Electronic Supplementary Material (ESI) for Dalton Transactions

Syntheses, structures and electrochemical properties of a class of 1-D double chain polyoxotungstate hybrids $[H_2dap][Cu(dap)_2]_{0.5}[Cu(dap)_2(H_2O)][Ln(H_2O)_3(\alpha\text{-}GeW_{11}O_{39})]\cdot 3H_2O$

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Electronic Supplementary Information

The refinement details in 1-7:

Due to the large structures of **1-7** and the existence of a large amount of weight atoms, their intensity data are not very good, leading to the ADP max/min ratio of some atoms, and it is very difficult to refine these large structures, therefore, some unit-occupancy atoms have been refined isotropically and restrainedly refined.

For **1**: The ISOR instruction is used for O6, O8W, O13, O20, O29, O34, O35, O36, O39, N2, O1W, O3, O18, O27, O32, O38, W1, W8, W10, GE1, O5, O25, W5, W11, O36, N7, O2 and O8. The DFIX instruction is used for C7 and C8, C12 and C10. The O3W, O7W, N5, N6, C1 and C4-C12 are refined isostropicallly. 657 parameters and 170 restraints are used in the refinement.

For **2**: The ISOR instruction is used for C8, N6, C11, O8 and O24. The DFIX instruction is used for N6 and C8, C4 and C5, C8 and C9, C10 and C11, C11 and C12, N7 and C10, C7 and C8. The DELU instruction is used for C5 and C6. The O3W, O7W and C4-C12 are refined isostropicallly. 672 parameters and 25 restraints are used in the refinement.

For **3**: The ISOR instruction is used for O5, O10, O15, O21, O24, O33, O34, O36, N8, O15, O18, O20, O27 and O39. The DFIX instruction is used for C7 and C8, C10 and C11. The O3W, O7W and C4-C12 are refined isostropicallly. 672 parameters and 86 restraints are used in the refinement.

For **4**: The ISOR instruction is used for O2, O5, O6, O11, O14, O17, O18, O20, O21, O32, O33, O34, O37, O38, O39, O25, N4, O23 and O4. The DFIX instruction is used for C7 and C8, C10 and C11, C2 and C3, C4 and C5, C5 and C6, N1 and C1, N3 and C4, N4 and C5, N5 and C7, N8 and C11. The DELU instruction is used for W2 and O7, SM1 and O7. The O3W, O7W, N5, N8 and C1-C12 are refined isostropicallly. 632 parameters and 149 restraints are used in the refinement.

For **5**: The ISOR instruction is used for O3, O4W, O6W, O8, O10, O19, O21, O22, O24, O30, O32, O33, O35, O38, O39, N1, N4, C1, C2, C3, O1W, O4, O6, O34, O25, O7, O39, O11, O2, O17, O28, O31 and O14. The DFIX instruction is used for C8 and C9, C7 and C8, C2 and C3, C5 and C6, C11 and C12, C4 and C5, Cu2 and C8, Cu2 and C9. The DELU instruction is used for CU1 and N3, W2 and O7. The O2W, O3W, O5, O7W, O8W, O9, O13, O15, O16, O18, O23, O26, O27, O37, N1-N8 and C1-C12 are refined isostropicallly. 587 parameters and 208 restraints are used in the refinement.

For **6**: The DFIX instruction is used for Cu2 and C8, Cu2 and C9, C11 and C12, C10 and C11, C4 and C5, C5 and C6, N8 and C11, N7 and C10, N5 and C7. The O2W, O3W, O5, O7W, O8W, O9W, O13 and C1-C12 are refined isostropicallly. 658 parameters and 11 restraints are used in the refinement.

For **7**: The ISOR instruction is used for O4, O7, O9, O18, O14, O22, O17, O36, C1, O23, O26, N8, O25 and O22. The DFIX instruction is used for Er1 and O3W, O2W and O3W, O4W and O3W, C7 and C8. The W5, W6 and W8 split respectively into two positions. The O2W, O3W, O4, O7W, O21, N1, N2 and C1-C12 are refined isostropicallly. 658 parameters and 88 restraints are used in the refinement.

