Supplementary Information

The rare-earth derivant of mixed-polyoxoniobates clusters with high proton release capacity†

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EXPERIMENTAL SECTION

Materials. $K_7[HNb_6O_{19}]\cdot 13H_2O$ and $K_{12}[H_2P_2W_{12}O_{48}]\cdot 24H_2O$ were prepared according to the literature procedure.[S1–2] Purity was confirmed by IR spectroscopy. All reagents and solvents were of commercially available grade and used without any previous purification

Synthesis of $K_{12}(NH_4)_{10}[\{Nb_{12}P_4W_{24}O_{122}\}_2\{Ln(H_2O)_5\}_4\{Nb_4O_4(OH)_6\}]\cdot xH_2O$ (Ln = Sm, Eu, Tb, Dy, Er, Tm and Yb for **1-7**.

Synthesis of 1: $K_7[HNb_6O_{19}]\cdot 13H_2O$ (2.0 g, 1.46 mmol) was dissolved in a solution consisting of 13.5 mL of 30% aqueous H_2O_2 and 165 mL of water with moderate stirring. Next, 1 M HCl (13 mL) was added dropwise and $K_{12}[H_2P_2W_{12}O_{48}]\cdot 24H_2O$ (5.75 g, 1.46 mmol) was then added immediately under rapidly stirring. Stirring of the resulting solution was continued for approximately 15 mins (pH is ca. 2.0 at this point). Then, about 1 hour later, an aqueous solution of $SmCl_3\cdot 6H_2O$ (5.33 g, 14.6 mmol) was added by dropwise. The mixture was adjusted to pH 2.2~2.4. The resultant solution was refluxed to colorless and then cooled to room temperature. Ammonium chloride (NH_4Cl, 1.56 g, 29.2 mmol) was added to the filtrate, which was stirred for another hour. And, the result solution was heated at 60 °C for 0.5 hour in an open beaker and then cooled to room temperature, filtered. Crystals obtained within one week (yield based on tungsten: 2.8 g, 41%). IR (KBr pellet, cm^{-1}): ν = 3453(s), 3205(s), 2048(m), 1617(m), 1425(m), 1088(s), 1071(s), 1010(w), 959(s), 903(s), 781(s), 694(w), 520(w). CHN analysis calculated: H 1.37, N 0.74; found for H 1.48, N 0.73. ICP-MS analysis show an elemental molar ratio of 3:2:12:7:1 for K:P:W:Nb:Sm.

Synthesis of 2: The synthetic method is the same as above except employing $EuCl_3\cdot 6H_2O$ (5.35 g, 14.6 mmol) instead of $SmCl_3\cdot 6H_2O$ (5.33g, 14.6 mmol). Yield (based on tungsten): 3.5 g, 52%. IR (KBr pellet, cm^{-1}): ν = 3455(s), 3203(s), 2049(m), 1615(m), 1422(m), 1089(s), 1070(s), 1008(w), 958(s), 903(s), 782(s), 692(w), 518(w). CHN analysis calculated: H 1.17, N 0.76; found for H 1.21, N 0.79. ICP-MS analysis show an elemental molar ratio of 3:2:12:7:1 for K:P:W:Nb:Eu.

Synthesis of 3: The synthetic method is the same as above except employing $TbCl_3\cdot 6H_2O$ (5.45 g, 14.6 mmol) instead of $SmCl_3\cdot 6H_2O$ (5.33g, 14.6 mmol) . Yield (based on tungsten): 3.2 g, 46%. IR (KBr pellet, cm^{-1}): ν = 3451(s), 3206(s), 2048(m), 1615(m), 1428(m), 1086(s), 1070(s), 1012(w), 957(s), 901(s), 783(s), 695(w), 521(w). CHN analysis calculated: H 1.36, N 0.74; found for H 1.47, N 0.73. ICP-MS analysis show an elemental molar ratio of 3:2:12:7:1 for K:P:W:Nb:Tb.

Synthesis of 4: The synthetic method is the same as above except employing $DyCl_3\cdot 6H_2O$ (5.50 g, 14.6 mmol) instead of $SmCl_3\cdot 6H_2O$ (5.33g, 14.6 mmol) . Yield (based on tungsten): 3.1 g, 45%. IR (KBr pellet, cm^{-1}): ν = 3452(s), 3202(s), 2048(m), 1615(m), 1424(m), 1087(s), 1075(s), 1012(w), 957(s), 902(s), 784(s), 695(w), 522(w). CHN analysis calculated: H 1.36, N 0.74; found for H 1.43, N 0.77. ICP-MS analysis show an elemental molar ratio of 3:2:12:7:1 for K:P:W:Nb:Dy.

Synthesis of 5: The synthetic method is the same as above except employing $ErCl_3\cdot 6H_2O$ (5.57 g, 14.6 mmol) instead of $SmCl_3\cdot 6H_2O$ (5.33g, 14.6 mmol) . Yield (based on tungsten): 3.4 g, 49%. IR (KBr pellet, cm^{-1}): ν = 3451(s), 3204(s), 2045(m), 1617(m), 1426(m), 1086(s), 1074(s), 1008(w), 957(s), 901(s), 779(s), 692(w), 520(w). CHN analysis calculated: H 1.36, N 0.74; found for H 1.44, N 0.79. ICP-MS analysis show an elemental molar ratio of 3:2:12:7:1 for K:P:W:Nb:Er.

Synthesis of 6: The synthetic method is the same as above except employing $TmCl_3\cdot 6H_2O$ (5.59 g, 14.6 mmol) instead of $SmCl_3\cdot 6H_2O$ (5.33g, 14.6 mmol) . Yield (based on tungsten): 3.3 g, 48%. IR (KBr pellet, cm^{-1}): ν = 3454(s), 3206(s), 2047(m), 1616(m), 1427(m), 1085(s), 1071(s), 1012(w), 958(s), 905(s), 780(s), 694(w), 522(w). CHN analysis calculated: H 1.36, N 0.74; found for H 1.43, N 0.76. ICP-MS analysis show an elemental molar ratio of 3:2:12:7:1 for K:P:W:Nb:Tm.

Synthesis of 7: The synthetic method is the same as above except employing $YbCl_3 \cdot 6H_2O$ (5.66 g, 14.6 mmol) instead of $SmCl_3 \cdot 6H_2O$ (5.33g, 14.6 mmol) . Yield (based on tungsten): 2.9 g, 42%. IR (KBr pellet, cm^{-1}): ν = 3454(s), 3204(s), 2049(m), 1616(m), 1425(m), 1086(s), 1071(s), 1010(w), 958(s), 903(s), 782(s), 696(w), 520(w). CHN analysis calculated: H 1.36, N 0.74; found for H 1.43, N 0.75. ICP-MS analysis show an elemental molar ratio of 3:2:12:7:1 for K:P:W:Nb:Yb.

