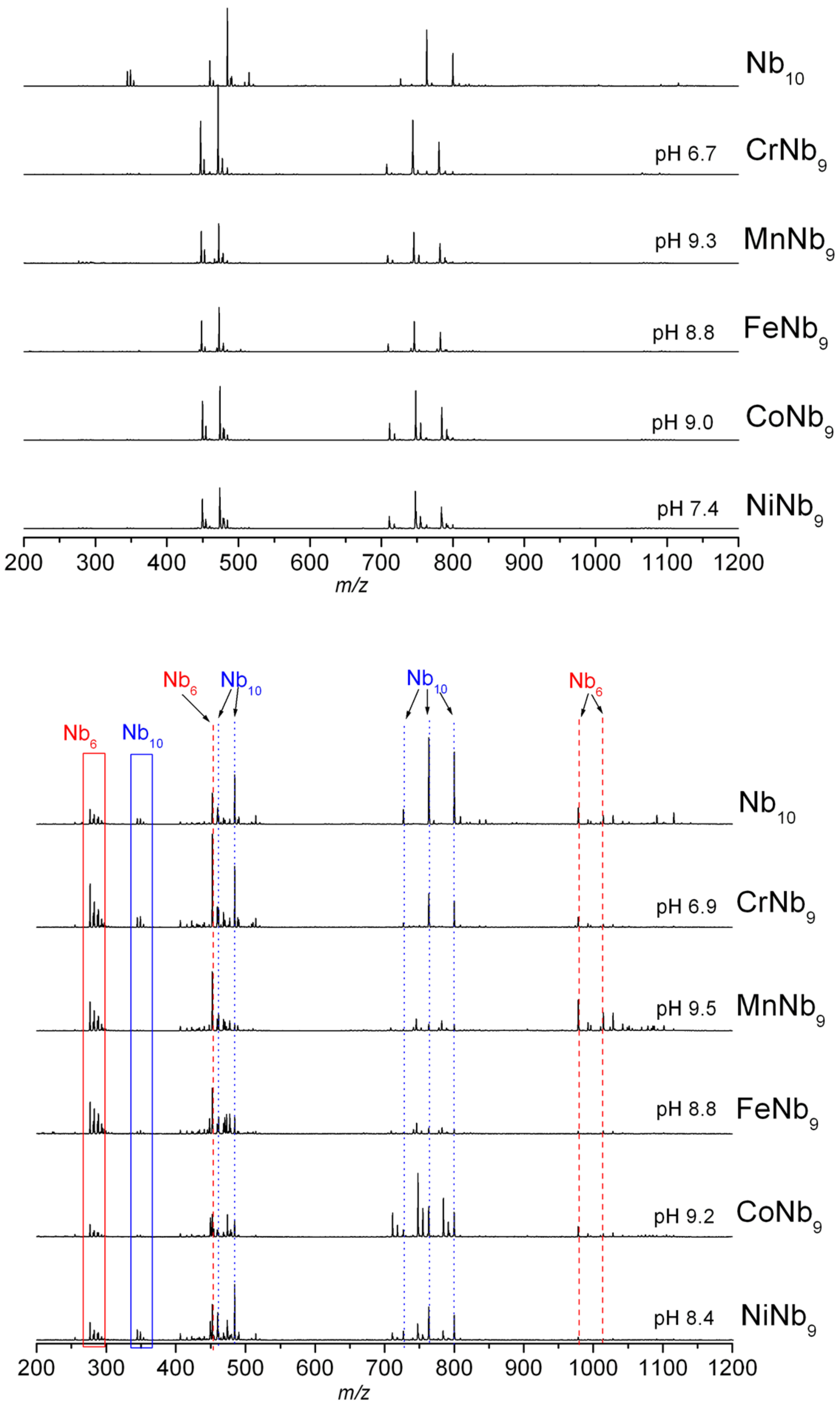


Fig. S11 ESI-MS of 0.2 g of samples in 50 mL MeOH/water (20% v/v) solution before (top) and after (bottom) irradiation