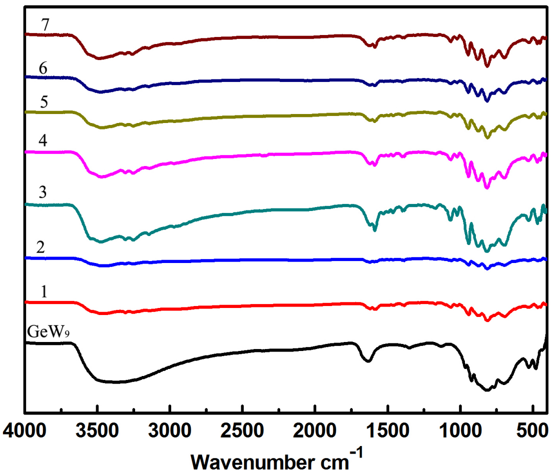

Fig. S1A The IR spectra between 4000 and 400 cm^{-1} of **1–7** and $K_8Na_2[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot 25H_2O$ (GeW_9)

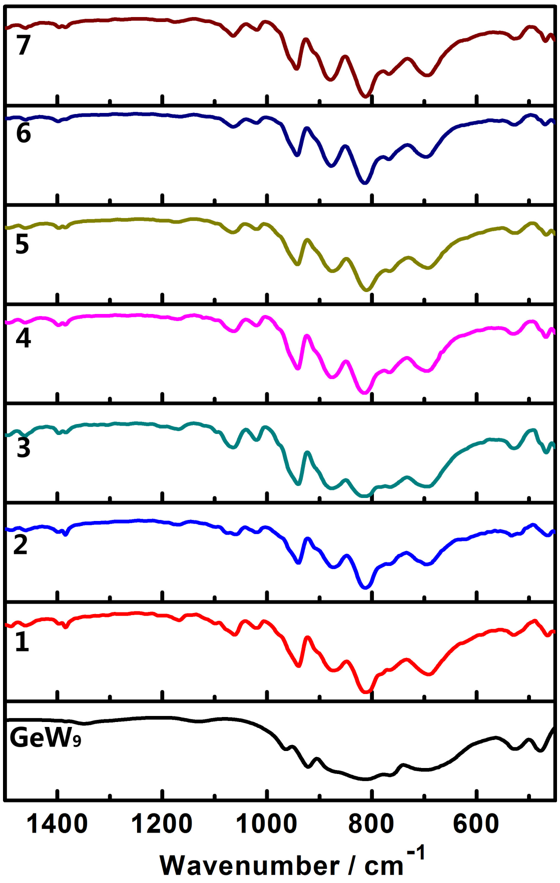

Fig. S1B The IR spectra between 1500 and 450 cm^{-1} of **1**–**7** and $K_8Na_2[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot 25H_2O$ (GeW$_9$)

Table S1 Bond valence sum (BVS) calculations of all W, Cu and Ln atoms in **1**–**7.**

Atoms	BVS values (**1**)	BVS values (**2**)	BVS values (**3**)	BVS values (**4**)	BVS values (**5**)	BVS values (**6**)	BVS values (**7**)
Ln	3.19	3.21	2.97	2.64	3.05	3.05	2.98
Cu1	2.20	2.11	2.14	2.25	2.34	2.08	2.18
Cu2	2.06	2.12	1.98	1.88	2.28	1.81	1.84
W1	6.27	6.11	6.17	6.35	6.39	5.87	6.01
W2	6.13	6.37	6.32	6.30	5.68	5.89	6.05
W3	6.08	6.08	5.77	5.78	6.01	5.85	5.94
W4	6.28	6.29	6.01	6.28	6.42	6.00	5.89
W5	6.28	6.13	5.90	6.16	6.06	5.77	5.99
W6	6.08	6.26	5.92	6.10	6.15	5.80	6.11
W7	6.11	6.16	5.93	6.43	6.15	5.76	6.09
W8	5.91	6.29	6.06	5.99	5.88	5.81	5.89
W9	6.37	6.41	6.27	6.17	6.16	5.90	6.08
W10	6.05	6.10	5.78	5.89	6.15	5.58	5.88
W11	6.28	6.06	5.95	5.95	5.83	5.80	5.89

