Supporting materials:

1. General methods

All reagents were purchased and used without further purification. Elemental analysis (C, H, N) was carried on a Perkin-Elmer 2400CHN elemental analyzer. The metal atom analysis (W, Al) was carried on an X Series 2 ICP-MS. Powder X-ray diffraction (XRD) was determined by a Bruker AXS D8 Advance diffractometer. FTIR spectra were recorded in KBr pellets with a FTIR-8900 IR spectrometer in the range of 400–4000 cm^{-1}. TG-DSC analysis was performed on a Perkin-Elmer Pyris Diamond TG/DTA instrument in a flow of N_2 with a heating rate of 10 ºC min^{-1}.

2. X-ray crystallography

Single crystal of compound **1** was selected for data collection performed on a Smart Apex CCD diffractometer at 296(2) K with Mo Ka monochromated radiation (λ = 0.71073 Å). The structure of **1** was solved by a direct method and refined by the full-matrix least squares methods on F^2 using the SHELXTL crystallographic software package.(G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997; G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.) Anisotropic thermal parameters were used to refine all non-hydrogen atoms. No hydrogen atoms of organic cation, monoprotonated -OH and solvent water molecules, were included in the final structure according to the disorder and the weak diffraction, but they were included in the total molecular formula. Hydrogen atoms of the coordinated water molecules were added from the Fourier map and fixed. All the refinement details for the compound **1** were given in Table S1-S2. The CCDC reference number is 1489188. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table S1 Crystal data and structure refinement details for compound **1**.

Empirical formula	$C_{12}H_{26}Al_{4.50}W_{8.5}N_2O_{44}$
Formula weight	2586.48
Crystal system	Monoclinic
Space group	*P2(1)/m*
a/ Å	10.005(4)
b/ Å	14.757(5)
c/ Å	17.197(6)
α/°	90
β/°	100.266(5)
γ/°	90
Volume/ Å^3	2498.5(15)
Z	2
F(000)	2303
Density(calculated)/(Mg·m^{-3})	3.438
θ/(°)	1.83 to 25.01°
Absorption coefficient/(mm^{-1})	19.672
Index range	-11≤h≤11, -14≤k≤17, -17≤l≤20
Reflections collected	11985
Independent reflections/ $R_{(int)}$	4568(0.0364)
Completeness	99.6
Absorption correction(%)	Semi-empirical
Max. and min. transmission	0.078 and 0.041
Data / restraints / parameters	4568 / 744 / 375
Goodness-of-fit on F^2	1.043
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0404, wR_2 = 0.1111
R indices (all data)	R_1 = 0.0444, wR_2 = 0.1141

Table S2 Selected bond lengths [Å] for compound **1**.

W(1)-O(13)	1.736(8)	W(3)-O(3)$^{\#1}$	2.269(8)	Al(1)-O(3)$^{\#1}$	1.780(8)
W(1)-O(15)	1.814(8)	W(4)-O(23)	1.730(9)	Al(1)-O(3)	1.780(8)
W(1)-O(22)	1.935(4)	W(4)-O(24')	1.915(10)	Al(1)-O(11)	1.790(11)
W(1)-O(16)	1.986(8)	W(4)-O(7)	1.928(7)	Al(2)-O(17)	1.870(8)
W(1)-O(10)	2.049(8)	W(4)-O(9)	1.931(8)	Al(2)-O(8)$^{\#1}$	1.891(9)
W(1)-O(3)$^{\#1}$	2.253(7)	W(4)-O(6)	1.954(15)	Al(2)-O(19)	1.904(8)
W(2)-O(18)	1.739(9)	W(4)-O(24)	1.971(11)	Al(2)-O(4)	1.905(8)
W(2)-O(10)	1.926(9)	W(4)-O(6')	2.010(15)	Al(2)-O(5)	1.936(8)
W(2)-O(1)	1.939(2)	W(4)-O(2)	2.311(7)	Al(2)-O(11)	2.008(8)
W(2)-O(14)	1.951(8)	W(5)Al(5)-O(20)	1.687(13)	Al(2)-Al(2)$^{\#1}$	2.967(7)
W(2)-O(7)	1.969(8)	W(5)Al(5)-O(6)$^{\#1}$	1.938(15)	Al(3)-O(21)	1.895(12)
W(2)-O(3)$^{\#1}$	2.282(7)	W(5)Al(5)-O(6)	1.938(15)	Al(3)-O(15)	1.904(9)
W(3)-O(12)	1.750(9)	W(5)Al(5)-O(19)$^{\#1}$	1.954(8)	Al(3)-O(15)$^{\#1}$	1.904(9)
W(3)-O(8)	1.809(8)	W(5)Al(5)-O(19)	1.954(8)	Al(3)-O(5)	1.903(8)
W(3)-O(16)	1.944(8)	W(5)Al(5)-O(2)	2.237(11)	Al(3)-O(5)$^{\#1}$	1.903(8)
W(3)-O(9)	1.951(8)	Al(1)-O(2)	1.763(11)	Al(3)-O(11)	2.008(11)
W(3)-O(14)	2.082(8)				

symmetry code: #1 =x,-y+3/2,z

Table S3. The BVS results for atoms in crystal **1**.

