Supporting Information

Assembly of niobium-phosphate cluster and *in-situ* transition-metal-containing derivatives

Shufang Zhao, Zhijie Liang, Qiaohua Geng, Pengtao Ma, Chao Zhang, Jingyang Niu and Jingping Wang**

Henan Key Laboratory of Polyoxometalate Chemistry, Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P. R. China.

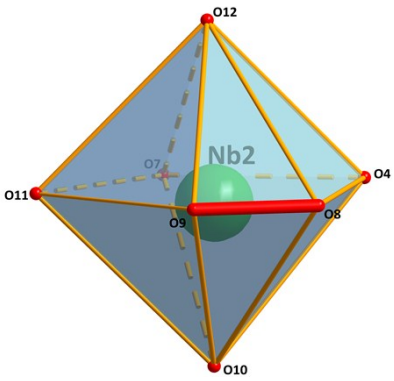


Fig. S1 The coordination environments of Nb2 of **1a.**

Table S1 The bond valence sum calculations of all the oxygen atoms on **1a.**

Atom	Bond valence	Atom	Bond valence	Atom	Bond valence
O1	1.34	O7	2.04	O13†	0.92
O2†	0.88	O8	1.90	O14†	0.87
O3†	0.89	O9†	0.86	O15	1.81
O4	1.32	O10†	0.90	O16	1.89
O5	1.89	O11	1.75	O17	1.32
O6	1.76	O12	2.03	O18	1.35

† represent peroxo oxygen atoms.

Table S2 The bond valence sum calculations of all the oxygen atoms on **2a.**

Atom	Bond valence	Atom	Bond valence	Atom	Bond valence
O1	1.92	O8	1.93	O15†	0.83

O2	1.31	O9†	0.87	O16*	0.33
O3	2.07	O10	1.81	O17	2.04
O4	1.68	O11	1.79	O18	1.71
O5	2.01	O12†	0.86	O19†	0.92
O6†	0.87	O13†	0.87	O20*	0.31
O7	1.86	O14	1.32		

† and ∗ represent peroxo oxygen atoms, H_2O groups, respectively.

Table S3 The bond valence sum calculations of all the oxygen atoms on **3a.**

Atom	Bond valence	Atom	Bond valence	Atom	Bond valence
O1†	0.89	O7†	0.80	O13†	0.87
O2†	0.95	O8†	0.87	O14†	0.82
O3	1.97	O9Ψ	1.27	O15Ψ	1.28
O4	1.40	O10Ψ	1.13	O16	1.88
O5	1.78	O11	2.03	O17	1.70
O6	1.87	O12	1.71	O18	1.88

† and Ψ represent peroxo oxygen atoms, mono-pronated groups, respectively.

Table S4 The bond valence sum calculations of all the oxygen atoms on **4a.**

Atom	Bond valence	Atom	Bond valence	Atom	Bond valence
O1†	0.90	O7†	0.86	O13†	0.90
O2†	0.97	O8†	0.85	O14†	0.81
O3	1.98	O9Ψ	1.29	O15Ψ	1.25
O4	1.48	O10	1.84	O16	1.89
O5	1.83	O11	2.06	O17	1.68
O6	1.93	O12	1.69	O18	1.92

† and Ψ represent peroxo oxygen atoms, mono-pronated groups, respectively.

Table S5 The bond valence sum calculations of all the oxygen atoms on **5a.**

Atom	Bond valence	Atom	Bond valence	Atom	Bond valence
O1†	0.83	O7	1.96	O13†	0.95
O2†	0.88	O8†	0.93	O14	1.86
O3	1.32	O9†	0.86	O15	1.33
O4	1.51	O10	2.04	O16	1.95
O5	1.88	O11	1.74	O17	1.97
O6	2.11	O12†	0.99	O18	1.76

† represent peroxo oxygen atoms.

Table S6 The bond valence sum calculations of all the oxygen atoms on **6a.**

Atom	Bond valence	Atom	Bond valence	Atom	Bond valence
O1†	0.86	O7	1.92	O13†	0.95
O2†	0.89	O8†	0.84	O14	1.78
O3	2.00	O9†	0.82	O15	1.89

O4	1.33	O10	1.51	O16	1.69
O5	1.76	O11	1.82	O17	2.04
O6	1.92	O12†	0.99	O18	1.74

† represents peroxo oxygen atoms.

