Supporting Information

Organic–inorganic hybrids based on monovacant Keggin-type polyoxotungstates and 3d-4f heterometals

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The details during the course of the structural refinements of 1-4:

Because structures of **1-4** 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 N1, N2, N4, N6, N8, $C and $O. The DFIX instruction is used for C1 and N1, C3 and C4, C4 and N4, C5 and C6. The SIMU instruction is used for C5 and C3. Now, 493 restraints are used in the refinement.

2: The ISOR instruction is used for N1, N2, N5, N8, $C and $O. The DFIX instruction is used for C4 and N4, C6 and N6, C8 and N8. The SIMU instruction is used for C3. Now, 414 restraints are used in the refinement.

3: The ISOR instruction is used for N4, $C and $O. The SIMU instruction is used for C9. Now, 384 restraints are used in the refinement.

4: The ISOR instruction is used for O5, O13, O14, O25, O26, C3, C6, C7, C9, C10 and C11. The DFIX instruction is used for C5 and H6A, C6 and H6B, C6 and N4. The SIMU instruction is used for C10 and C6. Now, 69 restraints are used in the refinement.

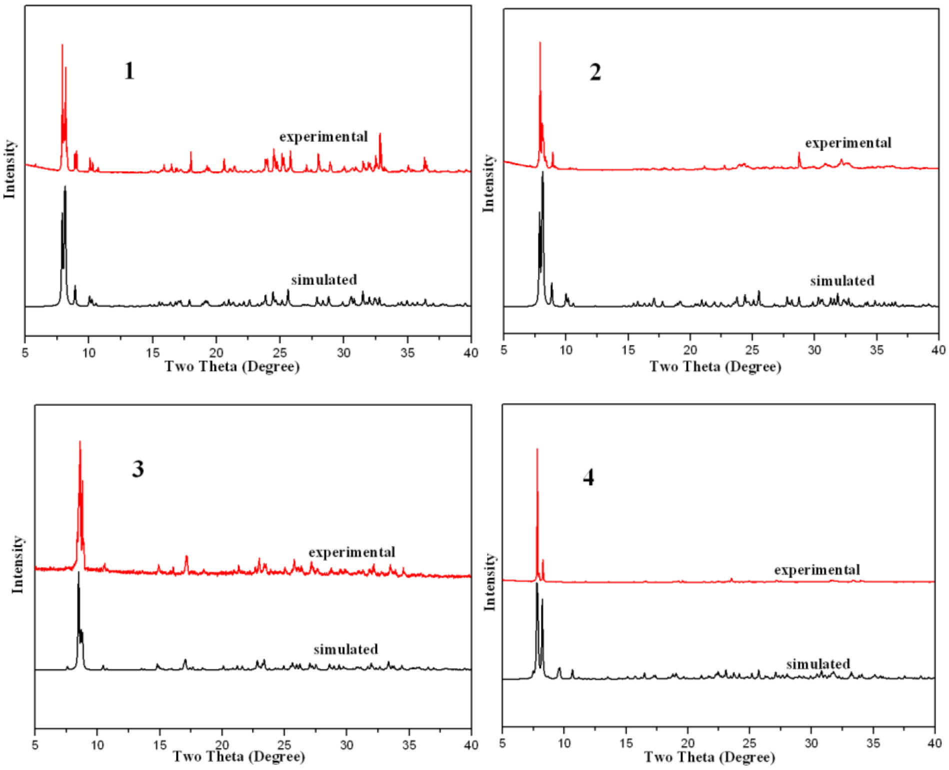

Fig. S1 Comparison of the simulated and experimental PXRD patterns of **1-4**.

The experimental PXRD patterns of **1-4** are in good agreement with the simulated PXRD patterns from the single-crystal X-ray diffraction, suggesting the good phase purity of samples (Fig. S1). The differences in intensity between them may be due to the variation in preferred orientation of the powder sample during collection of the experimental PXRD pattern.

