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A Large Molecular Cluster with High Proton Release Capacity

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Materials and Methods

Materials: Salts and solvents were purchased from Sigma-Aldrich and used without further purification.

Methods: Elemental analysis was carried out on an Agilent 700 Series Inductively coupled plasma - optical emission spectrometry (ICP-OES). A series of calibration standards with corresponding metals were used to obtain calibration curves and blank experiments were performed by using deionized water. pH measurements were performed on a SevenExcellence pH meter from Miller Toledo; UV-Vis spectra were conducted on an Agilent Technologies 8453 UV-Vis spectrophotometer from Agilent Technologies and analyzed by UV-Vis Chem Station Software; The SAXS studies were performed at the 12-ID-C station with X-ray energy of 20 keV at the Advanced Photon Source (APS) of the Argonne National Laboratory (ANL). The sample-to detector distance was about 2 m. A Pilatus detector (Dectris Ltd.) was used to acquire images with typical exposure times in the range of 0.01 to 1.0 s for a single measurement. Dialysis membrane with 1000 cut-off from Spectrum Labs was used for dialysis study.

Basic information about cluster K-1 and its aqueous solution and pH measurements on K-1 aqueous solution upon adding KOH

Compound **K-1** used in the current study were prepared by the established procedures published previously[1] and characterized by X-ray analysis, FTIR and elemental analysis.

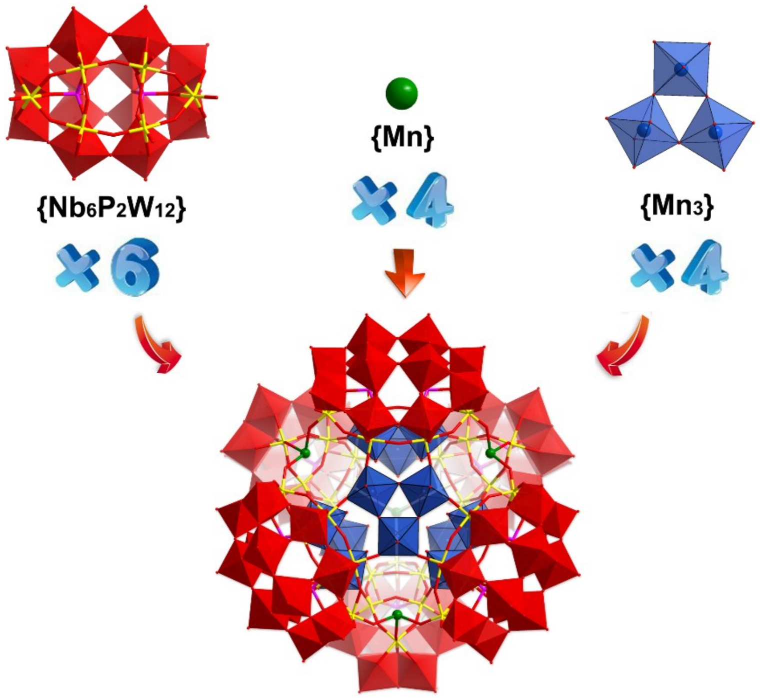

Figure S1. Combined polyhedral/ball-and-stick representation of polyanion of **K-1**, consisting of six {$P_2W_{12}Nb_6$} units connected together by four trinuclear {$Mn_3(OH)_3(H_2O)_6$} clusters and four {$Mn(H_2O)_4$} moieties. W: red, Nb: yellow, {Mn_3}: blue, {Mn}: green, P: pink, O: red.

Table S1. Crystal Data and Structure Refinement of Compound 1.

	Previously reported in 2015	This work
crystal system	Monoclinic	Monoclinic
space group	*P2(1)/m*	*P2(1)/m*
a / Å	27.2942(14)	27.2983(11)
b / Å	37.253(2)	37.2341(15)
c / Å	31.5972(16)	31.5228(14)
β / deg	110.5440(10)	110.5210(10)
V / $Å^3$	30084(3)	30007(2)
Z	2	2
D_c / g cm^{-3}	2.812	2.815
μ / mm^{-1}	14.845	14.882
F_{000}	22480	22440
Theta range for data collection, deg	1.76–25.00	1.38–25.00
reflns collected / unique	157106 / 53732	156060 / 53651
Rint	0.1909	0.1072
goodness-of-fit on F^2	1.017	1.013
${}^aR_1$,${}^bwR_2[I>2\sigma(I)]$	0.0833, 0.1334	0.0682, 0.1630
R indices(all data)	0.2394, 0.1535	0.1587, 0.2149

${}^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ${}^bwR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table S2. Elemental analysis for **K-1** ($K_{41}H_{144}NaMn_{15}P_{12}Nb_{36}W_{72}O_{450}$).

	K	Na	Nb	W	N_K/N_{Nb}	N_K/N_W
Calcd (%)	5.99	0.09	12.50	49.48	1.14	0.57
Found (%)	5.80	0.08	10.77	48.07	1.28	0.57

N_K, N_{Nb} and N_W is the number of potassium, niobium and tungsten atoms, respectively. N_K/N_{Nb} and N_K/N_W represents the ratio between the number of potassium and niobium, potassium and tungsten, respectively.

Table S3. The basic information of the stock solution of cluster studied in this paper.

