Supporting Information for

A novel 2-D coordination polymer constructed from high-nuclearity waist drum-like pure Ho_{48} clusters

Lei Chen[a], Jiu-Yu Guo[a], Xiao Xu[a], Wei-Wei Ju[a], Deng Zhang[a], Dun-Ru Zhu[a] and Yan Xu [*a,b]

1. General Experimental.

Single crystals of compound **1** were glued by a thin glass fiber with epoxy glue in air for data collection; diffraction data were performed on a Bruker Apex Ⅱ CCD with Mo-Kα radiation (λ = 0.71073 Å) at 296 K using ω-2θ scan method. The empirical absorption correction was applied. The crystal structures were figured out by direct method and refined on $|F|^2$ by full-matrix least-squares methods using the SHELX97 program package. All non-hydrogen atoms were refined anisotropically. All the metal atoms were refined anisotropically, while the remaining O, C, and N atoms of the organic ligands were refined isotropically. The hydrogen atoms of the organic moieties were placed in calculated positions, assigned isotropic displacement parameters, and allowed to ride on their parent atoms. However, H atoms for all water and OH^- groups are not located. Crystallographic data and relevant information are presented in Tab. S1.

All reagents were of commercially origin and were used without further purification. The element analysis of C, H and N were performed on a Perkin-Elemer 2400 CHN elemental analyzer. The Infrared (IR) spectra of the two compounds were implemented with a pressed KBr pellets on a Nicolet Impact 410 FTIR spectrometer. TG analysis was carried out in flowing N_2 atmosphere from 25 to 1100 ℃ with a heating rate of 10 ℃·min^{-1} with a Diamond thermogravimetric analyzer. Since Crystals of compound 1 (Ho48) were obtained together with some byproduct of Ho26, the recollected PXRD data were performed with selected single crystals from the bulk reaction product.

2. **Syntheses of complexe 1.** A mixture of Ho_2O_3 (0.1887 g, 0.5 mmol), $Mn(OAc)_2{\cdot}4H_2O$ (0.0354 g, 0.15 mmol), HIN (0.2459 g, 2.00 mmol), KBr (0.0071 g, 0.06 mmol), HCOOH (88%, 0.0293 g, 0.64 mmol), and H_2O (8 ml) was placed in a 25 mL Teflon-lined autoclave. Then, adjusted the pH of the solution to 3.2 with HNO_3 (65%) and sealed the solution after stirring for 12 h. When heated at 170 °C for 7 days, the idocrase-like nearly colorless crystal was obtained (0.0937 g, yield of 27.3% based on Ho). Elemental analysis (%): calcd.: C, 21.68, H, 2.22, N, 4.09; found: C, 21.62, H, 2.28, N, 4.12. IR of compound (cm^{-1}): 3432(s), 1605(vs), 1549(vs), 1418(vs), 1146(w), 769(m), 678(m), 560(m).

During the synthesis of compound **1**, it must be noted that the use of $Mn(OAc)_2{\cdot}4H_2O$ is extremely important. Actually, we supposed to get 3d-4f clusters by adding it. And we tried to replace $Mn(OAc)_2{\cdot}4H_2O$ with $Co(OAc)_2{\cdot}4H_2O$, $Ni(OAc)_2{\cdot}4H_2O$, $Zn(OAc)_2{\cdot}2H_2O$, $Cu(OAc)_2{\cdot}2H_2O$, $Cd(OAc)_2{\cdot}2H_2O$, alkali acetate or acetic acid, but we can only obtain Ho_{26} cluster (unit cell: a = 21.043 Å, b = 21.128 Å, c = 35.140 Å, α = 85.83, β = 74.90, γ = 85.41°). $Mn(OAc)_2{\cdot}4H_2O$ seems to have played a big role in the formation of **1**. What's more, the use of HCOOH is necessary, although it is not concerned in the final structure. Anyway, we can't get compound **1** without $Mn(OAc)_2{\cdot}4H_2O$ and HCOOH. And no isomorphous compounds can be obtained with other lanthanide metals.

Tab. S1. Crystal data and structure refinements for **1**.