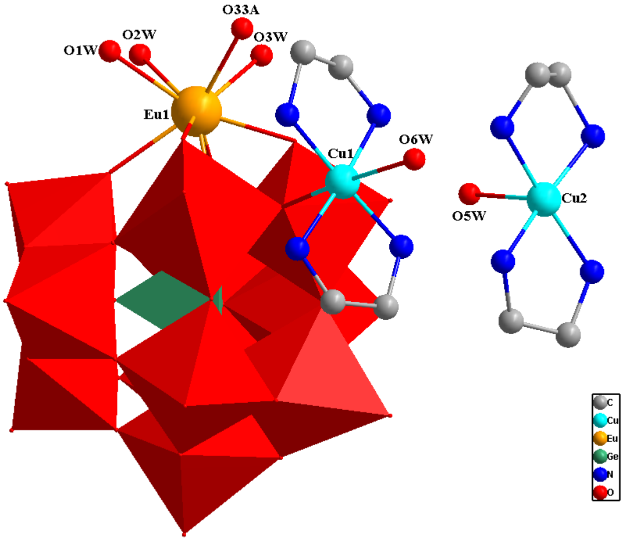

Fig. S2 Polyhedral/ball-and-stick representation of the molecular structural unit of **2**, H atoms and lattice water molecules are omitted for clarity. The atom with the suffix A is generated by the symmetry: A: 1+x, y, z.

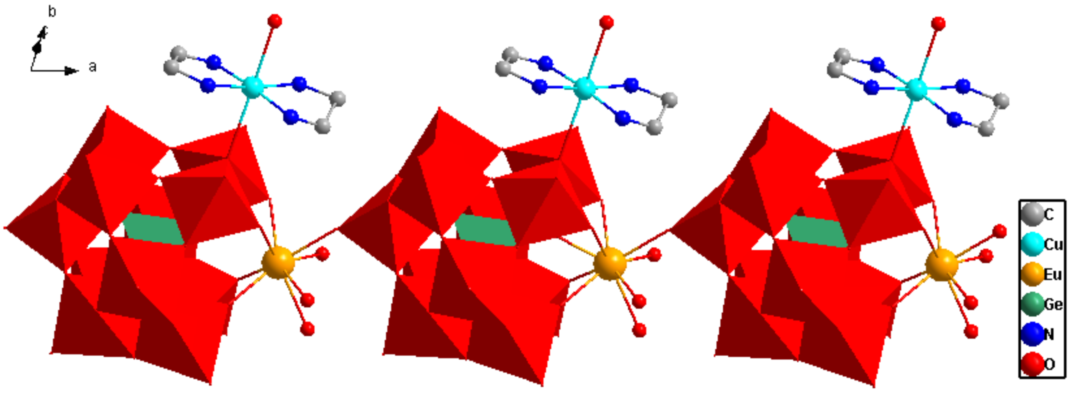

Fig. S3 View of the 1D chain of **2** along the *a*-axis.

Single-crystal X-ray analysis reveals that **2** crystallizes in the triclinic space group $P1$. The asymmetrical structural unit of **2** consists of one mono-Eu^{III} substituted Keggin-type $[\alpha\text{-GeW}_{11}O_{39}Tb(H_2O)_3]^{5-}$ fragment, one supporting $[Cu(en)_2(H_2O)]^{2+}$ cation, one discrete $[Cu(en)_2(H_2O)]^{2+}$ cation, one proton and 12 lattice water molecules (Fig. S2). The Eu1^{3+} cation incorporated into the vacant site of the $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ subunit exhibits an eight-coordinate distorted square antiprism geometry, in which three coordinate oxygen atoms come from three water ligands [Eu–O: 2.49(2)–2.54(3) Å], four from one $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ subunit [Eu–O: 2.335(19)–2.367(17) Å] and one from the other $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ subunit [Eu–O: 2.404(19) Å]. The pendant $[Cu1(en)_2(H_2O)]^{2+}$ ion shows the elongated octahedron defined by four nitrogen atoms from two en ligands with Cu–N distances of 1.97(2)–2.04(3) Å building the equatorial plane, one terminal O atom from the $[Tb(\alpha\text{-PW}_{11}O_{39})]^{4-}$ unit [Cu–O: 2.65(2) Å] and one water ligand [Cu–O: 2.59(4) Å], occupying two polar sites. The free $[Cu2(en)_2(H_2O)]^{2+}$ ion is defined by four N atoms from two en ligands with Cu–N distances of 1.94(3)–2.05(3) Å and one water ligand [Cu–O: 2.52(4) Å], exhibiting square pyramid geometry (Table S2). Each $\{[Cu(en)_2(H_2O)][Eu(\alpha\text{-GeW}_{11}O_{39})\ (H_2O)_3]\}^{3-}$ links two adjacent identical units through two W–O–Eu–O–W linkers and construct the beautiful 1-D chainlike structure (Fig. S3).