Conc.	*Vol*	*MW*	*pH(aqueous solution)*	*pH(deionized water)*
0.3 mg/mL	2.0 mL	26750 g/mol	8.14	6.69

Table S4. The amounts of released protons from CO_2 dissolved in water (2.0 mL) with the addition of KOH.

$n(OH^-)^a$	$pH_{measured}{}^b$	$n(OH^-)_{added}$ (mol)^b	$n(OH^-)_{measured}$ (mol)^b
0	6.69	~0	~0
0.09	6.79	1.98×10^{-9}	1.26×10^{-10}
0.19	6.95	4.37×10^{-9}	1.82×10^{-10}
0.36	7.18	8.35×10^{-9}	3.11×10^{-10}
0.70	8.06	1.63×10^{-8}	2.39×10^{-9}
1.94	8.87	4.53×10^{-8}	1.55×10^{-8}
3.79	9.31	8.88×10^{-8}	4.27×10^{-8}
6.85	9.67	1.61×10^{-7}	9.82×10^{-8}
12.89	10.03	3.06×10^{-7}	2.27×10^{-7}
51.57	10.73	1.22×10^{-6}	1.12×10^{-6}

^{a} $n(OH^-)$ is calculated by $c(OH^-)/1.12\times10^{-5}$, latter is the concentration of **K-1** solution; $^b pH_{measured}$, $n(OH^-)_{measured}$, $n(OH^-)_{added}$, are the measured pH values of the water with different amounts of hydroxide ions, the amounts of measured and added hydroxide ions. When titrating KOH solution into deionized water as a control group, the measured pH values are still slightly lower than the calculated values, indicating that still a small amount of CO2 was dissolved in ionized water and cannot be removed by boiling method. However, such small consequent pH change, the amount of CO2 will not affect the titration result as its effect can be excluded by control group.

Table S5. The pH measurements on the aqueous solution of **K-1** upon the addition of KOH.

$n(KOH)$ (mol)	$pH_{measured}$	$n(OH^-)_{measured}$ (mol)	$n(H^+)_{released}$ (mol)	$n(H^+)_{released}$ per cluster
1.52×10^{-9}	8.17	1.98×10^{-10}	1.32×10^{-9}	0
3.80×10^{-9}	8.15	6.46×10^{-11}	3.74×10^{-9}	0
7.60×10^{-9}	8.15	6.49×10^{-11}	7.54×10^{-9}	0.01
1.52×10^{-8}	8.22	5.70×10^{-10}	1.46×10^{-8}	0.07
4.10×10^{-8}	8.27	9.85×10^{-10}	4.00×10^{-8}	0.55
7.98×10^{-8}	8.38	2.09×10^{-9}	7.77×10^{-8}	1.53
1.44×10^{-7}	8.47	3.24×10^{-9}	1.41×10^{-7}	3.58
2.73×10^{-7}	8.68	7.08×10^{-9}	2.66×10^{-7}	8.23
6.22×10^{-7}	8.98	1.70×10^{-8}	6.05×10^{-7}	19.04
1.14×10^{-6}	9.35	4.39×10^{-8}	1.10×10^{-6}	34.41
2.02×10^{-6}	9.84	1.42×10^{-7}	1.87×10^{-6}	57.54

$pH_{measured}$, $n(KOH)$, $n(OH^-)_{measured}$, $n(H^+)_{released}$, and $n(H^+)_{released}$ per cluster represent the measured pH value, , the amount of added hydroxide ions, the amount of measured hydroxide ions, the amount of released protons per cluster, respectively. $n(H^+)_{released}$ per cluster has been corrected by control group.

Discussion about the stability of POM cluster 1 in water with or without additional KOH

As confirmed in the previous publication, the aqueous solution of **K-1** is stable.[1] The excellent buffer behavior of **K-1** is also matched by its good stability (no decomposition), which was confirmed by the very characteristic IR (Figure S2), ESI-MS (Figures S3-5), UV (Figures S6-7), SAXS (Figure S8 and Table S6) and dialysis studies (Figures S9-10).

The IR spectra of **K-1** almost retain before (black) and after (red) the addition of KOH used in this paper in the range between 3800 and 450 cm^{-1} (Figure S2).

In ESI-MS, the three major peak envelopes in the range of 1900-2300 assigned as an assembly of related clusters with differing numbers of cations and water molecules retain very well before and after the addition of different amounts of KOH (Figures S3 and S4). In addition, the ESI-MS of this cluster is almost unchanged with the titration of different amounts of HCl (Figure S5).

The UV-Vis spectra of **K-1** do not show any obvious change within two months (Figure S6), and exhibit the same spectral patterns consistent with its original pure stock solution upon the titration of different amounts of KOH (Figure S7).

A concentrated **K-1** aqueous solution (5.0 mg/mL, 0.187 mM) was used for SAXS study to generate enough signals. Different amounts of 100 mM KOH aqueous solution were added into 1.0 mL this solution (0.187 μmol), and the change of its radius of gyration (R_g) was monitored. The cluster is considered as stable as its R_g value does not change greatly when 0-35 μL KOH solution was added (Figure S8). After that, more KOH (50 μL, 5.0 μmol, n(OH$^-$)/n(POM) = 27) will strongly bind **1** as some precipitation with large R_g was observed (Table S6).

