Supplementary Information

Two New Members of the Niobium-substituted Polytungstophosphate Family Based on Hexalacunary $[H_2P_2W_{12}O_{48}]^{12-}$ Building Block

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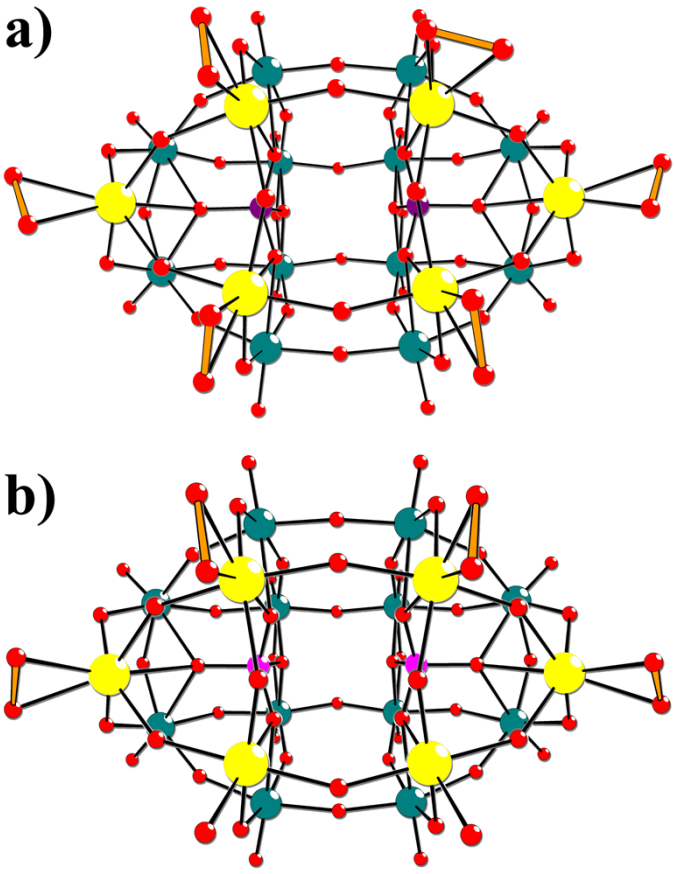

Fig. S1 a) Representation of polyanion $[Nb_6(O_2)_6P_2W_{12}O_{56}]^{12-}$ reported by Hill in 1997, b) Representation of polyanion $[Nb_6(O_2)_4P_2W_{12}O_{57}]^{10-}$ in **1a**. All cations and crystal waters are omitted for clarity. Teal balls W; yellow balls Nb; purple balls P; red balls O.