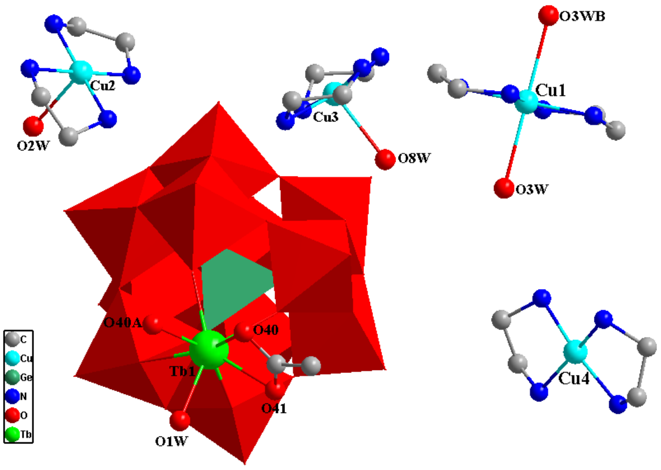

Fig. S4 Polyhedral/ball-and-stick representation of the asymmetric structure fragment of **4**, H atoms and lattice water molecules are omitted for clarity. The atoms with the suffixes A, B are generated by the symmetry: A: 0.5-x, 0.5-y, 1-z; B: -x, 1-y, -z).

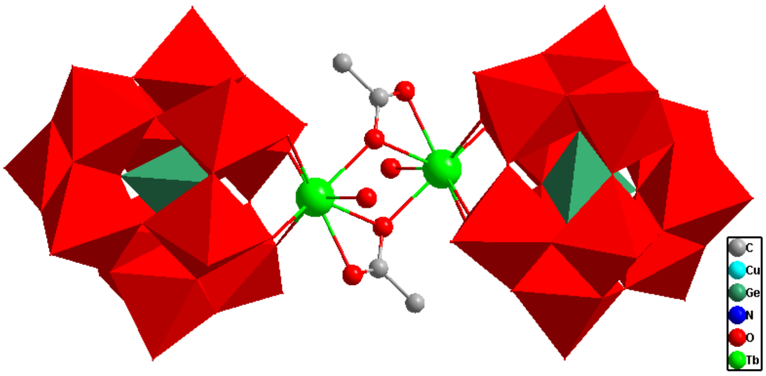

Fig. S5 View of the inorganic-organic hybrid dimeric unit of **4**.