Additional experimental evidence against the possible major dissociation of **K-1** with the addition of KOH comes from dialysis. The 1.0 mL **K-1** solution (0.3 mg/mL) with 18 times KOH was dialyzed against water at room temperature. After the dialysis, the UV-Vis spectrum of the outer water solution is as low as the background level (Figure S9), indicating that there is no noticeable dissociation. There is no significant difference in the UV-Vis spectra of **1** before and after dialysis (Figure S9). In addition, a concentrated **K-1** aqueous solution (1.0 mg/mL, 0.037 mM) with 18 times KOH was also dialyzed to detect the absorption peak in the visible region (Figure S10), which retains very well before and after dialysis. The data consistently indicate that this POM cluster is stable within the pH range studied in this paper.

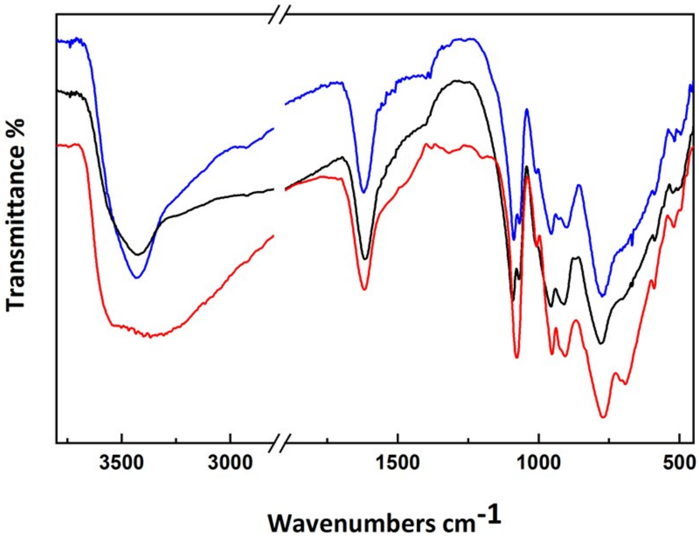

Figure S2. The IR spectrum of compound K-1 previously reported (blue) compared to those of before (black) and after (red) the addition of KOH used in this paper in the range between 3800 and 450 cm^{-1}.

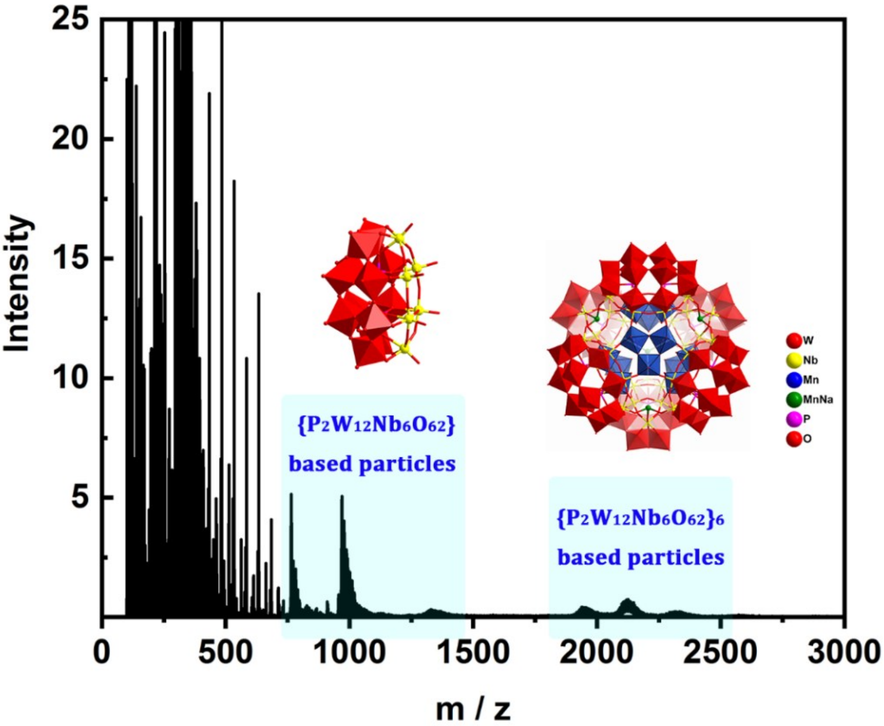

Figure S3. The negative-ion ESI mass spectra of compound used in this paper. The detection of {$P_2W_{12}Nb_6O_{62}$} was due to ionization during measurements.