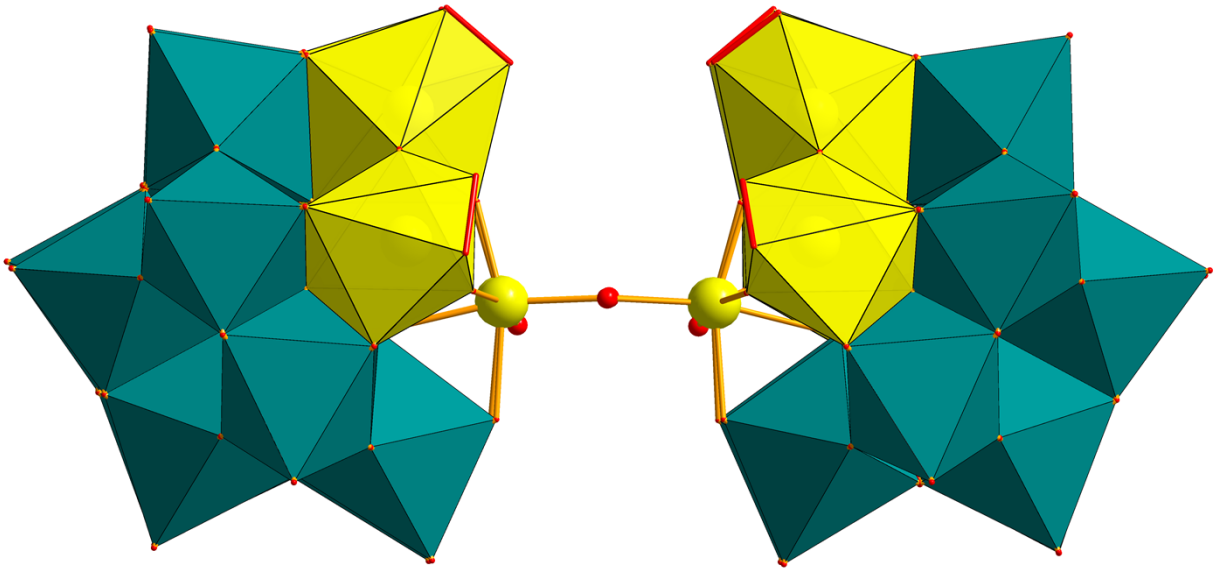

Fig. S2 Viewing from different direction of the combined polyhedral/stick representation of polyanion **1**. All cations and crystal waters are omitted for clarity. Teal polyhedra {WO_6}; yellow polyhedral {$Nb(O_2)O_5$}; yellow balls Nb; purple balls P; red balls O.

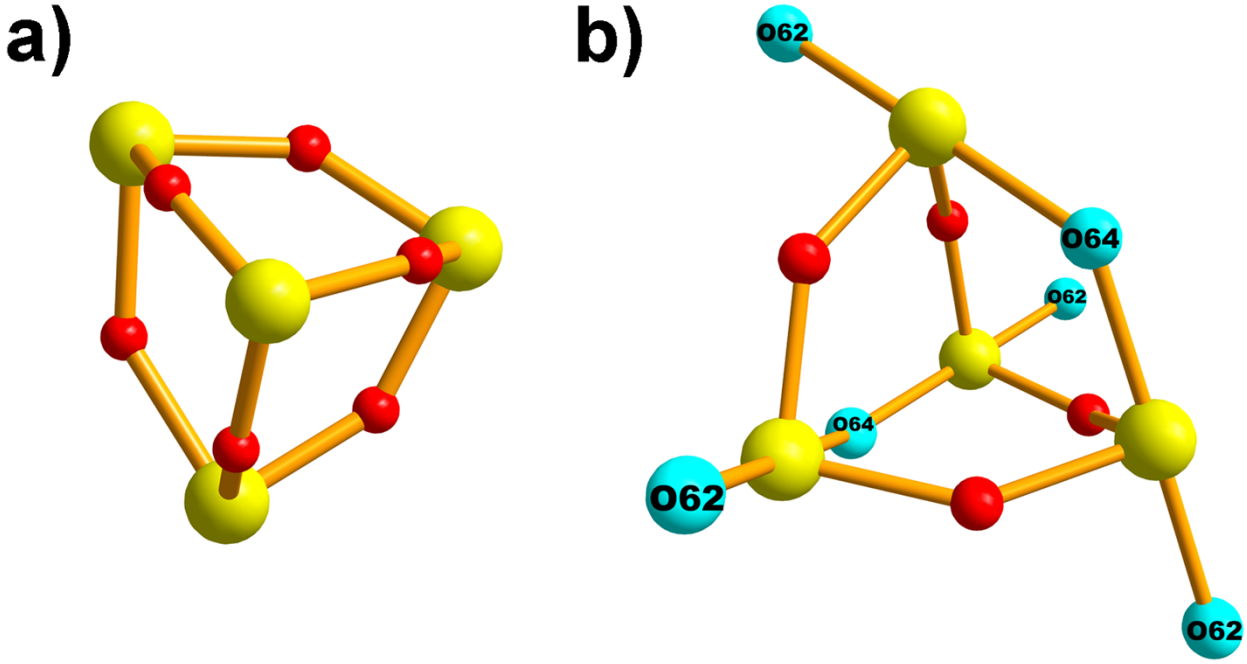

Fig. S3 a) Representation of the adamantane {Nb_4O_6} in **2** and b) highlighting the protonated oxygens. Yellow balls Nb; red balls O; turquoise balls OH. The BVS values of the four terminal oxygens (O62) and two of the six bridging Nb–O–Nb oxygen atoms (O64) are -0.80 and -1.32, respectively.