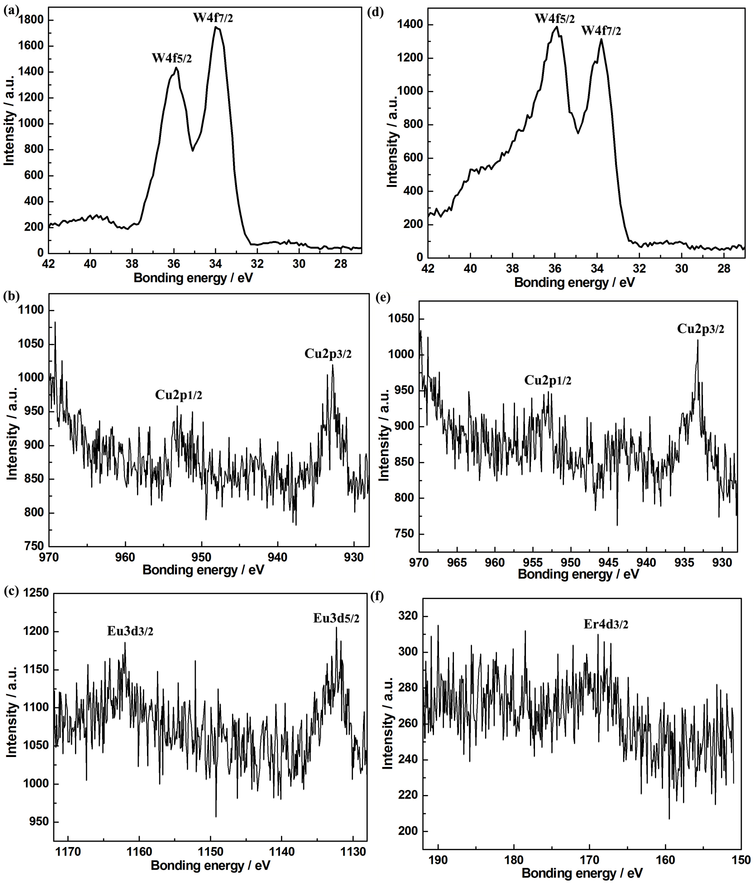

Fig. S2 (a) The XPS spectrum for W4f$_{7/2}$ and W4f$_{5/2}$ in **5**; (b) The XPS spectrum for Cu2p$_{3/2}$ and Cu2p$_{1/2}$ in **5**; (c) The XPS spectrum for Eu3d$_{5/2}$ and Eu3d$_{3/2}$ in **5**; (d) The XPS spectrum for W4f$_{7/2}$ and W4f$_{5/2}$ in **7**; (e) The XPS spectrum for Cu2p$_{3/2}$ and Cu2p$_{1/2}$ in **7**; (f) The XPS spectrum for Er4d$_{3/2}$ in **7**.

