Electronic Supplementary Information

Novel 1–D double–chain organic–inorganic hybrid polyoxotungstates constructed from dimeric copper–lanthanide heterometallic silicotungstate units

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The details during the course of the refinements of structures of 1-10

Fig. S1 IR spectra of **1**–**9**.

Fig. S2 The IR spectrum of the monovacant Keggin-type $K_8[\alpha\text{-}SiW_{11}O_{39}]\cdot 13H_2O$.

Fig. S3 The IR spectrum of the trivacant Keggin-type $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 18H_2O$.

Fig. S4 UV spectra of **1**–**9**.

Fig. S5 Visible spectra of **1**–**9**.

Fig. S6 Thermogravimetric curves of **2, 3, 5, 6, 7, 8**.

Table S1. The BVS values of all the oxygen atoms except the lattice water molecules in **1**.

The details during the course of the refinements of structures of 1-9:

Because structures of **1-9** are larger than those simple coordination complexes and there are a large amount of weight atoms in the structures, it is very difficult to refine these large structures. Moreover, the quality of crystals is not very good and the absorption coefficient is large, which usually leads to the case that the quality of intensity data is not perfect, as a result, some atoms have the ADP max/min ratios. Therefore, some unit-occupancy atoms have been isotropically refined and restrainedly refined.

1: The ISOR instruction is used for O8 and O26. The DFIX instruction is used for C7 and C8, C1 and C2, N5 and C7. O1W-O3W, O5W, O6W, N5, N6, C1-C3 and C7-C9 are refined isotropically. Now, 16 restraints are used in the refinement.

2: The ISOR instruction is used for O4, O15, O23, O31, O3, O21, O9, O13, O26, O17, C5, O1W, O2W, O5W, O7W, O8W and O9W. The DFIX instruction is used for C7 and C9, C7 and C8. O10W, O11W, C1-C4, C7-C9, N5 and N6 are refined isotropically. Now, 104 restraints are used in the refinement.

3: The ISOR instruction is used for O9W, O1, O2, O3, O4, O6, O9, O10, O11, O17, O19, O22, O24, O27, O28, O30, O39, C4, O29, O34, N2, Si1, O32, O33, O3W, O12, O13, O14, O15, O18, O20, O23, O26, N3, C6, O16, O37, O4W, O8W, O5 and O21. The DFIX instruction is used for N5 and C9, C9 and C7, C7 and N6, C9 and C8, Cu2 and C8, Cu2 and C7, Cu2 and C9, N5 and C8. O1W, O5W, O6W, O7, O8, O25, O31, O36, N5, N6, C1, C2, C3, C7, C8 and C9 are refined isotropically. Now, 254 restraints are used in the refinement.

4: The ISOR instruction is used for O2, O10, O12, O21, O19, O23, O27, O29, O31, O33, O7, N1, O4W, O7W, O8W and O9W. The DFIX instruction is used for C7 and C9, C7 and C8, N2 and C2, N5 and C7, N6 and C8, C1 and C2, C9 and C8. O1W, O2W, O3W, O5W, O6W, O10W, N5, N6, C1, C2, C3, C7, C8 and C9 are refined isotropically. Now, 109 restraints are used in the refinement.

5: The ISOR instruction is used for O17, O1, O16, O2W, O3W, O4W, O7W and O8W. The DFIX instruction is used for N5 and C7, Cu2 and O1, C7 and C8. O1W, O5W, O6W, O8, O29, O31, N5, N6, C1, C2, C3, C7, C8 and C9 are refined isotropically. Now, 51 restraints are used in the refinement.

6: The ISOR instruction is used for O4, O6, O11, O31, O32, O34, O39, N3, N4, O15, O17, O18, O25, O29 and O19. The DFIX instruction is used for C7 and C9, C4 and C5, C2 and C3, C7 and C8. O1W, O2W, O3W, O5W, O6W, N5, N6, C1, C2, C3, C7, C8 and C9 are refined isotropically. Now, 94 restraints are used in the refinement.

7: The ISOR instruction is used for O4, O10 and O23. The DFIX instruction is used for C7 and C8, C8 and C9, Tb1 and O2W. O1W, O2W, O3W, O5W, O6W, N5, N6, C1, C2, C3, C8 and C7 are refined isotropically. Now, 20 restraints are used in the refinement.

8: The ISOR instruction is used for O1, O4, O17, O20, O7, O13, O15, O16, O24, O30, O34, O2, C5, O25, O26, O6W, O7W, O5, O11, O35, O14, N3, O38, N4, C4, O8, O19, O29, O39, O9W, O37, O4W, O8W and O28. The DFIX instruction is used for N2 and C2, C1 and C2, C4 and C6, C7 and C8, N5 and C7. The SIMU instruction is used for N5 and C7. O1W, O2W, O5W, O31, N5, N6, C7, C8, C9, N1, C1, C2 and C3 are refined isotropically. The W11 site is split into two sites (W11 and W11') and the Dy1 site is split into two sites (Dy1 and Dy1'). Now, 210 restraints are used in the refinement.