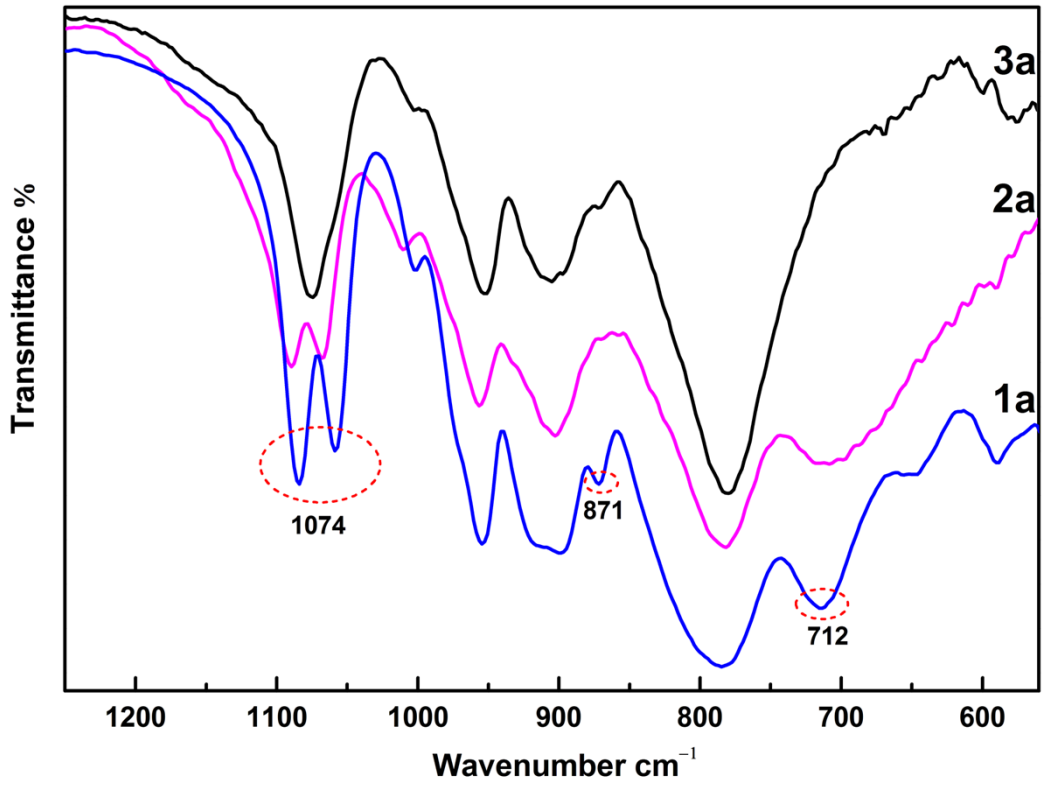

Fig. S4. IR spectra of **1a**, **2a** and **3a** in the region between 1250 and 400 cm^{-1}.