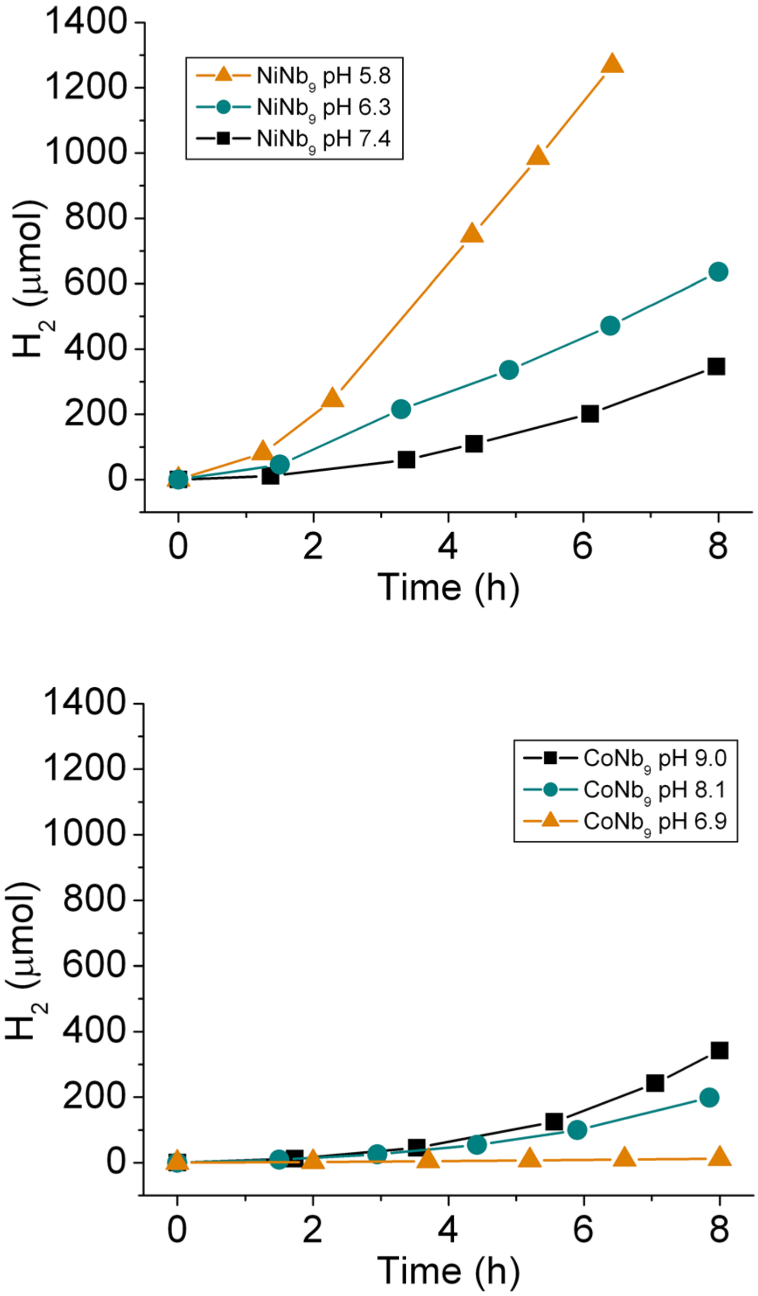
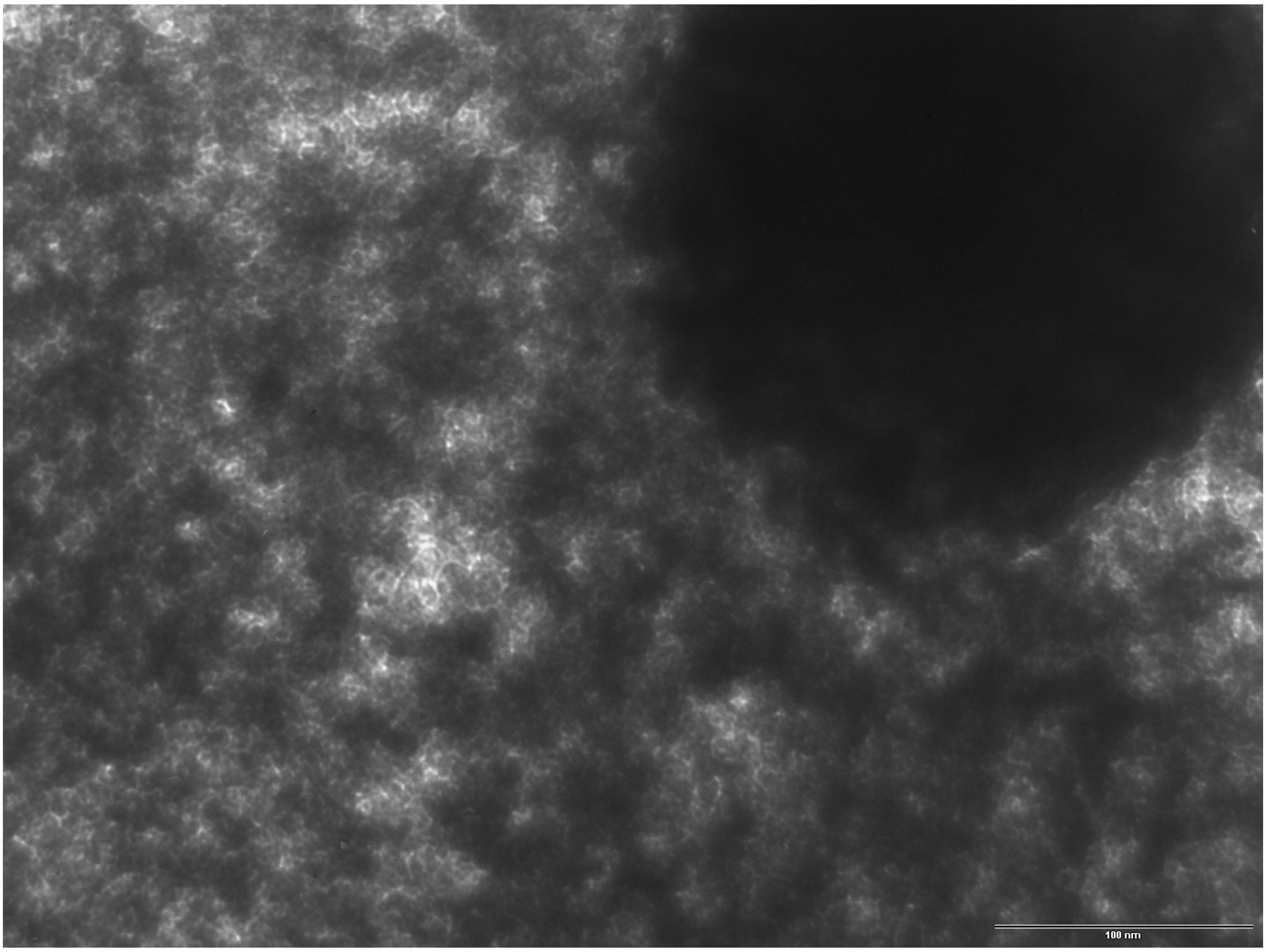