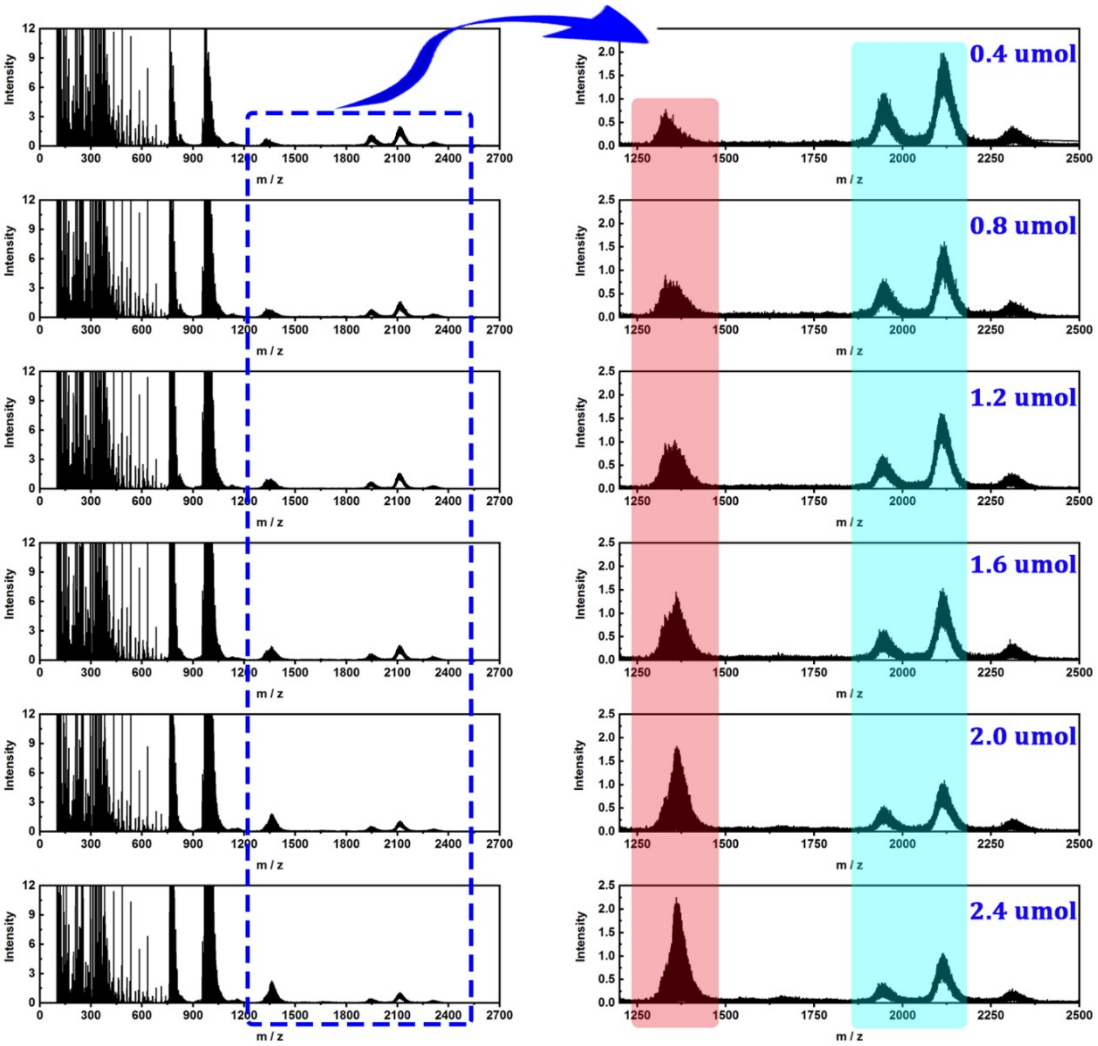

Figure S4. The negative-ion ESI mass spectra of compound (0.8 mg/mL, 2 mL) used in this paper after the addition of different amounts of KOH (13, 26, 40, 53, 67, 80 equivalents, respectively). Cluster **1-K** can be detected during all the titration process.

