ESI

Novel organic–inorganic hybrid one-dimensional chain assembled by oxalate-bridging terbium-substituted phosphotungstate dimers and dinuclear copper(II)–oxalate clusters

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Experimental section

The lacunary POM precursors $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot nH_2O$ and $K_{12}[\alpha\text{-}H_2P_2W_{12}O_{48}]\cdot 24H_2O$ were prepared according to the literature[1] and their purities were identified by IR spectra. All other chemicals were obtained from commercial sources and used without further purification. Elemental analyses of C, H and N were carried out with a Vario EL III elemental analyzer. IR spectra (KBr pellets) were recorded on a Smart Omni-Transmission spectrometer. X-ray diffraction data were collected on a Gemini diffractometer with graphite-monochromated MoK_α (λ = 0.71073 Å) at room temperature. The program SADABS was used for the absorption correction.[2] The structures were solved by the direct method and refined on F^2 by full-matrix least-squares methods using the SHELX97 program package.[3] Powder XRD patterns were obtained using a Philips X'Pert-MPD diffractometer with CuKα radiation (λ = 1.54056 Å). Variable temperature susceptibility measurements were carried out in the temperature range 2-300 K at a magnetic field of 1 kOe for **1** on polycrystalline samples with a Quantum Design MPMS XL-5 SQUID magnetometer. All the magnetic susceptibility data were corrected for magnetization of the sample holder and for diamagnetic contribution estimated from Pascal's constants.

1 (a) A. P. Ginsberg. *Inorg. Synth.*, 1990, **27**, 85; (b) R. Contant. *Inorg. Synth.*, 1990, **27**, 108.

2 G. M. Sheldrick SADABS, Program for Siemens Area Detector Absorption Corrections (University of Göttingen, Göttingen, Germany, 1997.

3 (a) G. M. Sheldrick SHELXS97, Program for Crystal Structure Solution; University of Göttingen, Germany, 1997; (b) G. M. Sheldrick SHELXL97, Program for Crystal Structure Refinement; University of Göttingen, Germany, 1997.

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

Cu(1)–O(45)	1.962(9)	Cu(1)–O(44)	1.965(7)	Cu(1)–N(2)	1.962(9)
Cu(1)–N(1)	1.976(1)	Cu(1)–O(7)	2.658(7)	Cu(2)–N(4)	1.987(1)
Cu(2)–N(3)	1.990(1)	Cu(2)–N(5)	1.990(1)	Cu(2)–O(42)	2.627(1)
Cu(2)–N(6)	1.985(1)	Cu(3)–N(10)	2.009(1)	Cu(3)–N(8)	2.038(2)
Cu(3)–-O(46)	2.416(8)	Cu(3)–N(7)	1.980(1)	Cu(3)–N(9)	2.002(1)
O(1)–Tb(1)	2.340(8)	O(2)–Tb(1)	2.378(8)	O(3)–Tb(1)	2.334(8)
O(4)–Tb(1)	2.327(7)	O(40)–Tb(1)	2.442(9)	O(41)–Tb(1)	2.451(1)
O(42)–Tb(1)	2.511(8)	O(43)–Tb(1)	2.380(9)		

As shown in Fig. 1 and Table S1, the $Tb1^{III}$ cation is eight-coordinated, adopting a distorted square antiprism geometry (pseudo-D_{4d}). The Tb1 center is bound to four available O atoms of the lacunary site of the $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ moiety, two O atoms from the $C_2O_4^{2-}$ ligand and two O atoms from water ligands with $Tb1^{III}$–O diatances of 2.327(7) –2.511(8) Å. Three crystallographic independent copper ions all exhibit square pyramid geometry, but the coordinated N atoms and O atoms are from different ligands with Cu–O bond lengths ranging from 1.962(9) to 2.658(7) Å and Cu–N bond lengths ranging from 1.962(9) to 2.038(2) Å, respectively.