Single-crystal X-ray analysis reveals that **4** crystallizes in the monoclinic space group *C*2/*c*. The skeleton of **4** is composed of one $[(\alpha\text{-GeW}_{11}O_{39})Tb(H_2O)(\eta^2,\mu\text{-}1,1)\text{-}CH_3COO]^{6-}$ polyanion, three discrete cooper-organic cations ($[Cu1(en)_2(H_2O)_2]^{2+}$, $[Cu2(en)_2(H_2O)]^{2+}$, $[Cu3(en)_2(H_2O)]^{2+}$, and $[Cu4(en)_2]^{2+}$) (Fig. S4), one Na^+ cation and five lattice water molecules. It should be noted that both $[Cu1(en)_2(H_2O)_2]^{2+}$ and $[Cu4(en)_2]^{2+}$ cations are situated on the special sites with the site occupancy of 0.5 for each, whereas the $[Cu2(en)_2(H_2O)]^{2+}$ and $[Cu3(en)_2(H_2O)]^{2+}$ cations are situated on the usual sites with the site occupancy of 1 for each. In **4**, the Tb1 cation is in the distorted square antiprismatic geometry, occupied by four O atoms from the defect site of the tetradentate $[\alpha\text{-GeW}_{11}O_{39}]^{8-}$ ligand [Tb–O: 2.307(11)–2.338(10) Å], three O atoms from a bidentate acetate ligand and another acetate ligand on the other polyanion subunit [Tb–O: 2.447(11)–2.497(12) Å] and a terminal water molecule [Tb–O: 2.443(12) Å] (Table S4). The two Tb^{III} cations are therefore doubly bridged by two (η^2, μ-1,1)-acetate ligands, separated by the Tb···Tb distance of 4.148 Å. The Cu1 atom is defined by four N atoms of two en molecules [Cu–N: 1.988(18)–2.008(15) Å] in the equatorial plane and two H_2O molecules [Cu–O: 2.560(11) Å] in the axial positions, adopting the six-coordinate octahedral geometry. The Cu2 and Cu3 ions inhabit in the square pyramidal geometry built by four N atoms from two en molecules with Cu–N distances of 1.929(15)–2.032(18) Å in the equatorial plane and one water molecule [Cu–O: 2.390(16)–2.403(14) Å]. The $[Cu4(en)_2]^{2+}$ cation is defined by four N atoms of two en molecules [Cu–N: 1.993(16)–1.998(16) Å] (Table S2). As shown in Fig. S5, the head-to-head inorganic–organic hybrid dimeric core $\{[Tb(\alpha\text{-GeW}_{11}O_{39})(CH_3COO)(H_2O)]\}_2^{12-}$ is built up of two identical symmetrically related mono-Tb-substituted moieties $\{[Tb(\alpha\text{-GeW}_{11}O_{39})(CH_3COO)(H_2O)]\}^{6-}$ bridged by two (η^2, μ-1,1)-acetate ligands.

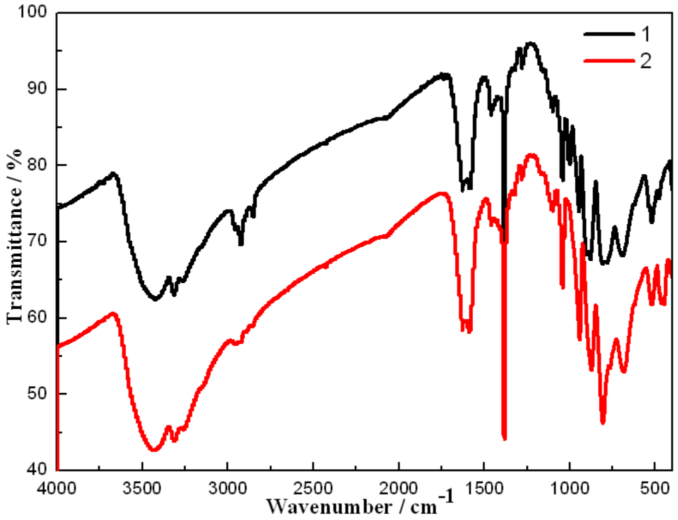

Fig. S6 IR spectra of **1** and **2**.

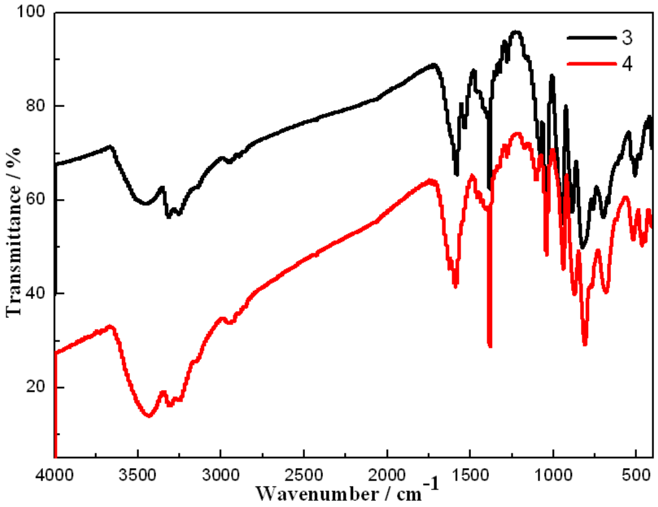

Fig. S7 IR spectra of **3** and **4**.

Table S1. Selected bond lengths (Å) for **1**.