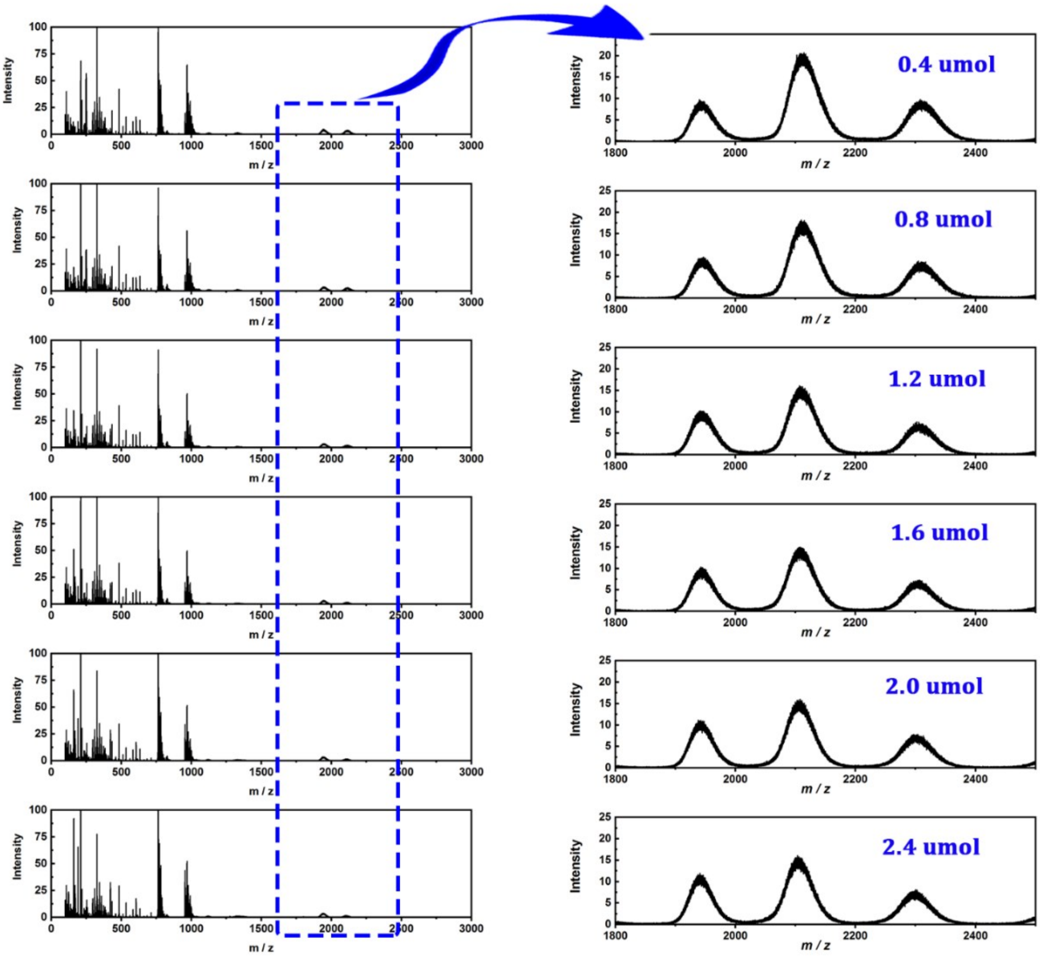

Figure S5. The negative-ion ESI mass spectra of compound (0.8 mg/mL, 2 mL) used in this paper after the addition of different amounts of HCl. No detectable change was detected during the measurements.

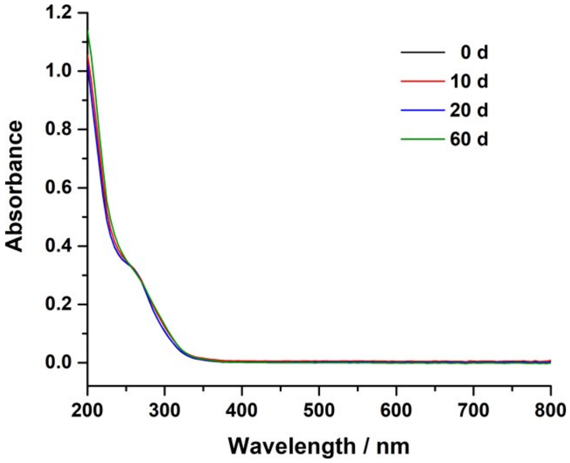

Figure S6. Time-resolved UV-Vis spectra of compound **K-1** used in this paper.

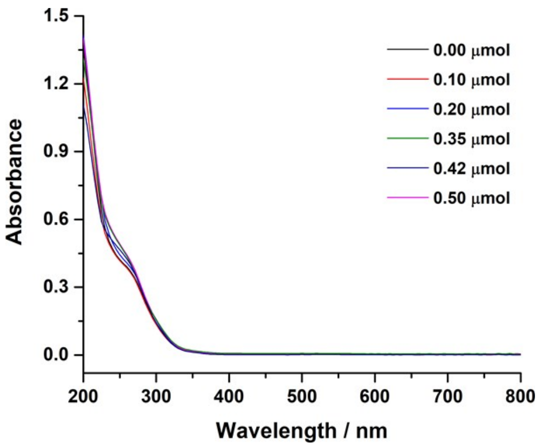

Figure S7. UV-Vis spectra of compound used in this paper with the addition of different amounts of KOH.

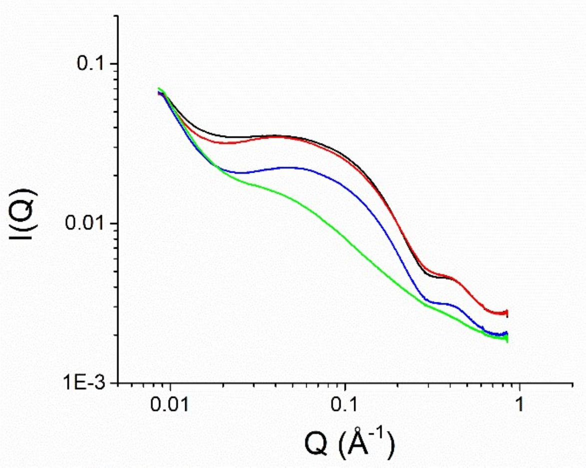

Figure S8. SAXS curves of POM cluster **1** in the presence of different amounts of KOH. 5.0 mg/mL **K-1** aqueous solution with no KOH (black), 20 µL (red), 35 µL (blue), and 50 µL (green) 100 mM KOH. Intensity changes due to dilution.

Table S6. SAXS study on the radius of gyration (R_g) of POM cluster **1** in the presence of different amounts of KOH.

Vol (KOH)	Radius of Gyration (R_g, Å)[a]
0	10.85
20 µL	10.67
35 µL	10.85
50 µL	19.05[b]

[a] Moore method[2] is used for R_g calculation.

[b] R_g increment indicates large aggregation formation due to high ionic strength.