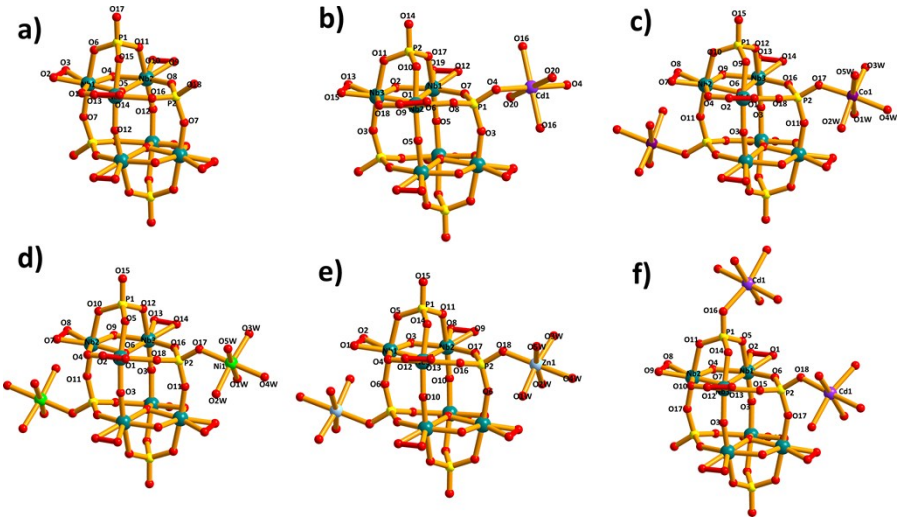


Fig. S2 Ball-and-stick representations with atomic label of **1a**–**6a**.

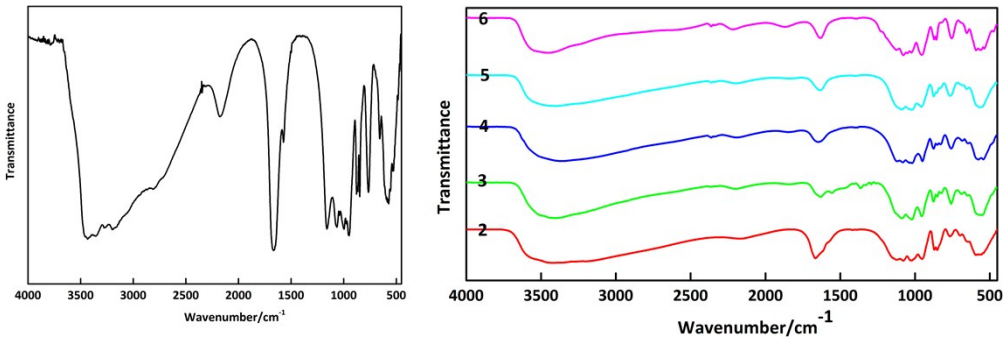


Fig. S3 FT-IR spectra of **1**–**6** between 4000-450cm^{-1}.