Instrumentation. IR spectra were recorded on a Bruker VERTEX 70 IR spectrometer spectrometer in the 4000–400 cm^{-1} range using crystalline sample in KBr pellet. The elemental analysis was carried out on an Agilent Technologies 700 Series ICP-OES in Akron. C, H and N elemental analysis were carried out on a VarioElcube CHNS S3analyzer. TGA analyses were carried out on a TGA/DSC3+ analyzer under N_2 atmosphere with 10 °C·min^{-1} heating rate. Electrospray ionization mass spectrometry were performed on an AB SCIEX Triple TOF 4600 instrument at Declustering Potential of -10 V, Collision Energy of -5 V and flow rate of 20 μL/min, the solutions of the investigated systems were prepared in water (1 mg/mL).

The SevenExcellenceTM bench meter was applied for measuring pH values. 4063 Traceable Portable Conductivity Meter was applied for conductivity measurements. Solution preparation and pH measurements were conducted in the glovebox of the N_2 environment at room temperature. All deionized water used in experiments was boiled to get rid of CO_2 dissolved. pH values and conductivities of the 1mg/mL aqueous solution of $\{Ln_4Nb_{28}\}$ clusters were measured to give the original state of clusters before introducing KOH. For each type of $\{Ln_4Nb_{28}\}$ cluster, two groups of aqueous solutions were prepared and used for pH measurements: a group of 1mg/mL clusters solution containing a monotonically increasing amount of KOH, i.e., 10, 20, … up to 100 equivalents, with the volume of each solution of 2 mL; a control group of deionized water containing the same amount of KOH, with the volume of each solution of 2 mL.

X-ray Crystallography. Suitable single crystal for **1-7** were selected and placed in a thin glass tube due to efflorescence. Single-crystal X-ray diffraction data were recorded on a Bruker Apex-II CCD diffractometer at 296(2) K with monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods, and non-H atoms were refined anisotropically by a least-squares method on F^2 using the *OLEX2* program.[S3] Selected details of the data collection and structural refinement of compounds **1-7** can be found in Tab. S1 and and full details are available in the corresponding CIF file, which was deposited at http:// www.ccdc.cam.ac.uk/data_request/cif with the CCDC numbers 2194738-2194744. Because of disorder, these guest water molecules were removed using SQUEEZE.[S4] The molecular formula finally determined according to the charge balance, ICP-OES, CHN elemental analysis and TGA.

S1 M. Filowitz, R. K. C. Ho, W. G. Klemperer and W. Shum, Oxygen-17 nuclear magnetic resonance spectroscopy of polyoxometalates. 1. Sensitivity and resolution, *Inorg. Chem.,* 1979, **18**, 93−103.

S2 R. Contant, Potassium Octadecatungstodiphosphates(V) and Related Lacunary Compounds, *Inorg. Synth.,* 1990, **27**, 104−111.

S3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *OLEX2*: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.,* 2009, **42**, 339−341.

S4 A. L. Spek, *PLATON SQUEEZE*: a tool for the calculation of the disordered solvent contribution to the calculated structure factors, *Acta Crystallogr., Sect. C: Struct. Chem.,* 2015, **71**, 9−18.

Tab. S1 Crystal Data and Structure Refinement of **1**-**7**.

Identification code	**1**	**2**	**3**
Empirical formula	$Sm_4K_8Nb_{29.6}O_{290}P_8W_{48}$	$Eu_4K_8Nb_{28}O_{290}P_8W_{48}$	$Tb_4K_8Nb_{29.6}O_{290}P_8W_{48}$
Formula weight	17376.90	17234.68	17411.18
Temperature/K	296.15	296.15	296.15
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Fddd*	*Fddd*	*Fddd*
a/Å	24.297(9)	24.2194(19)	24.1165(17)
b/Å	44.446(16)	44.094(3)	43.830(3)
c/Å	70.43(2)	70.448(6)	70.337(5)
Volume/Å^3	76056(45)	75233(10)	74349(9)
Z	8	8	8
ρ_{calc}g/cm^3	3.035	3.043	3.111
μ/mm^{-1}	16.118	16.290	16.617
F(000)	60845.0	60352.0	60941.0
Crystal size/mm^3	0.4 × 0.31 × 0.3	0.33 × 0.19 × 0.16	0.53 × 0.36 × 0.19
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.466 to 50	3.292 to 50	3.856 to 50
Index ranges	-24 ≤ h ≤ 28, -52 ≤ k ≤ 52, -71 ≤ l ≤ 83	-28 ≤ h ≤ 28, -38 ≤ k ≤ 52, -83 ≤ l ≤ 83	-28 ≤ h ≤ 28, -51 ≤ k ≤ 51, -58 ≤ l ≤ 83
Reflections collected	95932	95831	94077
Independent reflections	16699 [R_{int}= 0.1336, R_{sigma}= 0.0977]	16548 [R_{int}= 0.0982, R_{sigma}= 0.0708]	16267 [R_{int}= 0.1014, R_{sigma}= 0.0733]
Data/restraints/parameters	16699/24/848	16548/1109/891	16267/593/900
Goodness-of-fit on F^2	0.965	0.991	0.980
Final R indexes [I>=2σ (I)]	R_1= 0.0535, wR_2= 0.1229	R_1= 0.0475, wR_2= 0.1167	R_1= 0.0456, wR_2= 0.1050
Final R indexes [all data]	R_1= 0.1143, wR_2= 0.1375	R_1= 0.0946, wR_2= 0.1274	R_1= 0.0859, wR_2= 0.1135
Largest diff. peak/hole / e Å^{-3}	3.88/-1.93	3.32/-2.81	2.62/-2.47