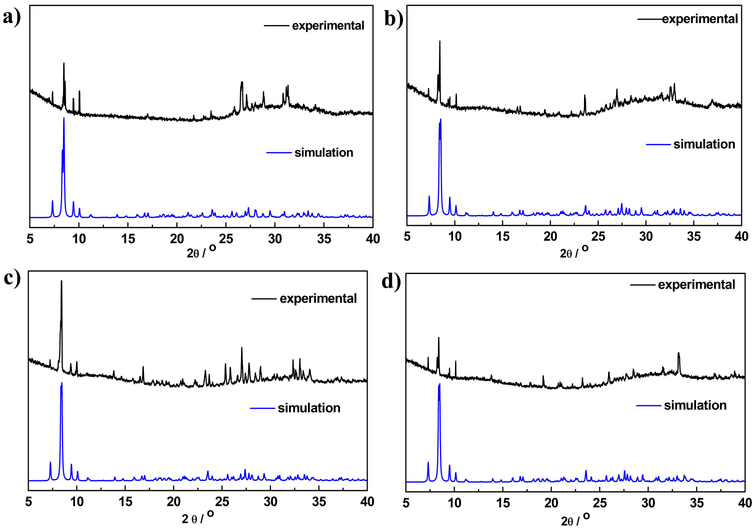

Fig. S3 Comparisons of the simulated and experimental PXRD patterns of **1** (a), **2** (b), **3** (c) and **4** (d).

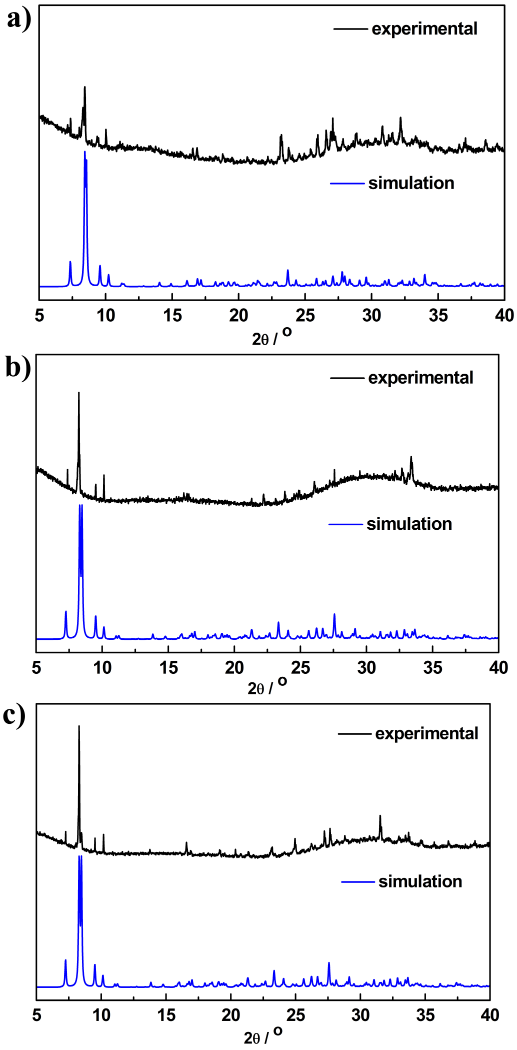

Fig. S4 Comparisons of the simulated and experimental PXRD patterns of **5** (a), **6** (b) and **7** (c).

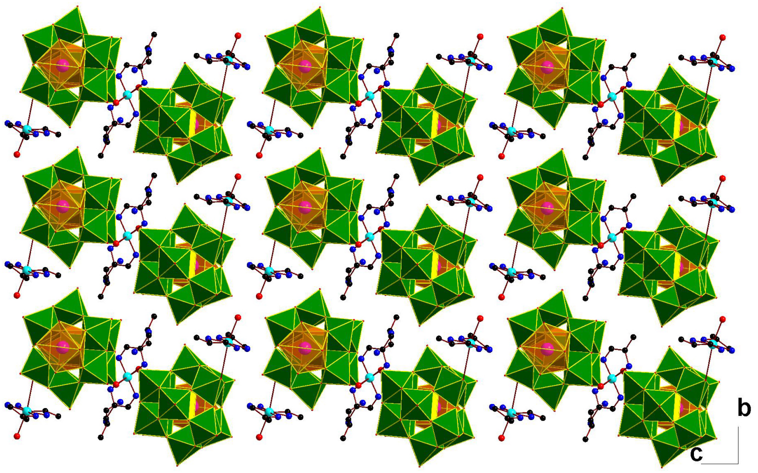

Fig. S5 Arrangement of 1-D double-chains in the crystallographical bc plane in **1** showing the mode of –AAA–.