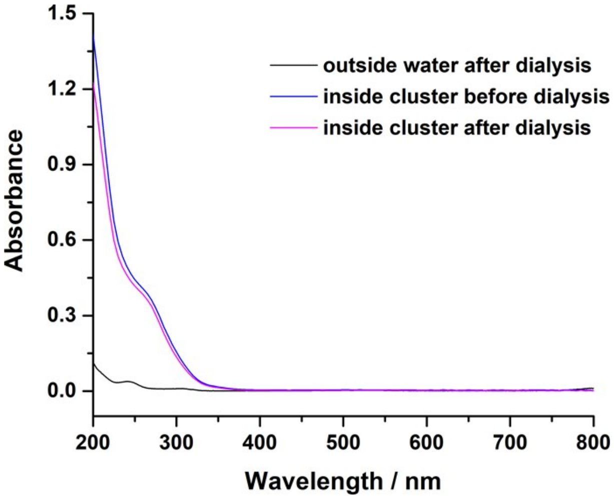

Figure S9. UV-Vis spectra of **K-1** (0.3 mg/mL) with the addition of 18 times KOH before and after dialysis.

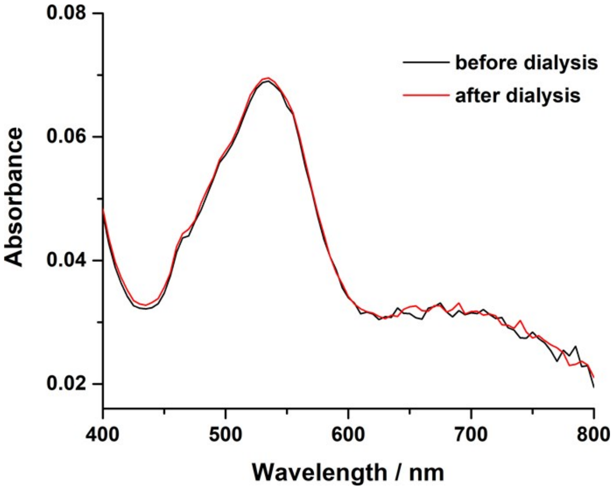

Figure S10. UV-Vis spectra of **K-1** (1.0 mg/mL) with the addition of 18 times KOH before and after dialysis, highlighting the absorption peak in the visible region.

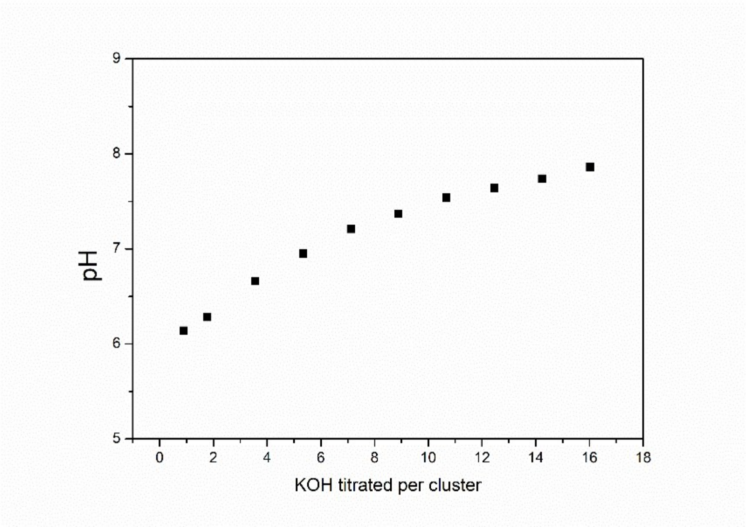

Figure S11. Titration curve of titrating concentrated KOH solution into 3.0 mL of 1.0 mg/mL **K-1** aqueous solution. Concentration of cluster, 1.0 mg/mL.

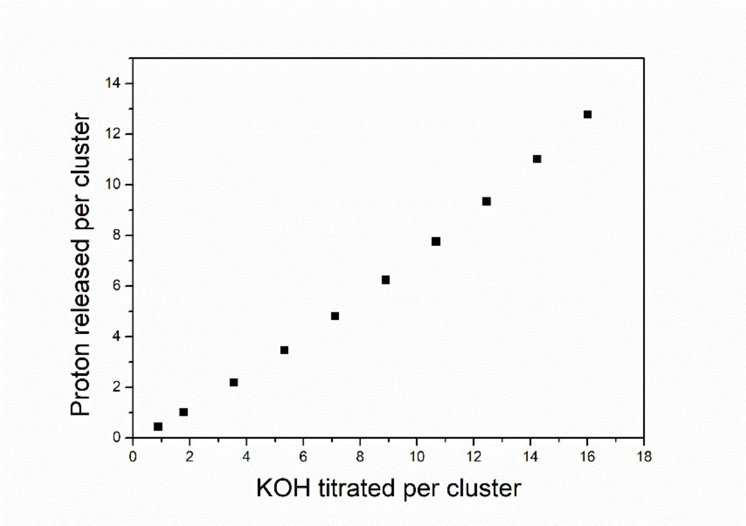

Figure S12. The number of released protons per cluster vs. the amount of added KOH per cluster. Concentration of cluster, 1.0 mg/mL.