9: The ISOR instruction is used for O1, O3, O6, O7, O8, O9, O10, O11, O17, O18, O19, O9W, O22, O25, O27, O28, O29, O33, O37, O39, C6, O12, N3, O30. The DFIX instruction is used for C8 and C9, C7 and C8. The DELU instruction is used for W8 and O30. The SIMU instruction is used for C4 and C6. O1W, O2W, O3W, O5W, O6W, N5, N6, C1, C2, C3, C4, C7, C8 and C9 are refined isotropically. Now, 156 restraints are used in the refinement.

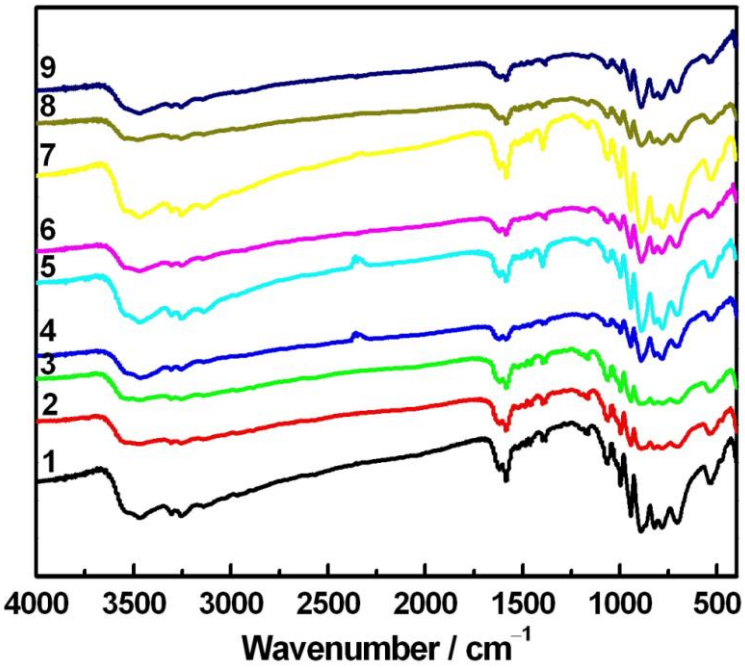

Fig. S1 IR spectra of **1**–**9**.

Table S1. The BVS values of all the oxygen atoms except the lattice water molecules in **1**.

Atoms	BVS values	Atoms	BVS values
O1	1.65	O21	1.88
O2	1.96	O22	1.84
O3	1.95	O23	1.60
O4	1.92	O24	2.36
O5	1.97	O25	1.90
O6	1.93	O26	1.64
O7	1.70	O27	1.90
O8	2.10	O28	1.87
O9	1.91	O29	1.99
O10	1.93	O30	1.65
O11	2.44	O31	1.93
O12	1.91	O32	2.08
O13	2.08	O33	1.74
O14	1.76	O34	1.96

O15	1.87	O35	1.76
O16	2.13	O36	2.37
O17	2.08	O37	2.01
O18	2.08	O38	1.52
O19	1.75	O39	2.33
O20	2.35		

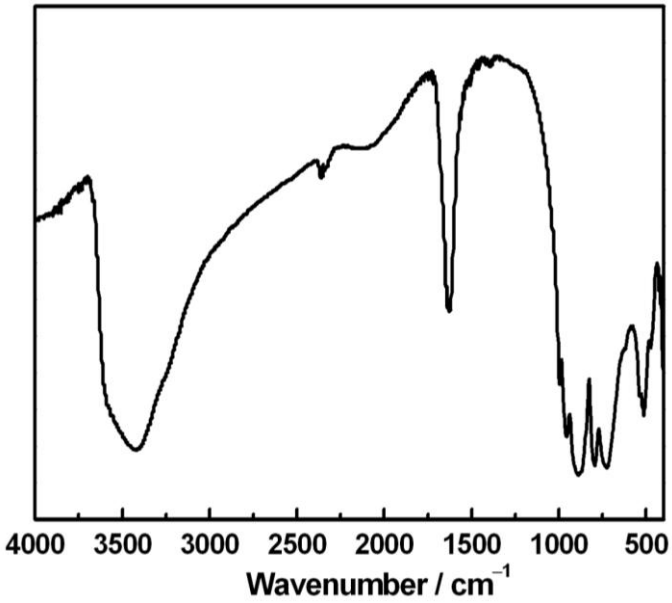

Fig. S2 The IR spectrum of the monovacant Keggin-type $K_8[\alpha\text{-}SiW_{11}O_{39}]\cdot 13H_2O$.