Identification code	**4**	**5**	**6**	**7**
Empirical formula	$Dy_4K_8Nb_{28}O_{290}P_8W_{48}$	$Er_4K_8Nb_{29.6}O_{290}P_8W_{48}$	$Tm_4K_8Nb_{29.6}O_{290}P_8W_{48}$	$Yb_4K_8Nb_{29.6}O_{290}P_8W_{48}$
Formula weight	17276.84	17444.54	17451.22	17467.66
Temperature/K	296.15	296.15	296.15	296.15
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*Fddd*	*Fddd*	*Fddd*	*Fddd*
a/Å	24.118(3)	23.722(5)	24.099(4)	23.878(8)
b/Å	43.890(5)	43.245(8)	43.796(7)	43.595(14)
c/Å	70.370(9)	69.648(13)	70.296(10)	69.78(2)
Volume/Å^3	74488(16)	71450(24)	74193(19)	72635(41)
Z	8	8	8	8
ρ_{calc}g/cm^3	3.081	3.243	3.125	3.195
μ/mm^{-1}	16.582	17.439	16.846	17.260
F(000)	60448.0	61037.0	61069.0	61101.0
Crystal size/mm^3	0.34 × 0.19 × 0.16	0.33 × 0.19 × 0.16	0.38 × 0.31 × 0.25	0.23 × 0.17 × 0.15
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.308 to 50	3.358 to 50	3.312 to 50	3.332 to 50
Index ranges	-28 ≤ h ≤ 20, -50 ≤ k ≤ 52, -83 ≤ l ≤ 73	-28 ≤ h ≤ 27, -51 ≤ k ≤ 46, -82 ≤ l ≤ 64	-28 ≤ h ≤ 24, -44 ≤ k ≤ 52, -83 ≤ l ≤ 75	-28 ≤ h ≤ 19, -31 ≤ k ≤ 51, -82 ≤ l ≤ 82
Reflections collected	95274	73554	94119	74800
Independent reflections	16391 [R_{int}= 0.1201, R_{sigma}= 0.0854]	15700 [R_{int}= 0.1623, R_{sigma}= 0.1169]	16293 [R_{int}= 0.1246, R_{sigma}= 0.0913]	15939 [R_{int}= 0.1381, R_{sigma}= 0.1211]
Data/restraints/parameters	16391/62/891	15700/663/900	16293/622/901	15939/98/900
Goodness-of-fit on F^2	0.956	1.011	1.018	0.963
Final R indexes [I>=2σ (I)]	R_1= 0.0510, wR_2= 0.1212	R_1= 0.0660, wR_2= 0.1537	R_1= 0.0572, wR_2= 0.1349	R_1= 0.0575, wR_2= 0.1230
Final R indexes [all data]	R_1= 0.1050, wR_2= 0.1339	R_1= 0.1182, wR_2= 0.1690	R_1= 0.1145, wR_2= 0.1493	R_1= 0.1086, wR_2= 0.1358
Largest diff. peak/hole / e Å^{-3}	4.33/-1.81	3.40/-3.53	2.78/-3.66	3.37/-3.51

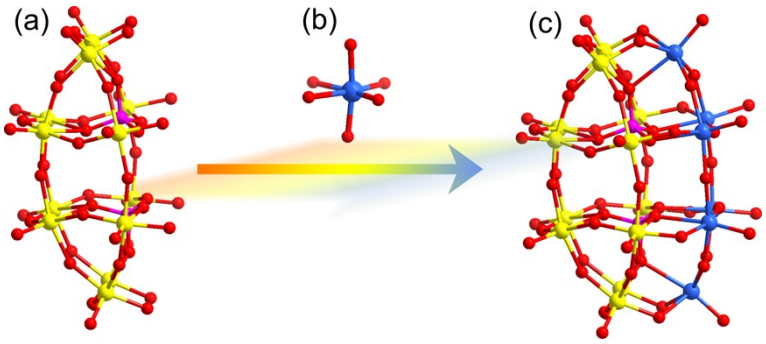

Fig. S1. The evolution from $[P_2W_{12}O_{48}]^{14-}$ to $[Nb_6P_2W_{12}O_{62}]^{12-}$. The ball-and-stick representation of $[P_2W_{12}O_{48}]^{14-}$ (a), NbO_6 (b) and $[Nb_6P_2W_{12}O_{62}]^{12-}$ (c). Color codes: W, yellow; Nb, blue; P, purple; O, red.

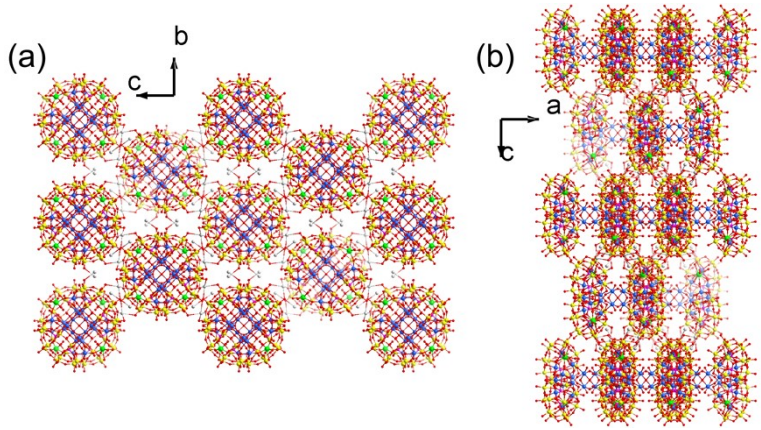

Fig. S2. The purely inorganic three-dimensional metal frame of **1**-**7**. Color codes: W, yellow; Nb, blue; P, purple; Ln, green; O, red; K, light grey.

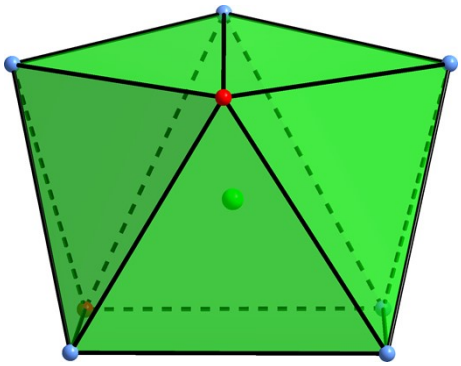

Fig. S3. The two-capped triangular prism geometry of LnO_8 polyhedral. Color codes: Ln, green; O of Nb-O-Ln, red; O of OH_2, light blue.

Tab. S2 Ln-O bond lengths in **1-7.**

Bond	Length	Bond	Length	Bond	Length	Bond	Length
Sm1—O57	2.3198(6)	Eu1—O57	2.3282(2)	Tb1—O57	2.2802(1)	Dy1—O57	2.2824(2)
Sm1—O49	2.3284(7)	Eu1—O49	2.3383(1)	Tb1—O49	2.2932(1)	Dy1—O49	2.2819(2)
Sm1—O4W	2.3489(7)	Eu1—O4W	2.3087(2)	Tb1—O4W	2.3922(1)	Dy1—O4W	2.3543(3)
Sm1—O3W	2.4276(8)	Eu1—O3W	2.3940(2)	Tb1—O3W	2.4160(2)	Dy1—O3W	2.4059(3)
Sm1—O6W	2.4849(7)	Eu1—O1W	2.5151(1)	Tb1—O5W	2.4397(1)	Dy1—O6W	2.4266(2)
Sm1—O2W	2.5182(5)	Eu1—O6W	2.5239(2)	Tb1—O6W	2.4456(1)	Dy1—O5W	2.4506(2)
Sm1—O1W	2.5225(6)	Eu1—O2W	2.5319(1)	Tb1—O1W	2.4572(1)	Dy1—O1W	2.4516(2)
Sm1—O5W	2.6288(6)	Eu1—O5W	2.5444(1)	Tb1—O2W	2.5020(1)	Dy1—O2W	2.4736(2)