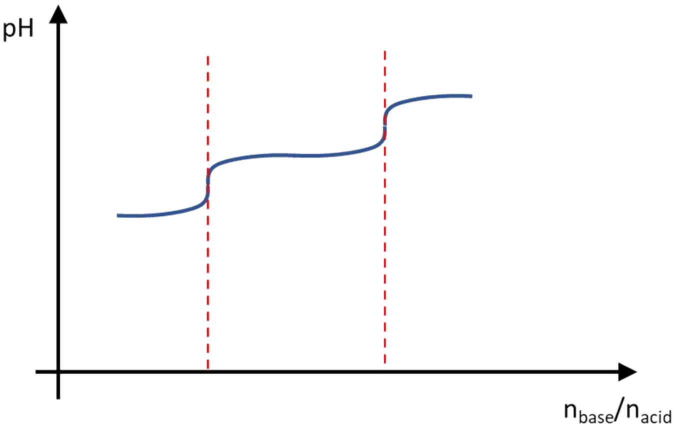

Figure S13. Typical titration curves of polyprotic acids by adding strong base.

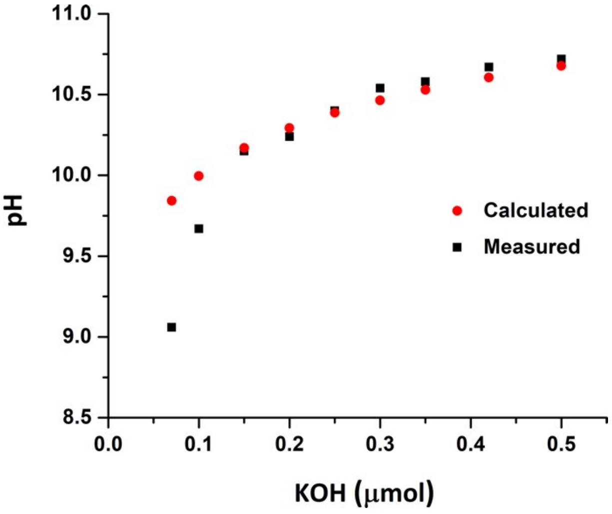

Figure S14. The pH upon the addition of KOH (10 mM) to 1.0 mL water in air without N_2 protection.

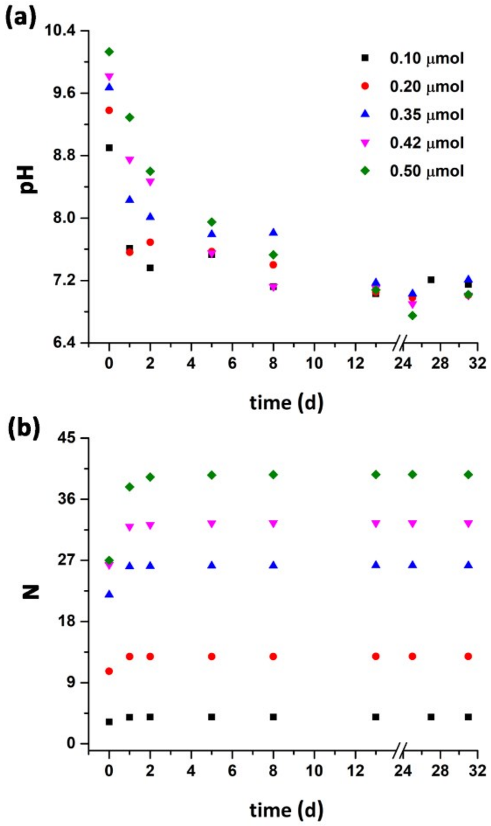

Figure S15. With CO_2 in air, (a) pH vs. time upon the addition of different amounts of KOH to the 0.30 mg/mL solution of **K-1** (1.0 mL). (b) The corresponding number of protons (N) released from each cluster.

Table S7. BVS calculation results of all the oxygen atoms in polyanion**.**

Oxygen Code	Bond Valence	Oxygen Code	Bond Valence	Oxygen Code	Bond Valence
O1	-1.71	O76	-2.00	O151	-1.95
O2	-1.95	O77	-1.89	O152	-1.96
O3	-1.99	O78	-1.68	O153	-1.81
O4	-2.03	O79	-2.15	O154	-1.96
O5	-1.98	O80	-2.04	O155	-1.84
O6	-1.89	O81	-1.97	O156	-1.89
O7	-1.73	O82	-1.93	O157	-2.08
O8	-1.96	O83	-1.76	O158	-2.01
O9	-1.98	O84	-2.00	O159	-1.84
O10	-1.85	O85	-2.02	O160	-1.84
O11	-1.68	O86	-1.49	O161	-1.77
O12	-2.18	O87	-1.78	O162	-1.85
O13	-2.00	O88	-1.95	O163	-2.16
O14	-2.05	O89	-1.81	O164	-2.07
O15	-1.92	O90	-1.63	O165	-1.99
O16	-1.66	O91	-1.64	O166	-2.03
O17	-2.04	O92	-1.80	O167	-1.91
O18	-2.07	O93	-2.02	O168	-1.61
O19	-1.94	O94	-2.00	O169	-2.12
O20	-1.68	O95	-1.83	O170	-2.04
O21	-2.14	O96	-1.99	O171	-2.10
O22	-2.07	O97	-2.08	O172	-1.91
O23	-1.70	O98	-1.81	O173	-1.90
O24	-1.88	O99	-1.93	O174	-2.12
O25	-2.03	O100	-1.67	O175	-1.99
O26	-1.80	O101	-1.91	O176	-2.21
O27	-1.80	O102	-1.99	O177	-1.75
O28	-1.83	O103	-2.01	O178	-2.02