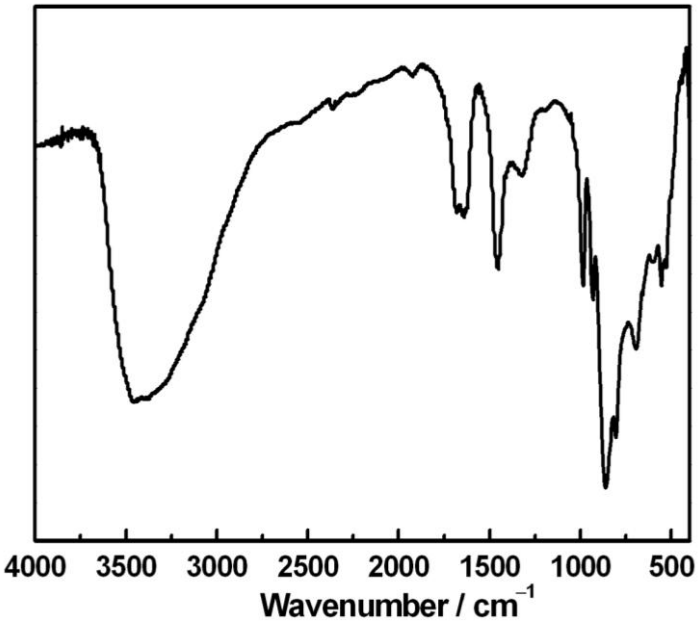

Fig. S3 The IR spectrum of the trivacant Keggin-type $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 18H_2O$.

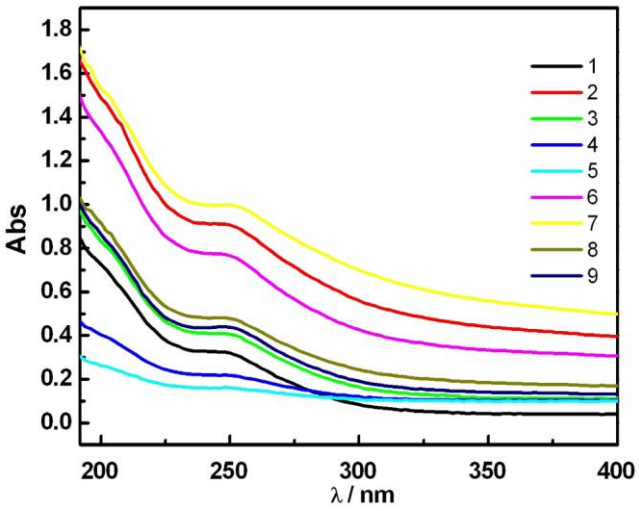

Fig. S4 UV spectra of **1**–**9**.

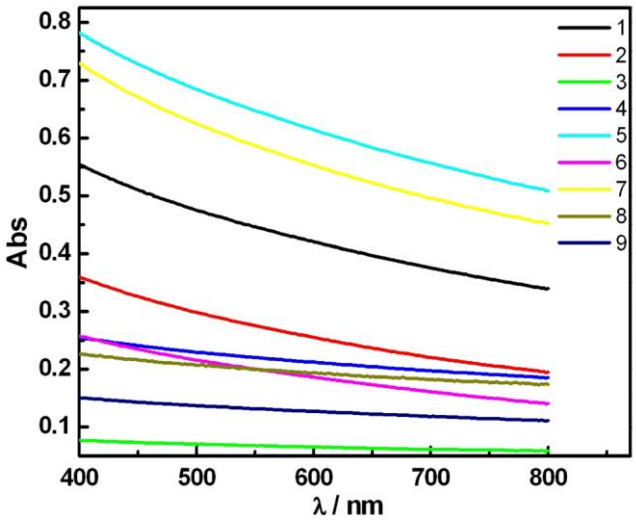

Fig. S5 Visible spectra of **1**–**9.**

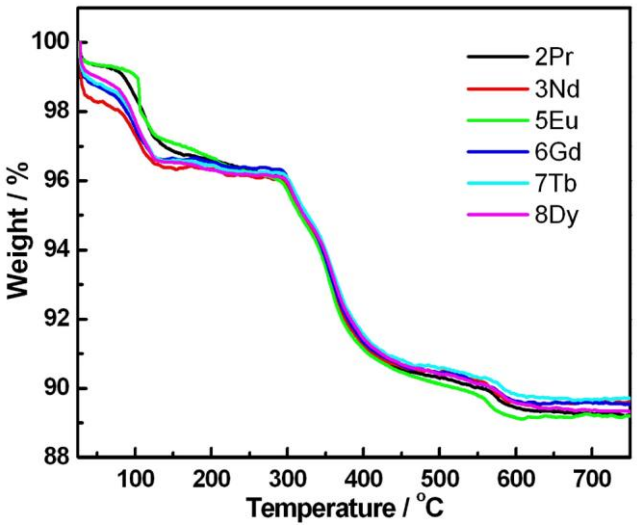

Fig. S6 Thermogravimetric curves of **2, 3, 5, 6, 7, 8**.