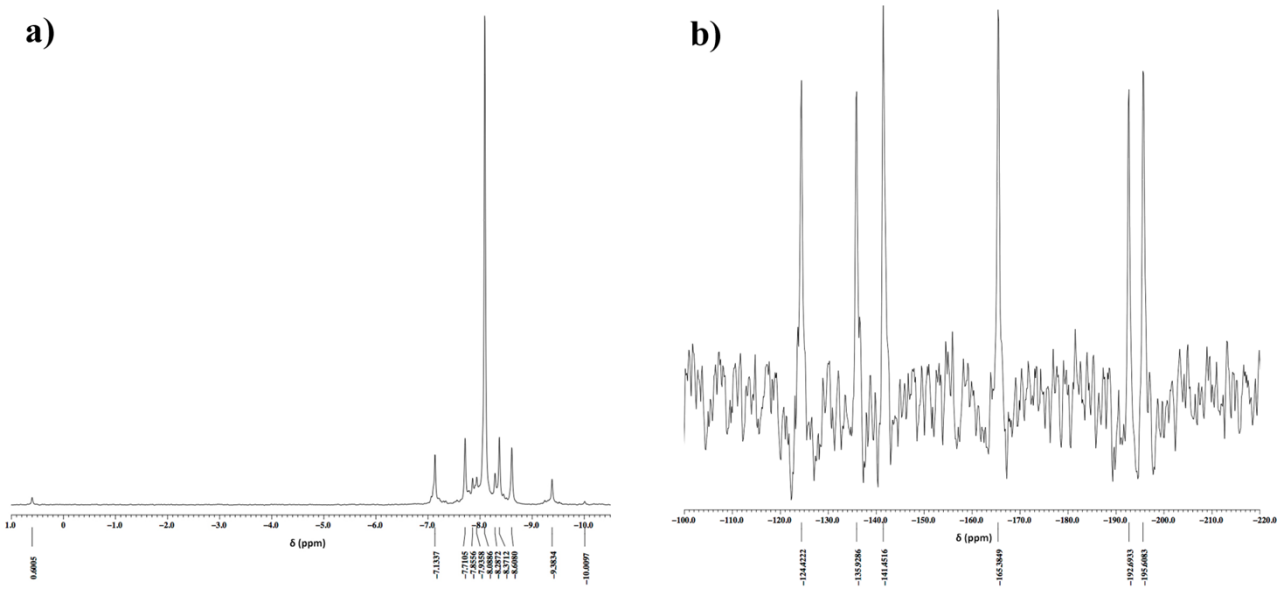

Fig. S5 Solution ^{31}P NMR (a) and ^{183}W NMR (b) spectra of compound **2a** redissolved in D_2O.

Fig. S6 The color changes of the reaction mixture during irradiation time.

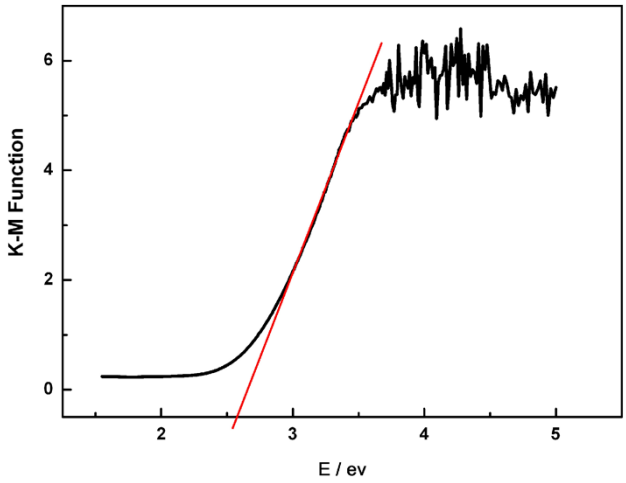

Fig. S7. The diffuse reflectance UV-vis-NIR spectrum of K-M function vs. energy of compound **1a**. The band gap of 1a is about 2.58 eV.

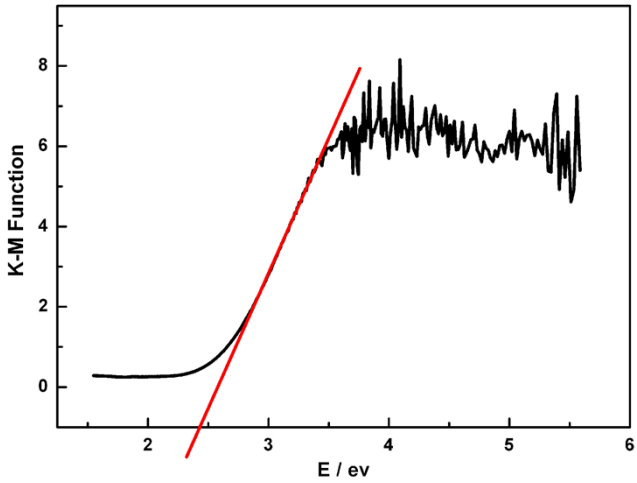

Fig. S8 The diffuse reflectance UV-vis-NIR spectrum of K-M function vs. energy of compound 2a. The band gap of **2a** is about 2.43 eV.