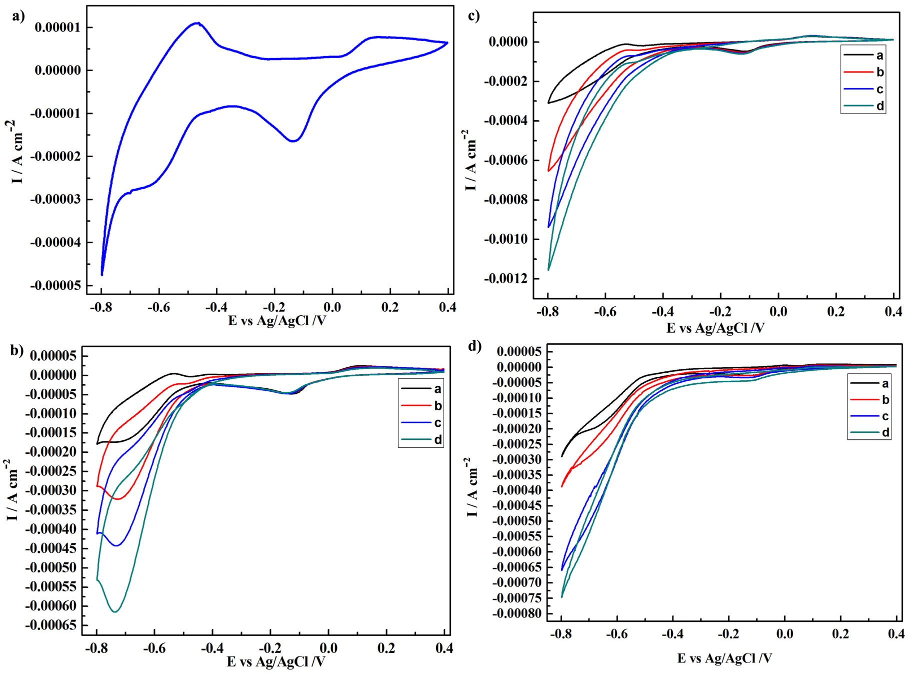

Fig. S6 (a) Cyclic voltammogram of **4**-CPE in pH = 1.35 0.5 mol·L^{-1} Na_2SO_4 + H_2SO_4 aqueous solution; (b) The evolution of cyclic voltammograms of **4**-CPE in pH = 1.34 0.5 mol·L^{-1} Na_2SO_4 + H_2SO_4 aqueous solution containing various H_2O_2 concentrations (a 5.88 × 10^{-3}, b 9.80 × 10^{-3}, c 1.37 × 10^{-2}, d 1.76 × 10^{-2} mol·L^{-1}); (c) The evolution of cyclic voltammograms of **4**-CPE in pH = 1.34 0.5 mol·L^{-1} Na_2SO_4 + H_2SO_4 aqueous solution containing various $NaBrO_3$ concentrations (a 1 × 10^{-3}, b 3 × 10^{-3}, c 5 × 10^{-2}, d 7 × 10^{-3}); (d) The evolution of cyclic voltammograms of **4**-CPE in pH = 1.34 0.5 mol·L^{-1} Na_2SO_4 + H_2SO_4 aqueous solution containing various $NaNO_2$ concentrations (a 3 × 10^{-3}, b 5 × 10^{-3}, c 7 × 10^{-3}, d 9 × 10^{-3} mol·L^{-1}). Scan rate: 50 mV s^{-1}.

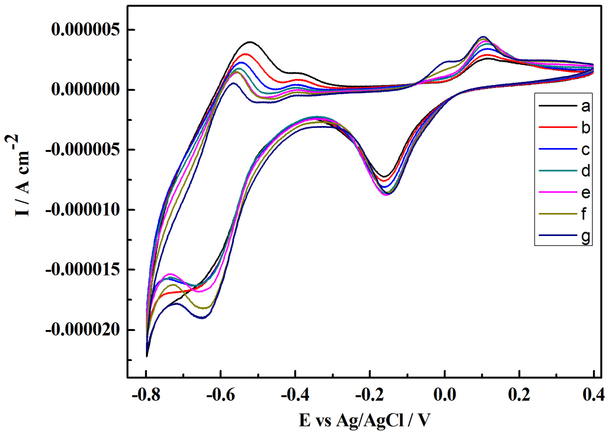

Fig. S7 Cyclic voltammorgrams of **3**-CPE in different pH (a 1.20; b 1.25; c 1.30; d 1.34; e 1.39; f 1.44; g 1.53).