O29	-1.99	O104	-1.84	O179	-1.93
O30	-2.01	O105	-1.97	O180	-1.94
O31	-1.84	O106	-1.71	O181	-1.89
O32	-1.60	O107	-1.99	O182	-1.66
O33	-2.09	O108	-1.91	O183	-1.89
O34	-2.02	O109	-2.02	O184	-1.98
O35	-1.93	O110	-1.75	O185	-1.98
O36	-1.87	O111	-2.14	O186	-1.75
O37	-1.80	O112	-1.88	O187	-1.87
O38	-1.82	O113	-2.04	O188	-1.99
O39	-2.01	O114	-1.91	O189	-1.86
O40	-2.02	O115	-1.54	O190	-2.01
O41	-1.75	O116	-1.98	O191	-1.84
O42	-2.05	O117	-2.10	O192	-1.96
O43	-2.13	O118	-1.95	O193	-1.81
O44	-1.95	O119	-1.74	O194	-1.85
O45	-2.04	O120	-2.10	O195	-1.81
O46	-1.91	O121	-2.06	O196	-1.40
O47	-1.76	O122	-1.80	O197	-1.40
O48	-1.66	O123	-1.94	O198	-1.29
O49	-1.96	O124	-2.07	O199	-1.28
O50	-1.90	O125	-1.87	O200	-1.35
O51	-1.93	O126	-1.62	O201	-0.51
O52	-1.70	O127	-2.06	O202	-1.33
O53	-1.93	O128	-2.00	O203	-1.33
O54	-1.90	O129	-1.87	O204	-0.58
O55	-1.95	O130	-1.84	O1W	-0.36
O56	-1.81	O131	-1.57	O2W	-0.27
O57	-1.92	O132	-2.00	O3W	-0.32
O58	-2.03	O133	-2.04	O4W	-0.35

O59	-1.86	O134	-1.79	O5W	-0.26
O60	-1.91	O135	-1.60	O6W	-0.26
O61	-1.81	O136	-2.15	O7W	-0.36
O62	-1.84	O137	-2.05	O8W	-0.21
O63	-1.73	O138	-1.67	O9W	-0.38
O64	-1.92	O139	-1.99	O10W	-0.21
O65	-2.01	O140	-1.93	O11W	-0.41
O66	-2.02	O141	-1.85	O12W	-0.18
O67	-1.84	O142	-1.72	O14W	-0.28
O68	-1.61	O143	-1.95	O15W	-0.32
O69	-1.79	O144	-1.89	O16W	-0.26
O70	-2.04	O145	-1.93	O17W	-0.35
O71	-2.07	O146	-1.69	O18W	-0.22
O72	-2.07	O147	-1.90	O19W	-0.21
O73	-1.51	O148	-1.79	O20W	-0.25
O74	-1.65	O149	-1.84	O21W	-0.26
O75	-2.06	O150	-1.90	O35W	-0.19

Red values indicate deprotonated oxygen atoms.

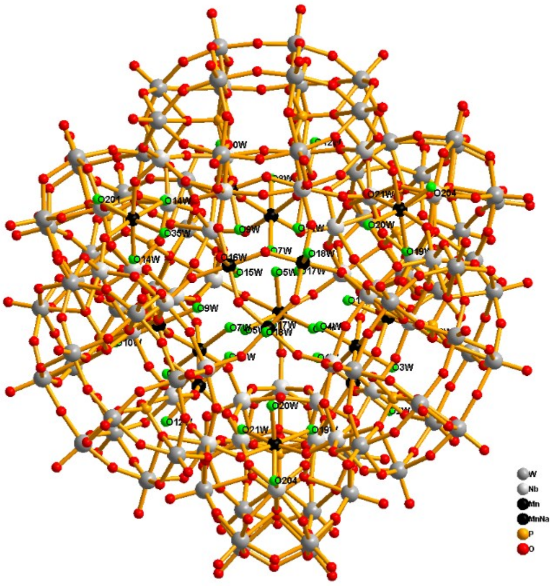

Figure S16. Ball-and-stick representation of polyoxoanion highlighting the diprotonated oxygens. Mn: blue, O: red, H_2O: green.

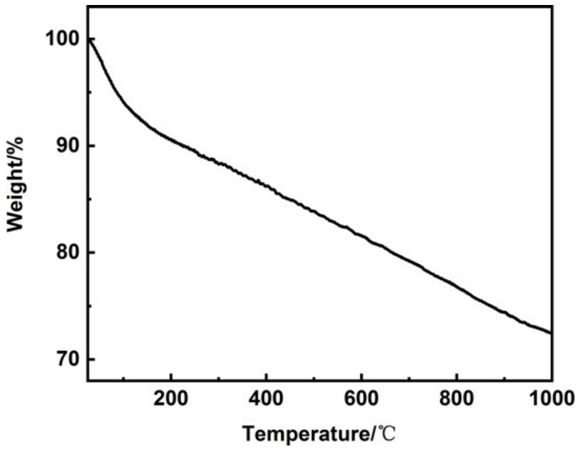

Figure S17. The TG curve of compound used in this paper.

References

[1] D. Zhang, F. Cao, P. Ma, C. Zhang, Y. Song, Z. Liang, X. Hu, J. Wang, J. Niu, *Chem. Eur. J.* **2015**, *21*, 17683-17690.

[2] P. B. Moore, *J. Appl. Crystallogr.* **1980**, *13*, 168-175.