O(1)-Tb(1)	2.28(3)	O(27)-Tb(1)	2.36(3)	O(33)-Tb(1)	2.27(3)
O(37)-Tb(1)	2.31(3)	O(14A)-Tb(1)	2.42(2)	O(1W)-Tb(1)	2.44(5)
O(2W)-Tb(1)	2.48(5)	O(3W)-Tb(1)	2.49(5)	Cu(1)-N(1)	1.94(4)
Cu(1)-N(2)	2.00(5)	Cu(1)-N(3)	1.98(5)	Cu(1)-N(4)	1.98(3)
Cu(2)-N(5)	2.01(5)	Cu(2)-N(6)	1.91(4)	Cu(2)-N(7)	1.91(5)
Cu(2)-N(8)	1.94(4)	Cu(1)-O(9W)	2.47(1)	Cu(2)-O(4W)	2.46(1)

Symmetry code: A, 1+x, y, z.

Table S2. Selected bond lengths (Å) for **2**.

Eu(1)-O(1)	2.347(18)	Eu(1)-O(2)	2.335(19)	Eu(1)-O(3)	2.362(17)
Eu(1)-O(4)	2.367(17)	Eu(1)-O(1W)	2.55(3)	Eu(1)-O(2W)	2.54(3)
Eu(1)-O(3W)	2.49(2)	Eu(1)-O(33A)	2.404(19)	Cu(1)-N(5)	2.04(2)
Cu(1)-N(6)	2.02(2)	Cu(1)-N(7)	1.97(2)	Cu(1)-N(8)	2.04(3)
Cu(2)-N(1)	2.05(3)	Cu(2)-N(2)	1.97(3)	Cu(2)-N(3)	2.05(3)
Cu(2)-N(4)	1.94(3)	Cu(1)-O(6W)	2.59(4)	Cu(2)-O(5W)	2.52(4)

Symmetry code: A, 1+x, y, z

Table S3. Selected bond lengths (Å) for **3**.

O(8)-Sm(1)	2.333(16)	O(16)-Sm(1)	2.342(15)	O(22)-Sm(1)	2.385(14)
O(35)-Sm(1)	2.338(15)	O(40)-Sm(1)	2.483(16)	O(1W)-Sm(1)	2.51(2)
O(41)-Sm(1)	2.592(16)	O(41A)-Sm(1)	2.479(16)	Cu(2)-N(1)	2.02(2)
Cu(2)-N(2)	2.029(19)	Cu(2)-N(3)	2.00(2)	Cu(2)-N(4)	2.048(17)
Cu(2)-O(4W)	2.27(2)	Cu(1)-N(5)	2.02(2)	Cu(1)-N(6)	2.02(3)
Cu(1)-N(7)	2.01(3)	Cu(1)-N(8)	1.97(3)	Cu(1)-O(5W)	2.43(4)

Symmetry code: A, 0.5–x, 1.5–y, 1–z.

Table S4. Selected bond lengths (Å) for **4**.

O(1)-Tb(1)	2.317(12)	O(2)-Tb(1)	2.330(10)	O(34)-Tb(1)	2.307(11)
O(35)-Tb(1)	2.338(10)	O(40)-Tb(1)	2.496(11)	O(41)-Tb(1)	2.497(12)
O(1W)-Tb(1)	2.443(12)	Tb(1)-O(40A)	2.447(11)	Cu(1)-N(1)	1.988(18)
Cu(1)-N(2)	2.008(15)	Cu(2)-N(4)	1.929(15)	Cu(2)-N(5)	1.978(17)
Cu(2)-N(6)	1.988(17)	Cu(2)-N(3)	1.990(17)	Cu(2)-O(2W)	2.403(14)
Cu(3)-N(8)	1.95(2)	Cu(3)-N(9)	1.98(2)	Cu(3)-N(10)	2.02(3)
Cu(3)-N(7)	2.032(18)	Cu(3)-O(8W)	2.390(16)	Cu(4)-N(11)	1.993(16)
Cu(4)-N(12)	1.998(16)	Cu(1)–O(3W)	2.560(11)		

Symmetry code: A, 0.5-x, 0.5-y, 1-z.