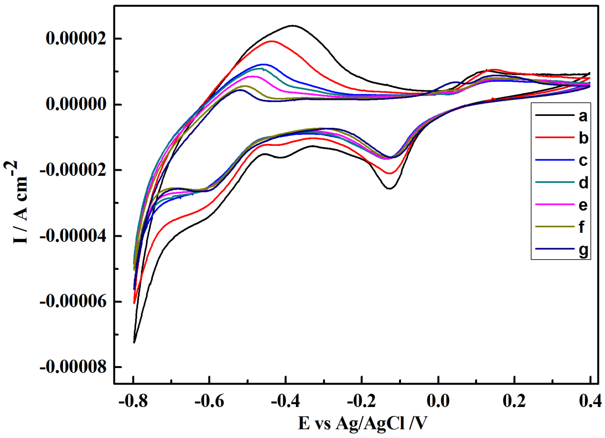

Fig. S8 Cyclic voltammorgrams of **4**-CPE in different pH (a 1.10, b 1.20, c 1.30, d 1.35, e 1.40, f 1.51, g 1.61).

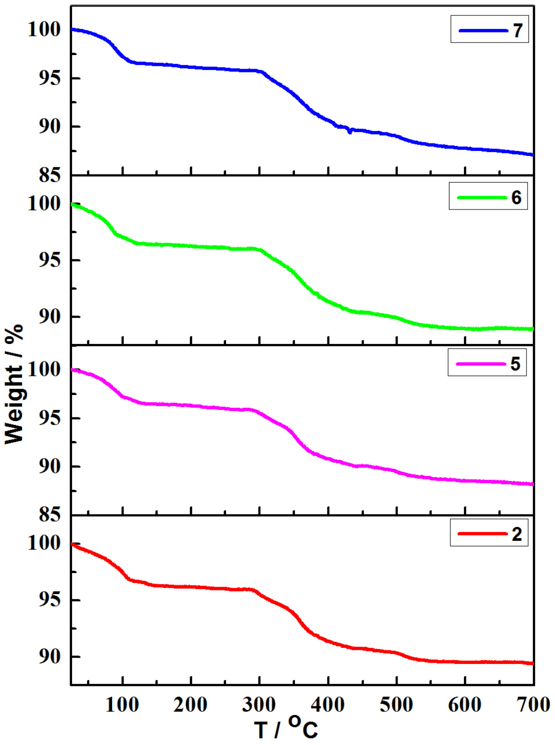

Fig. S9 The TG curves of **2**, **5**, **6** and **7**.

The thermal stability of **2**, **5**, **6** and **7** has been investigated on crystalline samples under N_2 atmosphere with a heating rate of 10 °C/min in the temperature range of 25–700 °C (Fig. S9). The TG curves indicate two steps of weight loss. The first weight loss of 4.06 % for **2**, 4.10 % for **5**, 4.02 % for **6** and 4.16 for **7** from 25 to 260 °C is approximately assigned to the removal of three lattice water molecules, one coordination water molecule and one dap ligand (calcd. 4.32 % for **2**, 4.30 % for **5**, 4.27 % for **6**, 4.28 % for **7**). The second weight loss of 8.73 % for **2**, 8.60 for **5**, 8.13 for **6** and 8.76 for **7** from 260 to 700 °C is attributable to the removal of three coordination water molecules, three dap ligands the dehydration of two protons (calcd. 9.09 % for **2**, 9.06 for **5**, 8.99 for **6**, 9.02 for **7**).