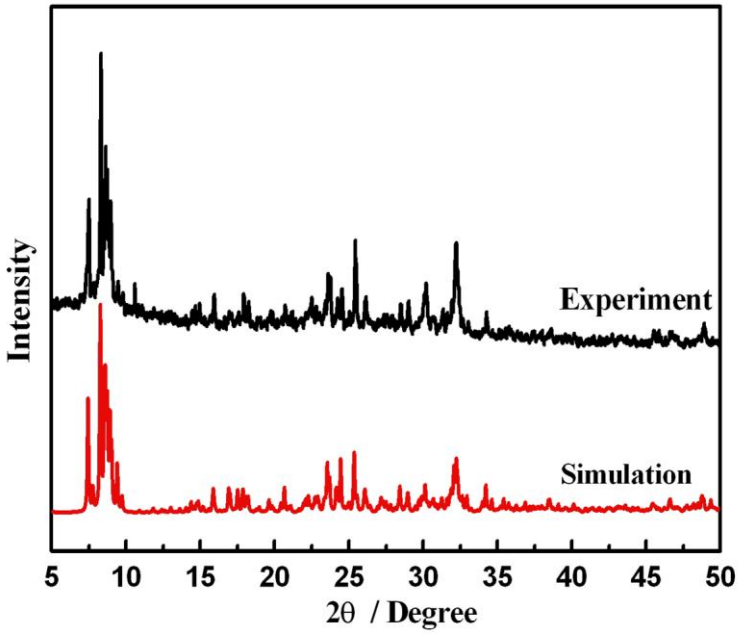

Fig. S1. Comparison of the simulated and experimental PXRD patterns of **1**.

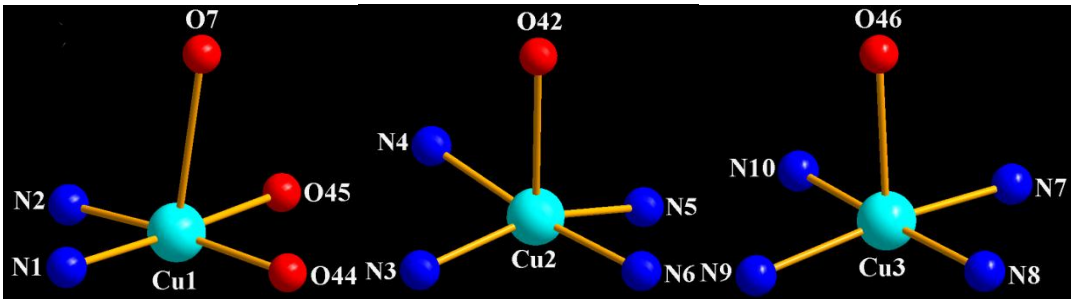

Fig. S2. The coordination environments of the Cu^{II} cations in **1**.

As is shown in Fig. S2, in **1**, three crystallographic independent copper ions all exhibit square pyramid geometry, but the coordinated N atoms and O atoms are from different ligands . The Cu1 ion is defined by two N atoms from the chelating en ligands with Cu–N bond lengths of 1.962(9) and 1.976(1) Å, two O atoms from the chelating ox ligands with Cu–O bond lengths of 1.962(9)–1.965(7) Å, one terminal O atom from the $[Tb(\alpha\text{-}PW_{11}O_{39})]^{4-}$ POA [Cu–O: 2.658(7) Å]. The Cu2 ion adopts the same geometry with four N atoms from two en ligands [Cu–N: 1.985(1)–1.990(1) Å] and one O atom from the chelating ox ligands [Cu–O: 2.627(1) Å]. The free $[Cu3(en)_2(H_2O)]^{2+}$ ion is defined by four N atoms from the chelating en ligands [Cu–N: 1.980(1)–2.038(2) Å] and one water ligand [Cu–O: 2.416(8) Å] (Table S1).