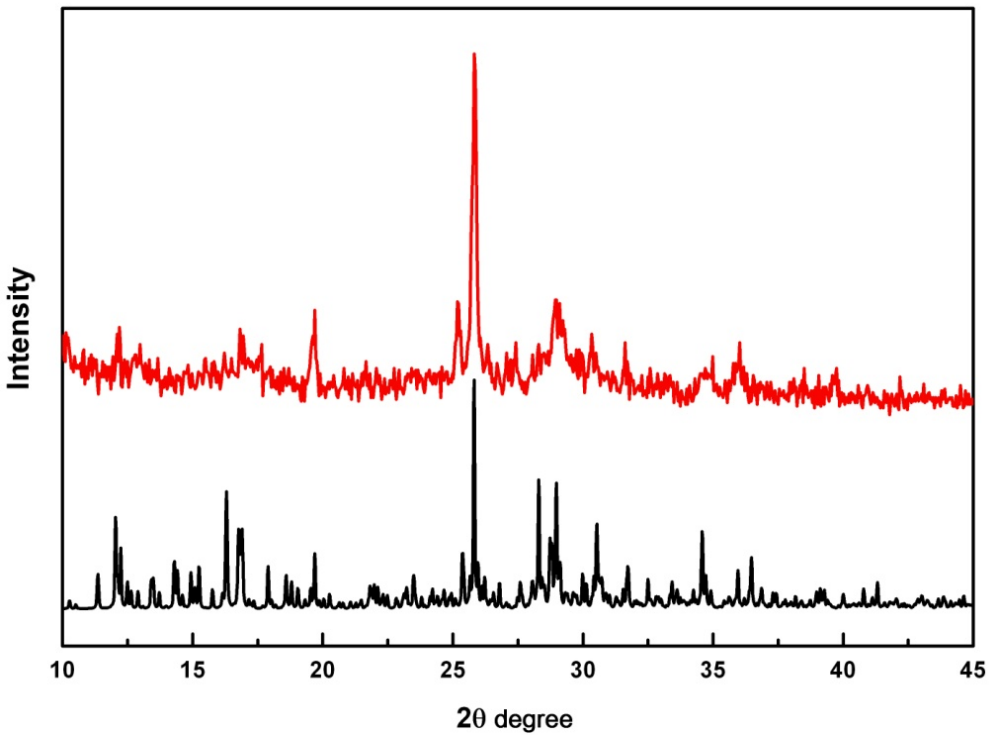

Fig. S9. XRD patterns of compound 1a (red), simulated XRD patterns of 1a (black). X-ray powder diffraction experiments were performed on a Bruker D8 Advance X-ray powder diffractometer operating at 40 kV and 40 mA.