Bond	Length	Bond	Length	Bond	Length	Average Length	
Er1—O57	2.2529(4)	Tm1—O57	2.2834(3)	Yb1—O57	2.2102(6)	**1** (Sm)	2.4474
Er1—O49	2.2550(4)	Tm1—O49	2.2380(3)	Yb1—O49	2.2135(6)	**2** (Eu)	2.4356
Er1—O3W	2.2549(4)	Tm1—O3W	2.3275(4)	Yb1—O6W	2.3073(7)	**3** (Tb)	2.4033
Er1—O4W	2.2681(4)	Tm1—O4W	2.3502(3)	Yb1—O3W	2.3109(7)	**4** (Dy)	2.3909
Er1—O1W	2.3758(3)	Tm1—O6W	2.3813(3)	Yb1—O5W	2.3167(6)	**5** (Er)	2.3297
Er1—O2W	2.3859(3)	Tm1—O1W	2.4187(2)	Yb1—O4W	2.3239(7)	**6** (Tm)	2.3597
Er1—O5W	2.4197(3)	Tm1—O5W	2.4284(3)	Yb1—O1W	2.3702(5)	**7** (Yb)	2.3073
Er1—O6W	2.4255(4)	Tm1—O2W	2.4500(2)	Yb1—O2W	2.4053(5)		

Tab. S3 BVS calculation results of all the atoms in **1-7**.

Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence
Sm1	2.99	W8	6.32	Nb3	4.87	O9	1.96	O33	1.95	O57	1.88
W1	6.17	W9	6.16	Nb4	4.88	O10	1.88	O34	2.01	O58	1.72
W2	6.23	W10	6.14	Nb5	5.13	O11	1.52	O35	1.86	O59	2.03
W3	5.90	W11	6.13	Nb6	4.85	O12	2.06	O36	1.71	O60	1.87
W4	5.94	W12	5.99	Nb7	4.93	O13	2.05	O37	2.13	O61	1.91
W5	6.04	Nb1	4.82	P1	4.66	O14	1.90	O38	2.02	O62	1.89
W6	6.39	Nb2	4.95	P2	4.79	O15	1.83	O39	1.73	O63	1.88
W7	5.99					O16	1.61	O40	1.94	O64	1.22
O1	1.84	O25	1.82	O49	1.89	O17	2.13	O41	2.12	O65	0.93
O2	1.90	O26	2.09	O50	1.79	O18	2.02	O42	1.77	O1W	0.31
O3	1.94	O27	1.65	O51	1.71	O19	1.93	O43	1.58	O2W	0.29
O4	1.98	O28	2.08	O52	2.05	O20	1.73	O44	1.88	O3W	0.36
O5	1.82	O29	1.92	O53	1.87	O21	1.61	O45	1.91	O4W	0.46
O6	1.81	O30	1.88	O54	2.06	O22	2.04	O46	1.86	O5W	0.21
O7	1.86	O31	1.81	O55	1.77	O23	1.84	O47	1.72	O6W	0.26
O8	1.94	O32	1.82	O56	2.02	O24	2.06	O48	1.85		

Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence
Eu1	2.60	W8	6.17	Nb3	4.96	O9	2.04	O33	2.00	O57	1.92
W1	6.17	W9	6.09	Nb4	5.04	O10	1.91	O34	2.06	O58	1.69
W2	6.24	W10	6.15	Nb5	5.15	O11	1.71	O35	1.82	O59	2.08
W3	6.26	W11	6.23	Nb6	4.94	O12	2.12	O36	1.65	O60	1.91
W4	6.10	W12	6.20	Nb7	4.92	O13	2.08	O37	2.12	O61	2.00
W5	6.16	Nb1	5.13	P1	4.77	O14	2.00	O38	2.02	O62	1.98

W6	6.31	Nb2	5.10	P2	4.75	O15	1.86	O39	1.73	O63	1.93
W7	6.28					O16	1.66	O40	1.97	O64	1.44
O1	1.80	O25	1.71	O49	1.89	O17	2.13	O41	2.03	O65	0.79
O2	1.89	O26	2.13	O50	1.79	O18	2.04	O42	1.82	O1W	0.31
O3	1.97	O27	1.75	O51	1.69	O19	2.03	O43	1.82	O2W	0.24
O4	2.00	O28	2.11	O52	2.09	O20	1.77	O44	1.88	O3W	0.35
O5	1.95	O29	1.97	O53	1.89	O21	1.61	O45	1.82	O4W	0.44
O6	1.90	O30	1.91	O54	2.07	O22	2.00	O46	1.87	O5W	0.23
O7	1.87	O31	1.83	O55	1.78	O23	1.81	O47	1.83	O6W	0.18
O8	1.97	O32	1.76	O56	2.09	O24	2.06	O48	1.80		

Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence
Tb1	3.04	W8	6.42	Nb3	5.09	O9	2.06	O33	2.06	O57	1.95
W1	6.24	W9	6.44	Nb4	5.02	O10	1.92	O34	2.06	O58	1.72
W2	6.34	W10	6.22	Nb5	5.23	O11	1.84	O35	1.76	O59	2.10
W3	6.41	W11	6.43	Nb6	5.20	O12	2.19	O36	1.84	O60	1.99
W4	6.39	W12	6.26	Nb7	5.00	O13	2.13	O37	2.15	O61	2.05
W5	6.39	Nb1	5.09	P1	4.72	O14	1.98	O38	2.06	O62	1.96
W6	6.36	Nb2	5.13	P2	4.67	O15	1.92	O39	1.73	O63	2.00
W7	6.19					O16	1.82	O40	2.02	O64	1.26
O1	1.75	O25	1.72	O49	2.03	O17	2.18	O41	2.05	O65	0.82
O2	1.91	O26	2.14	O50	1.84	O18	2.09	O42	1.86	O1W	0.35
O3	1.98	O27	1.84	O51	1.68	O19	2.04	O43	1.77	O2W	0.30
O4	2.07	O28	2.16	O52	2.09	O20	1.79	O44	1.94	O3W	0.34
O5	1.86	O29	1.99	O53	1.92	O21	1.79	O45	1.95	O4W	0.38
O6	1.87	O30	1.93	O54	2.11	O22	2.06	O46	1.91	O5W	0.26
O7	1.90	O31	1.84	O55	1.87	O23	1.86	O47	1.84	O6W	0.32
O8	2.02	O32	1.82	O56	2.13	O24	2.10	O48	1.83		

Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence
Dy1	3.00	W8	6.35	Nb3	4.95	O9	2.05	O33	2.03	O57	2.00
W1	6.45	W9	6.43	Nb4	5.15	O10	1.94	O34	2.06	O58	1.71
W2	6.24	W10	6.21	Nb5	5.19	O11	1.68	O35	1.80	O59	2.11
W3	6.38	W11	6.31	Nb6	4.99	O12	2.19	O36	1.74	O60	1.96
W4	6.21	W12	6.19	Nb7	5.01	O13	2.11	O37	2.18	O61	2.04
W5	6.25	Nb1	5.12	P1	4.78	O14	1.93	O38	2.04	O62	1.99
W6	6.52	Nb2	5.18	P2	4.70	O15	1.87	O39	1.78	O63	1.91
W7	6.25					O16	1.69	O40	2.02	O64	1.31
O1	1.93	O25	1.77	O49	1.94	O17	2.18	O41	2.07	O65	0.85
O2	1.96	O26	2.17	O50	1.88	O18	2.08	O42	1.84	O1W	0.36
O3	1.97	O27	1.72	O51	1.68	O19	2.00	O43	1.76	O2W	0.28
O4	2.03	O28	2.16	O52	2.10	O20	1.79	O44	1.89	O3W	0.36
O5	2.01	O29	2.02	O53	1.92	O21	1.62	O45	1.95	O4W	0.38
O6	1.89	O30	1.93	O54	2.11	O22	2.09	O46	1.90	O5W	0.32
O7	1.89	O31	1.86	O55	1.84	O23	1.88	O47	1.69	O6W	0.26
O8	1.99	O32	1.82	O56	2.07	O24	2.12	O48	2.12		

Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence
Er1	3.22	W8	6.42	Nb3	5.24	O9	2.09	O33	2.07	O57	2.08

W1	6.02	W9	6.25	Nb4	5.38	O10	2.09	O34	2.07	O58	1.76
W2	6.47	W10	6.52	Nb5	5.34	O11	1.94	O35	1.97	O59	2.18
W3	6.64	W11	6.34	Nb6	5.33	O12	2.18	O36	1.73	O60	2.01
W4	6.3	W12	6.3	Nb7	5.3	O13	2.11	O37	2.19	O61	2.12
W5	6.44	Nb1	5.42	P1	4.81	O14	2.06	O38	2.07	O62	2.11
W6	6.65	Nb2	4.95	P2	4.89	O15	1.86	O39	1.89	O63	1.99
W7	6.66					O16	1.72	O40	2.06	O64	1.35
O1	1.64	O25	1.89	O49	2.08	O17	2.21	O41	2.12	O65	0.9
O2	2.03	O26	2.19	O50	1.91	O18	2.09	O42	1.81	O1W	0.35
O3	2.02	O27	1.96	O51	1.74	O19	2.17	O43	1.86	O2W	0.34
O4	2.06	O28	2.23	O52	2.16	O20	1.85	O44	1.98	O3W	0.44
O5	1.9	O29	1.98	O53	1.95	O21	1.71	O45	1.88	O4W	0.49
O6	1.92	O30	2.02	O54	2.16	O22	2.06	O46	1.94	O5W	0.36
O7	1.77	O31	1.89	O55	1.88	O23	1.92	O47	1.81	O6W	0.25
O8	2.03	O32	1.7	O56	2.19	O24	2.16	O48	1.89		

Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence
Tm1	2.96	W8	6.35	Nb3	4.97	O9	2.04	O33	2.04	O57	2.05
W1	6.23	W9	6.36	Nb4	5.29	O10	2.00	O34	2.07	O58	1.77
W2	6.32	W10	6.12	Nb5	5.22	O11	1.74	O35	1.82	O59	2.12
W3	6.22	W11	6.23	Nb6	5.02	O12	2.18	O36	1.78	O60	1.96
W4	6.48	W12	6.41	Nb7	5.31	O13	2.12	O37	2.11	O61	2.02
W5	6.31	Nb1	5.26	P1	4.67	O14	2.00	O38	2.03	O62	1.96
W6	6.47	Nb2	5.05	P2	4.78	O15	1.90	O39	1.67	O63	1.95
W7	6.11					O16	1.73	O40	1.98	O64	1.31
O1	1.76	O25	1.80	O49	2.05	O17	2.19	O41	2.06	O65	0.85
O2	1.91	O26	2.10	O50	1.87	O18	2.09	O42	1.77	O1W	0.33
O3	2.00	O27	1.74	O51	1.81	O19	2.11	O43	1.68	O2W	0.26
O4	2.08	O28	2.13	O52	2.09	O20	1.76	O44	1.97	O3W	0.30
O5	1.89	O29	2.00	O53	1.87	O21	1.71	O45	2.02	O4W	0.46
O6	1.84	O30	1.97	O54	2.09	O22	2.00	O46	1.91	O5W	0.40
O7	1.69	O31	1.94	O55	1.89	O23	1.89	O47	1.82	O6W	0.28
O8	2.00	O32	1.85	O56	2.10	O24	2.06	O48	1.91		

Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence
Yb1	3.30	W8	6.56	Nb3	5.26	O9	2.06	O33	2.08	O57	1.91
W1	6.62	W9	6.48	Nb4	5.21	O10	1.93	O34	2.17	O58	1.86
W2	6.29	W10	6.52	Nb5	5.46	O11	1.70	O35	1.86	O59	2.16
W3	6.23	W11	6.43	Nb6	5.20	O12	2.24	O36	1.85	O60	2.02
W4	6.51	W12	6.28	Nb7	5.54	O13	2.16	O37	2.17	O61	2.07
W5	6.35	Nb1	5.27	P1	4.84	O14	1.95	O38	2.13	O62	2.07
W6	6.60	Nb2	5.33	P2	4.85	O15	3.30	O39	1.86	O63	2.03
W7	6.41					O16	1.77	O40	2.08	O64	1.14
O1	1.90	O25	1.71	O49	2.01	O17	2.21	O41	2.09	O65	1.26
O2	2.02	O26	2.19	O50	1.91	O18	2.13	O42	1.86	O1W	0.40
O3	2.10	O27	1.86	O51	1.91	O19	2.12	O43	6.16	O2W	0.35
O4	2.12	O28	2.24	O52	2.14	O20	1.86	O44	2.00	O3W	0.37
O5	1.93	O29	2.01	O53	1.98	O21	1.84	O45	2.01	O4W	0.33
O6	1.99	O30	1.99	O54	2.17	O22	2.17	O46	1.99	O5W	0.38

O7	1.89	O31	1.92	O55	1.87	O23	1.93	O47	1.70	O6W	0.40
O8	2.04	O32	1.69	O56	2.17	O24	2.14	O48	1.89		

Tab. S4 pH and conductivity measurements of 1mg/mL aqueous solution of $\{Ln_4Nb_{28}\}$.

POM	Sm	Eu	Tb	Dy	Er	Tm	Yb
pH	5.774	5.741	5.447	5.81	5.728	5.95	5.624
Conductivity (μS/cm)	83.2	71.9	89.2	87.0	89.3	84.5	85.9
Number of counterions dissociated per cluster	22.6	19.5	24.8	23.6	24.3	23.0	23.3

Number of counterions dissociated per cluster is calculated based on pH and conductivities. NH_4^+ and K^+ have comparable molar conductivity.