W1	5.901	W5(Al5)	6.047		
W2	5.752	Al1	2.837		
W3	5.840	Al2	2.928		
W4	5.767	Al3	2.920		
O1	1.906	O9	1.895	O17	0.553
O2	1.862	O10	1.694	O18	1.635
O3	1.880	O11	1.830	O19	1.420
O4	1.006	O12	1.588	O20	1.882
O5	0.969	O13	1.649	O21	0.517
O6	1.870	O14	1.569	O22	1.926
O7	1.860	O15	1.840	O23	1.676
O8	1.876	O16	1.779	O24	1.748

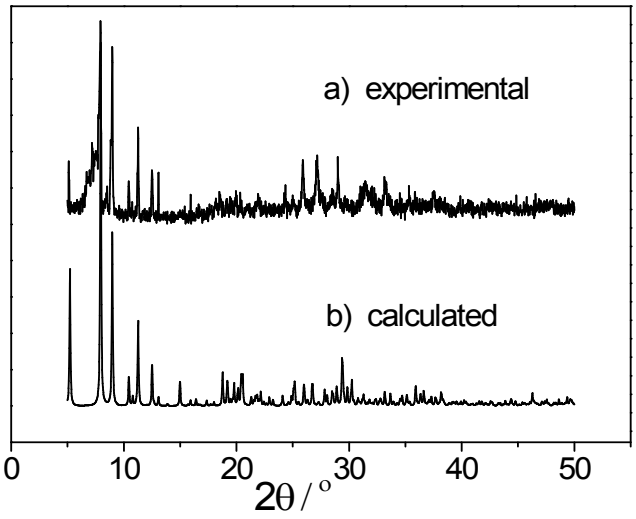
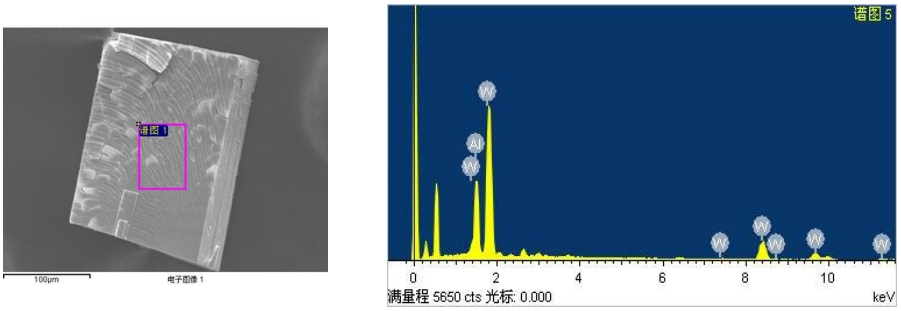


Figure S1. The experimental and calculated XRD patterns for crystal **1**.



Al:W ≈ 4.5:8.5

Figure S2. EDS (energy dispersive X-ray spectroscopy) for **1**.

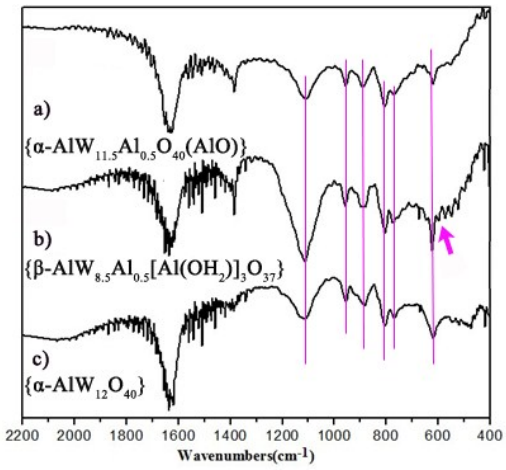


Figure S3. IR spectra showing the polyanionic structures: a) $(H_2bpe)_3[\alpha\text{-}AlW_{11.5}Al_{0.5}O_{40}(AlO)]\cdot 2H_2O$: b) crystal **1**; c) $(H_2bpe)_{2.5}[\alpha\text{-}AlW_{12}O_{40}]\cdot 4H_2O$.