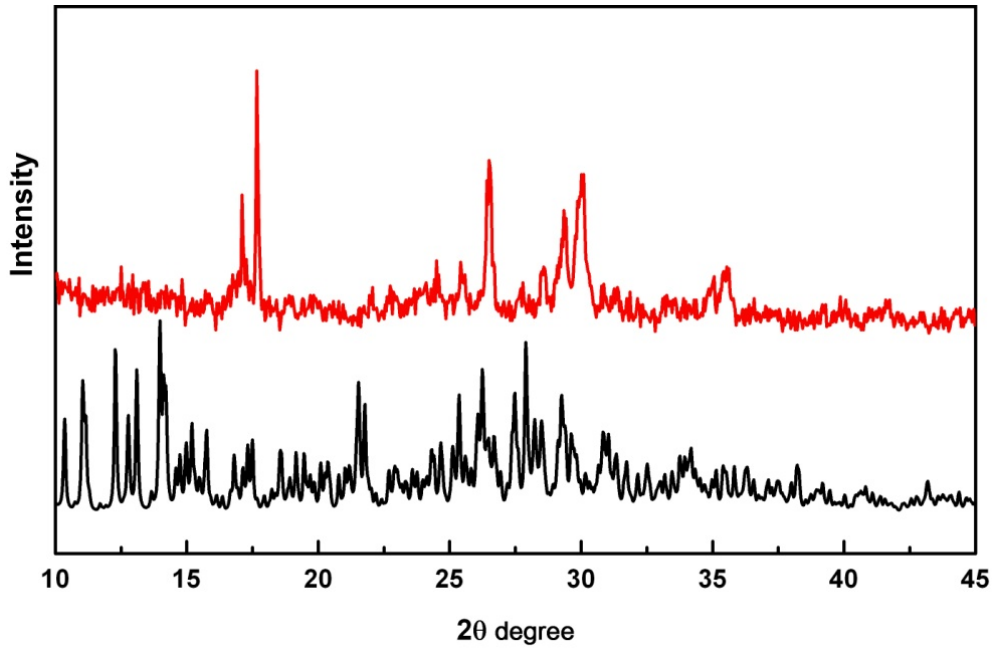

Fig. S10. XRD patterns of compound 2a (red), simulated XRD patterns of 2a (black). X-ray powder diffraction experiments were performed on a Bruker D8 Advance X-ray powder diffractometer operating at 40 kV and 40 mA.

Table S1. BVS calculation results of all the oxygen atoms on polyanion **1**.

Oxygen Code	Bond Valence	Oxygen Code	Bond Valence	Oxygen Code	Bond Valence
O1	-1.87	O23	-1.89	O45	-2.03
O2	-2.04	O24	-1.85	O46	-2.01
O3	-2.11	O25	-2.05	O47	-2.27
O4	-1.97	O26	-2.21	O48	-2.25
O5	-2.09	O27	-1.00	O49	-2.04
O6	-2.00	O28	-1.11	O50	-1.94
O7	-2.14	O29	-1.64	O51	-1.80
O8	-2.14	O30	-2.05	O52	-2.21
O9	-2.06	O31	-0.89	O53	-2.11
O10	-1.97	O32	-0.88	O54	-2.14
O11	-2.09	O33	-2.11	O55	-2.03
O12	-2.28	O34	-1.94	O56	-2.10
O13	-2.11	O35	-0.93	O57	-1.92
O14	-2.14	O36	-1.06	O58	-2.08
O15	-1.90	O37	-1.85	O59	-2.25
O16	-1.81	O38	-2.21	O60	-2.08
O17	-1.89	O39	-1.96	O61	-2.06
O18	-2.19	O40	-1.84	O62	-2.11
O19	-2.15	O41	-1.17	O63	-1.60
O20	-2.10	O42	-1.17	O64	-2.10
O21	-2.26	O43	-1.96	O65	-1.53
O22	-2.26	O44	-2.17		

Table S2. BVS calculation results of all the oxygen atoms on polyanion **2**.

Oxygen Code	Bond Valence	Oxygen Code	Bond Valence	Oxygen Code	Bond Valence
O1	-1.83	O24	-2.00	O47	-1.77
O2	-1.90	O25	-2.14	O48	-1.86
O3	-2.00	O26	-1.96	O49	-1.90
O4	-2.05	O27	-1.91	O50	-1.86
O5	-1.93	O28	-1.79	O51	-1.82
O6	-1.93	O29	-2.08	O52	-1.93
O7	-1.84	O30	-2.08	O53	-2.11
O8	-2.07	O31	-1.79	O54	-2.06
O9	-1.93	O32	-1.78	O55	-1.99
O10	-1.99	O33	-2.01	O56	-2.13
O11	-1.82	O34	-2.08	O57	-2.11
O12	-2.18	O35	-1.76	O58	-1.88
O13	-1.93	O36	-1.62	O59	-2.09
O14	-2.07	O37	-2.16	O60	-1.81
O15	-1.86	O38	-2.07	O61	-1.90
O16	-1.77	O39	-1.70	O62	-0.80
O17	-2.10	O40	-2.13	O63	-2.00
O18	-2.09	O41	-2.06	O64	-1.32
O19	-1.87	O42	-1.81	O65	-1.98
O20	-1.79	O43	-1.74	O66	-1.63
O21	-2.07	O44	-1.93	O67	-1.96
O22	-2.13	O45	-1.89		
O23	-1.89	O46	-1.90		