Tab. S5 Number of protons neutralizing KOH during the titration.

Molar ratio KOH:POM	Degree of hydrolysis	Number of H^+ contributed by NH_4^+ per $\{Sm_4Nb_{28}\}$ cluster	Total number of H^+ released per $\{Sm_4Nb_{28}\}$ cluster	Number of H^+ contributed by the anion part per $\{Sm_4Nb_{28}\}$ cluster
0	0	0	0	0
10	0.8	7.6	8.5	0.9
20	1.0	9.8	15.8	6.0
30	1.0	10.0	21.8	11.8
40	1.0	10.0	28.1	18.1

Example calculation of pK_a of $\{Sm_4Nb_{28}\}$ cluster with 20 equiv. of KOH:

Concentration of cluster solution [cluster] = 1mg/mL = $5.6 * 10^{-5}$ M

pH = 9.088 (Tab. S7)

Deprotonation efficiency ≈ 0.5 (after the subtraction of contribution by ammonium)

Each cluster with 20 coordinated water ligands is considered as 20 monoprotic acids (HA). Thus, the original concentration of HA can be calculated. $[HA]_{original}$ = [cluster] * 20 = $1.1 * 10^{-3}$ M

The concentrations of HA and A^- can be calculated based on the deprotonation efficiency.

[HA] = $1.1 * 10^{-3}$ M * (1 - 0.6) = $4.4 * 10^{-2}$ M

$[A^-] = 1.1 * 10^{-3}$ M * 0.6 = $6.6 * 10^{-2}$ M

There are three reactions in the solution:

1. $OH^-_{(aq)} + HA_{(aq)} \rightleftharpoons H_2O_{(l)} + A^-_{(aq)}$
2. $HA_{(aq)} \rightleftharpoons H+_{(aq)} + A^-_{(aq)}$
3. $H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)}$

$$K_{a1} = \frac{[A^-]}{[HA][OH^-]} = 9.6 * 10^4$$

$$K_{a2} = \frac{K_{a1}}{K_{a3}} = 1.0 * 10^9$$

pK_{a2} = 9.0

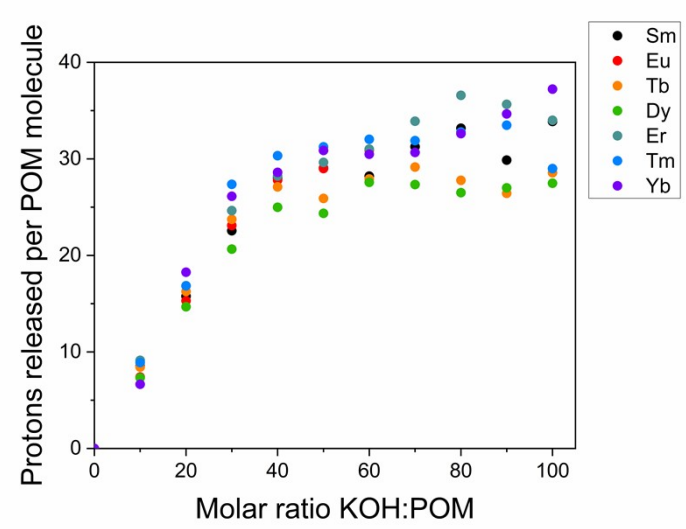

Fig. S4. The number of protons released per molecular cluster versus the molar ratio of KOH introduced to POM clusters.

Tab. S6 pH measurements of 1mg/mL aqueous solution (2 mL) of $\{Sm_4Nb_{28}\}$ and water (2 mL) containing the same amount of KOH.

Molar ratio KOH:$\{Sm_4Nb_{28}\}$	pH of POM solution containing KOH	pH of water containing KOH	Number of protons released per cluster
10	8.387	10.731	8.5
20	9.088	11.005	15.8
30	9.752	11.159	21.8
40	10.484	11.323	28.1
50	10.790	11.401	29.1
60	11.058	11.480	28.2
70	11.175	11.561	31.3
80	11.292	11.575	33.2
90	11.382	11.652	29.9
100	11.449	11.709	33.9

Tab. S7 pH measurements of 1mg/mL aqueous solution (2 mL) of $\{Eu_4Nb_{28}\}$and water (2 mL) containing the same amount of KOH.

Molar ratio KOH:$\{Eu_4Nb_{28}\}$	pH of POM solution containing KOH	pH of water containing KOH	Number of protons released per cluster
10	8.625	10.781	7.4
20	9.263	11.100	15.3
30	9.874	11.289	23.1
40	10.547	11.415	27.8
50	10.921	11.502	29.0
60	11.127	11.584	30.9

Tab. S8 pH measurements of 1mg/mL aqueous solution (2 mL) of $\{Tb_4Nb_{28}\}$ and water (2 mL) containing the same amount of KOH.

Molar ratio KOH:$\{Tb_4Nb_{28}\}$	pH of POM solution containing KOH	pH of water containing KOH	Number of protons released per cluster
10	8.660	10.680	8.4
20	9.183	10.969	16.3
30	9.792	11.149	23.7
40	10.502	11.273	27.1
50	10.879	11.350	25.9
60	11.069	11.441	27.9
70	11.200	11.511	29.1
80	11.318	11.570	27.8
90	11.402	11.606	26.4
100	11.462	11.655	28.6

Tab. S9 pH measurements of 1mg/mL aqueous solution (2 mL) of $\{Dy_4Nb_{28}\}$ and water (2 mL) containing the same amount of KOH.

Molar ratio KOH:$\{Dy_4Nb_{28}\}$	pH of POM solution containing KOH	pH of water containing KOH	Number of protons released per cluster
10	8.862	10.587	7.3
20	9.460	10.905	14.7
30	10.035	11.073	20.7
40	10.500	11.206	25.0
50	10.848	11.292	24.4
60	11.037	11.413	27.6
70	11.155	11.461	27.3
80	11.269	11.514	26.5
90	11.347	11.559	27.0
100	11.420	11.611	27.5

Tab. S10 pH measurements of 1mg/mL aqueous solution (2 mL) of $\{Er_4Nb_{28}\}$ and water (2 mL) containing the same amount of KOH.

Molar ratio KOH:$\{Er_4Nb_{28}\}$	pH of POM solution containing KOH	pH of water containing KOH	Number of protons released per cluster
10	8.584	10.686	9.1
20	9.113	10.958	16.9
30	9.888	11.144	24.6
40	10.544	11.271	28.2
50	10.857	11.364	29.6
60	11.040	11.435	31.0
70	11.181	11.525	33.9
80	11.283	11.592	36.6

90	11.381	11.634	35.7
100	11.469	11.676	34.0

Tab. S11 pH measurements of 1mg/mL aqueous solution (2 mL) of $\{Tm_4Nb_{28}\}$ and water (2 mL) containing the same amount of KOH.