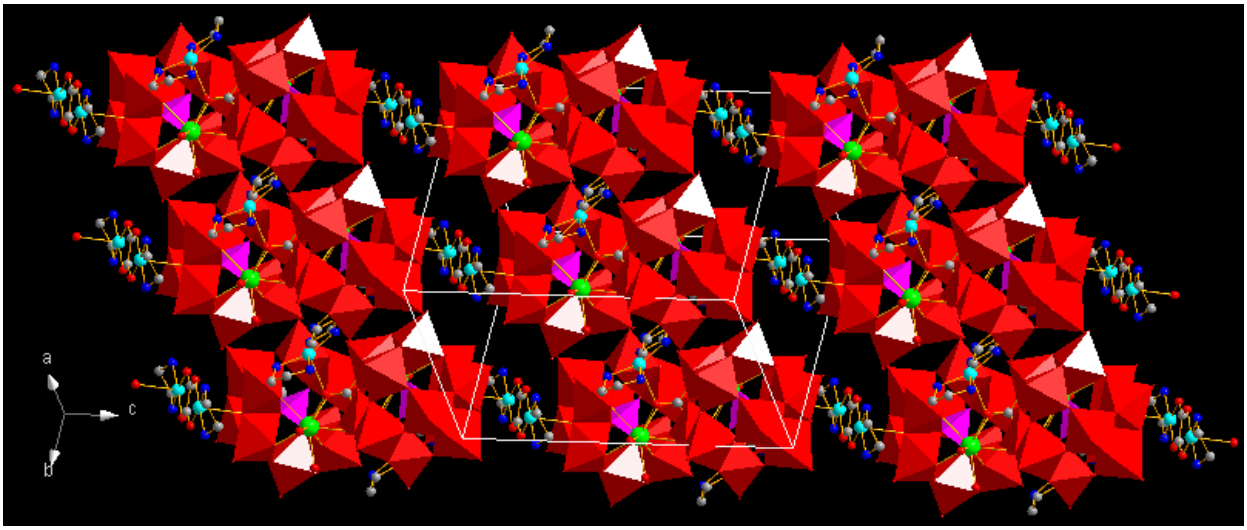

Fig. S3. The packing arrangement of compound **1**, free $[Cu(en)_2(H_2O)]^{2+}$ ions, H atoms and lattice water molecules are omitted for clarity. It can be found that this kind of hybrid compounds were all low dimensional structures, which may be due to the connection mode of oxalate ligands.

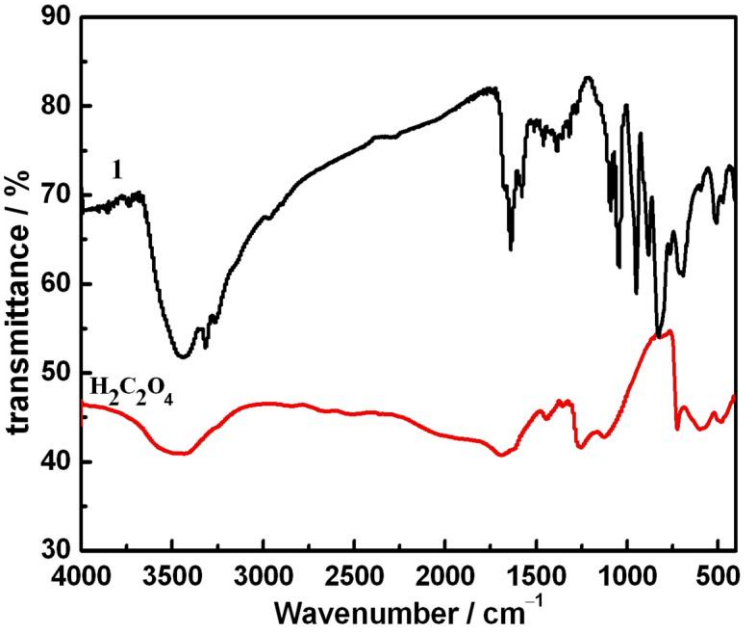

Fig. S4. IR spectra of **1** and the free $H_2C_2O_4$ ligand.

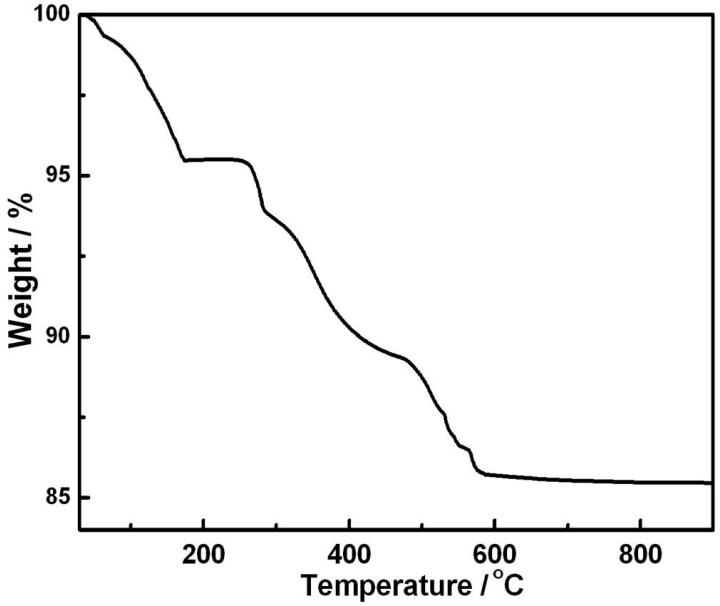

Fig. S5. The TG curve of **1**.