Fig. S12 H_2-evolution data of NiNb$_9$ (top) and CoNb$_9$ (bottom) dependent on pH



Element	Peak Area	Area Sigma	k factor	Abs Corrn.	Weight%	Weight% Sigma	Atomic%
C K	2472	232	2.134	1.000	7.36	0.65	21.63
O K	9370	193	1.765	1.000	23.09	0.47	50.92
Ni K	2544	118	1.322	1.000	4.70	0.22	2.82
Nb K	14694	236	3.162	1.000	64.86	0.67	24.63
Totals					100.00		

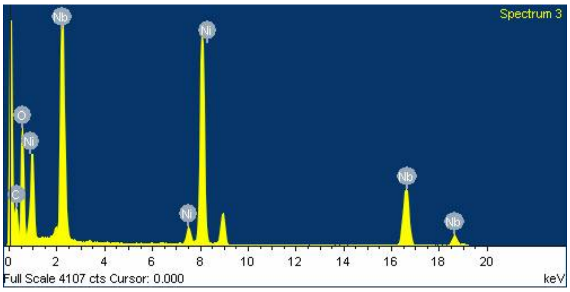


Fig. S13 TEM image of the precipitate from $NiNb_9$ solution at pH 5.8 formed after Xe-lamp irradiation for 8 hours and EDS analysis of this area. Carbon and copper peaks originate from the TEM grid.