Molar ratio KOH:$\{Tm_4Nb_{28}\}$	pH of POM solution containing KOH	pH of water containing KOH	Number of protons released per cluster
10	8.883	10.780	8.9
20	9.241	11.062	16.8
30	9.848	11.279	27.4
40	10.553	11.374	30.3
50	10.924	11.465	31.2
60	11.139	11.544	32.0
70	11.294	11.613	31.9
80	11.387	11.664	32.8
90	11.477	11.716	33.5
100	11.546	11.739	29.0

Tab. S12 pH measurements of 1mg/mL aqueous solution (2 mL) of $\{Yb_4Nb_{28}\}$ and water (2 mL) containing the same amount of KOH.

Molar ratio KOH:$\{Yb_4Nb_{28}\}$	pH of POM solution containing KOH	pH of water containing KOH	Number of protons released per cluster
10	8.832	10.620	6.6
20	9.457	11.033	18.3
30	9.942	11.168	26.1
40	10.571	11.303	28.6
50	10.927	11.414	30.9
60	11.123	11.472	30.5
70	11.251	11.550	30.7
80	11.362	11.611	32.6
90	11.441	11.667	34.7
100	11.499	11.715	37.2

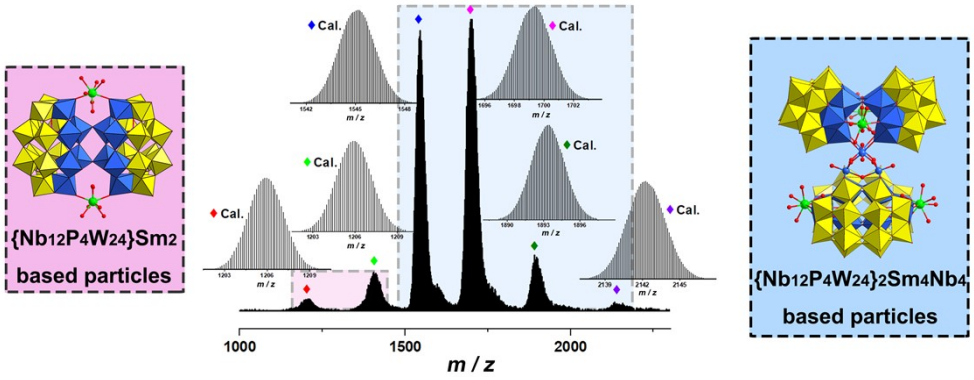

Fig. S5. The negative-ion ESI mass spectra of $\{Sm_4Nb_{28}\}$. The detection of $\{Nb_{12}P_4W_{24}\}Sm_2$ was due to ionization during measurements.

Tab. S13 Experimental and calculated *m/z* value of the isotopic envelopes for $\{Sm_4Nb_{28}\}$.

	Peak assignment	exp.*m/z*	cal.*m/z*
♦	$\{K_5(NH_4)_2\{Nb_{12}P_4W_{24}O_{122}\}\{Sm(H_2O)_5\}_2(H_2O)_7\}^{7-}$	1205.47	1205.92
♦	$\{K_7(NH_4)\{Nb_{12}P_4W_{24}O_{122}\}\{Sm(H_2O)_5\}_2(H_2O)_3\}^{6-}$	1404.56	1404.92
♦	$\{K_6(NH_4)_3(Nb_{12}P_4W_{24}O_{122})_2Sm_4(H_2O)_{20}Nb_4O_4(OH)_6H_2\}^{11-}$	1544.95	1545.07
♦	$\{K_5(NH_4)_5(Nb_{12}P_4W_{24}O_{122})_2Sm_4(H_2O)_{20}Nb_4O_4(OH)_6H_2\}^{10-}$	1699.54	1699.28
♦	$\{K_8(NH_4)(Nb_{12}P_4W_{24}O_{122})_2Sm_4(H_2O)_{20}Nb_4O_4(OH)_6H_4\}^{9-}$	1893.63	1893.33
♦	$\{K_{11}(Nb_{12}P_4W_{24}O_{122})_2Sm_4(H_2O)_{20}Nb_4O_4(OH)_6H_3\}^{8-}$	2142.03	2142.28

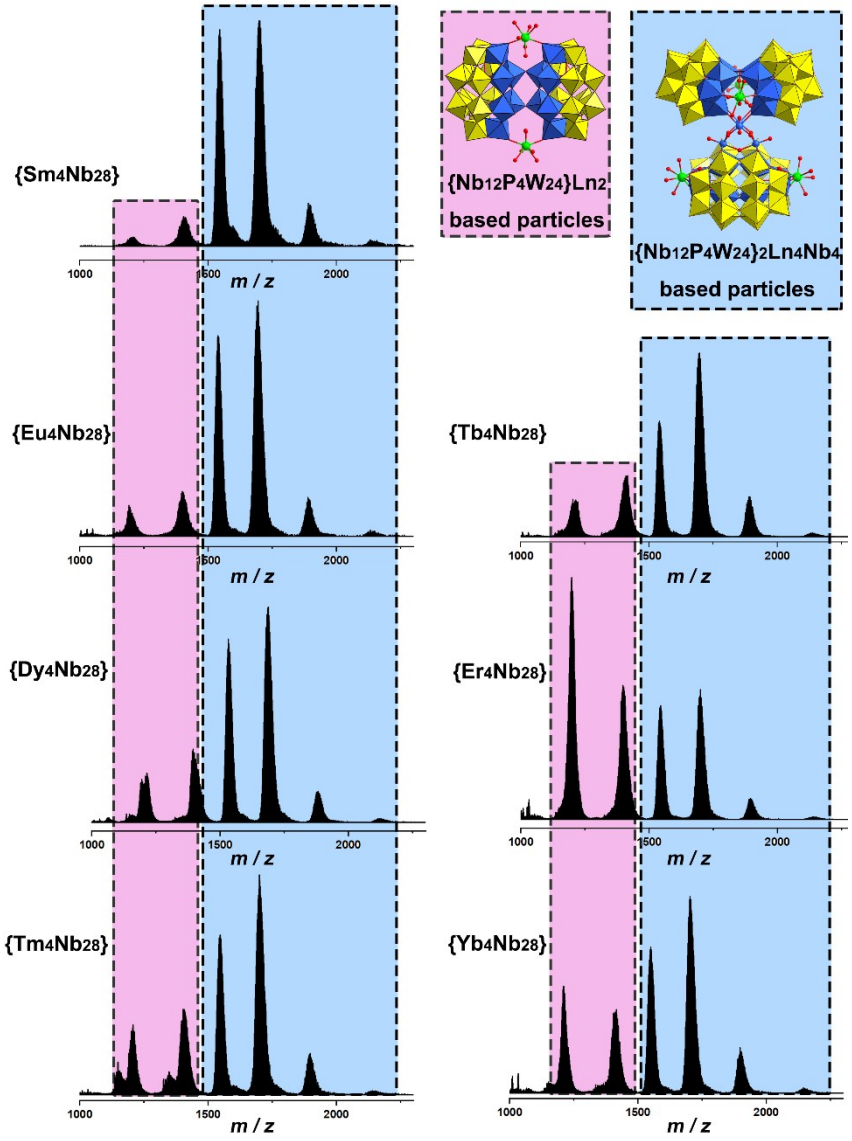

Fig. S6. The negative-ion ESI mass spectra of compounds used in this paper. The detection of $\{Nb_{12}P_4W_{24}\}Ln_2$ was due to ionization during measurements.