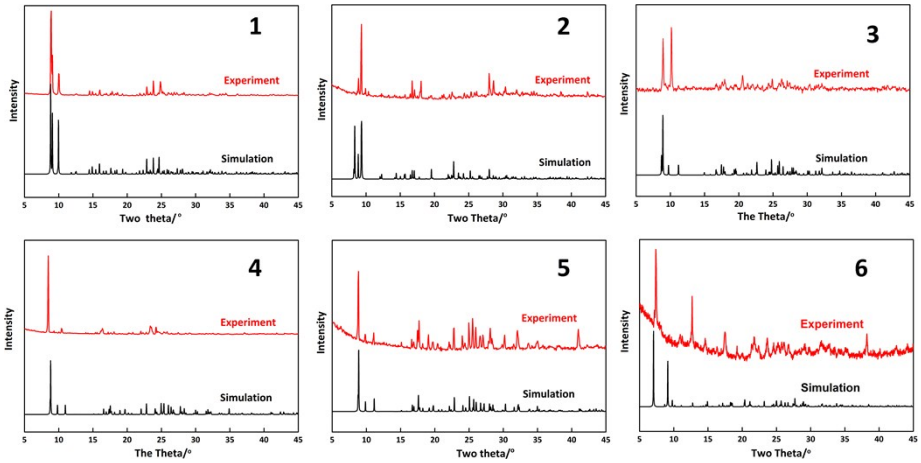


Fig. S4 The simulated and experimental powder XRD pattern of the bulk products **1**–**6** (a–g). Simulation based on the single crystal X-ray diffraction data.

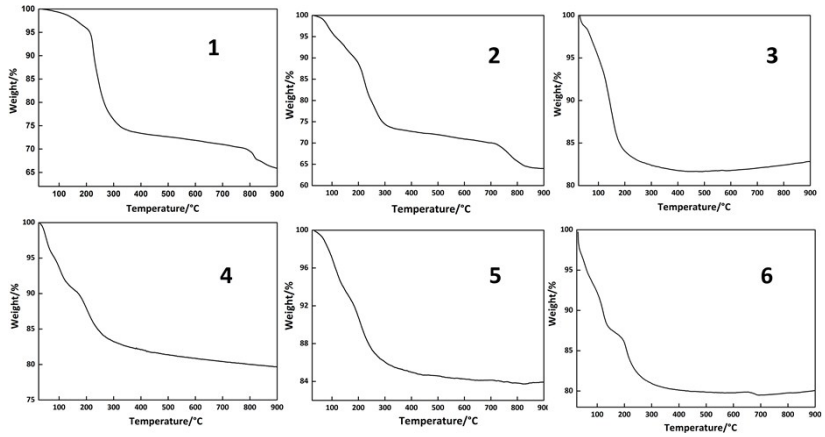


Fig. S5 The TGA curves of **1**–**6** were measured in the range of 25–900 °C under nitrogen gas atmosphere with the heating rate of 10 °C/min.

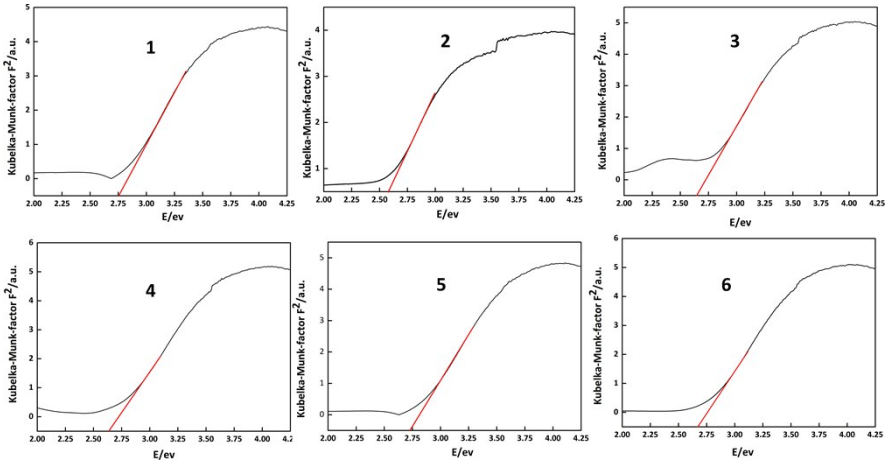


Fig. S6 The diffuse reflectance UV-vis spectra of K-M function vs. energy (eV) of compounds **1–6**.