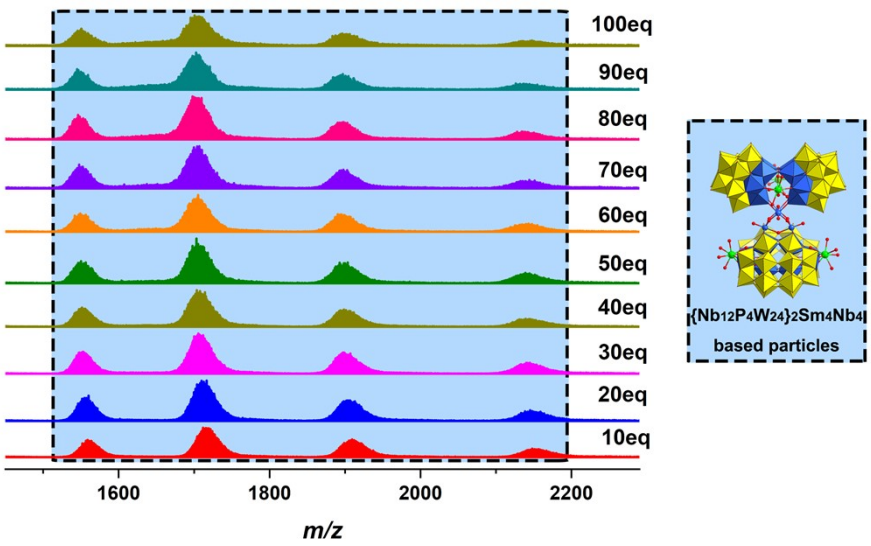

Fig. S7. The negative-ion ESI mass spectra of $\{Sm_4Nb_{28}\}$ used in this paper after the addition of different amounts of KOH (10, 20, 30, ⋯ 100 equivalents, respectively). Polyanion $\{Sm_4Nb_{28}\}$ can be detected during all the titration process.

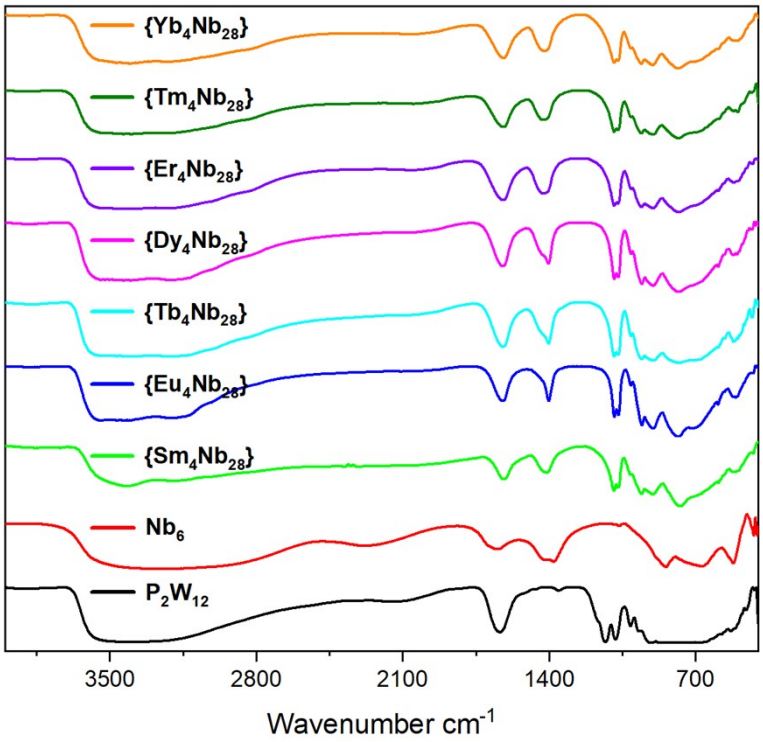

Fig. S8. The IR spectra of compounds **1-7**, $K_7[HNb_6O_{19}]$ $13H_2O$ (Nb_6) and $K_{12}[H_2P_2W_{12}O_{48}]$ $24H_2O$ (P_2W_{12}) in the region between 4000 to 400 cm^{-1}.

The Fourier transform infrared spectrum of compounds **1-7** shows medium or strong bands in the range of 1200-550 cm^{-1}, associated with the antisymmetric stretching vibrations of P⋯O, P⋯O⋯W, Nb⋯O⋯W, W⋯O⋯W bridges and the terminal W=O, Nb=O bonds, respectively. These results confirm with the fragment in **1-7**.

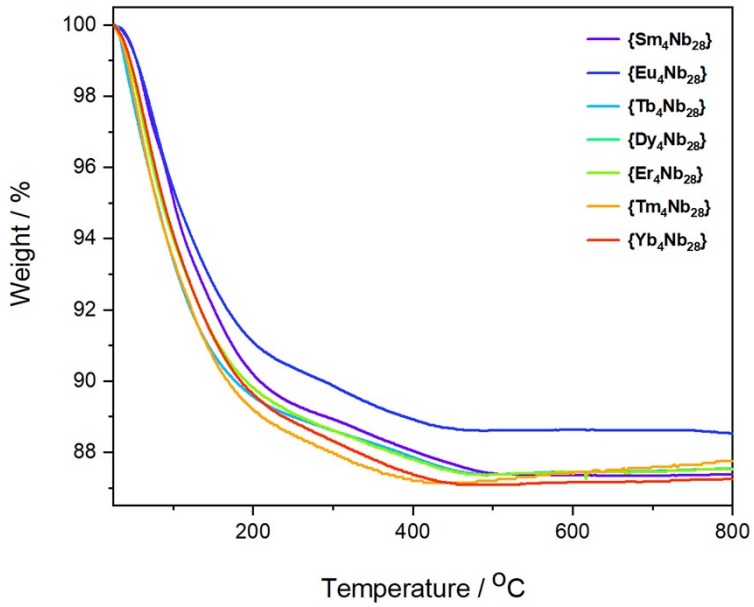

Fig. S9. TG curve of compounds **1**-**7** under N_2 atmosphere.