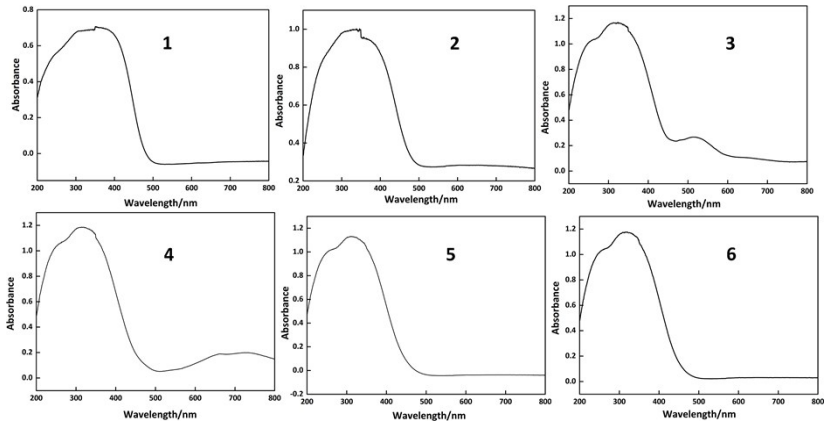


Fig. S7 The soild UV/Vis spectra of **1–6**.

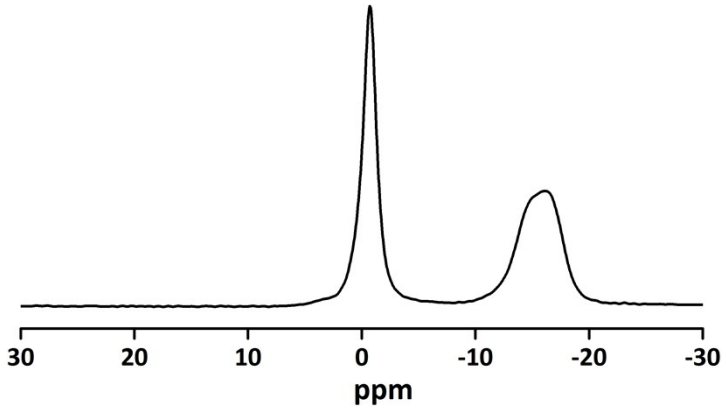
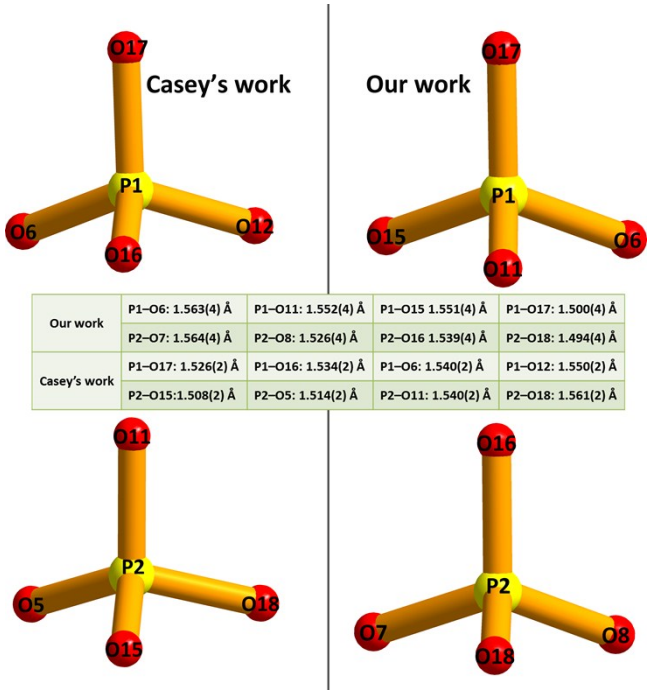


Fig. S8 Soild state ^{31}P MAS NMR of **1a.**



Our work	P1–O6: 1.563(4) Å	P1–O11: 1.552(4) Å	P1–O15 1.551(4) Å	P1–O17: 1.500(4) Å
	P2–O7: 1.564(4) Å	P2–O8: 1.526(4) Å	P2–O16 1.539(4) Å	P2–O18: 1.494(4) Å
Casey's work	P1–O17: 1.526(2) Å	P1–O16: 1.534(2) Å	P1–O6: 1.540(2) Å	P1–O12: 1.550(2) Å
	P2–O15:1.508(2) Å	P2–O5: 1.514(2) Å	P2–O11: 1.540(2) Å	P2–O18: 1.561(2) Å

Fig. S9 The connection patterns of PO_4 groups and P–O lengths of $\{P_4Nb_6(O_2)_6O_{24}\}$ by Casey's group and us.