Compound	**1**
Empirical formula	$K_2Ho_{48}Br_2N_{48}C_{297}O_{231}H_{410}$
Formula weight	16454.9
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
space group	$P2_1/c$
Unit cell dimensions (Å , °)	
a	24.1311(16)
b	23.3088(16)
c	40.600(3)
β	91.4810(10)
Volume($Å^3$), *Z*	22829(3), 2
Calculated density (g/cm^{-3})	2.370
Absorption coefficient (mm^{-1})	8.499
F(000)	14980
Crystal size(mm^3)	0.13 × 0.12 × 0.12
Limiting indices	$-29 \leq h \leq 25$; $-28 \leq k \leq 28$; $-49 \leq l \leq 48$
Reflections collected	163,602
Independent reflection	42340 [*R*(int) = 0.1258]
Max. and min. transmission	0.4287 and 0.4046
Refinement method	Full-matrix-block least-squares on F^2
Data/parameters	42340/1419
Goodness-of-fit on F^2	0.970

Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0608$, $wR_2 = 0.1432$
R indices (all data)	$R_1 = 0.1355$, $wR_2 = 0.1702$

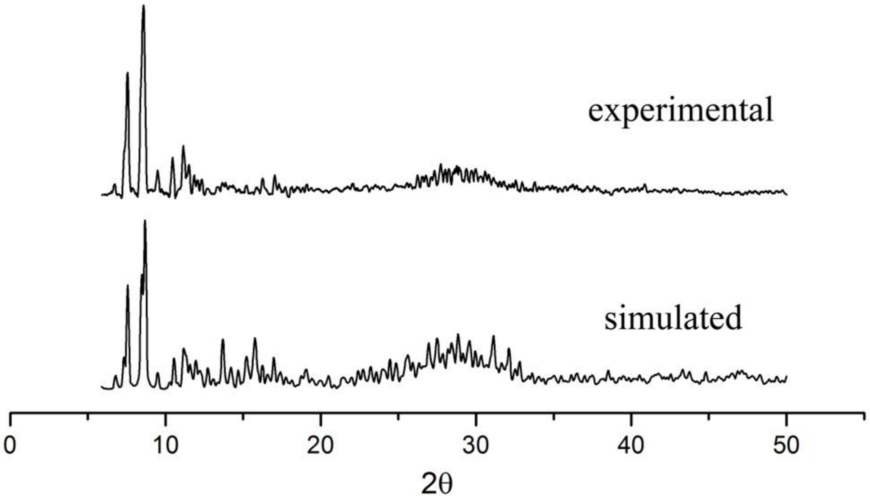

Fig. S1 The experimental and simulated XRD patterns for **1**.

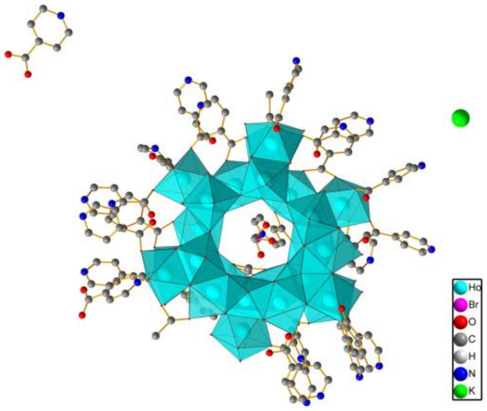

Fig. S2 View of the petaloid asymmetric unit of complex **1**. For clarity, hydrogen atoms and water molecules are omitted.

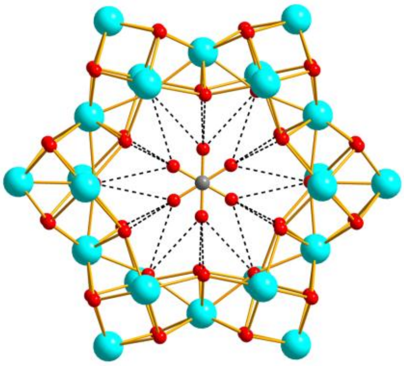

Fig. S3 The radially hydrogen-bond of the barrel of the drum templated by CO_3^{2-} ion.

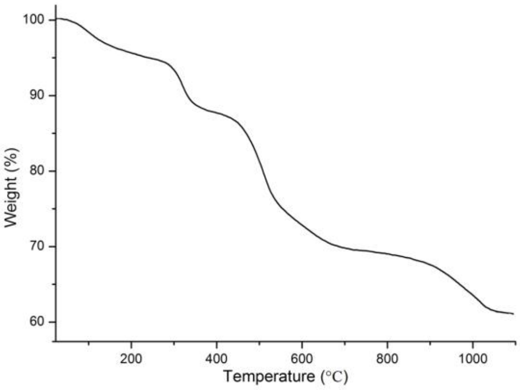

Fig. S4 The TG curve of compound **1**.

The thermal analysis of compound **1** was carried out in the temperature range of 25-1100 °C. As shown in Fig. S5, the weight loss of 2.58% from 25 to 124 °C is ascribed to the loss of lattice H_2O molecules (Calcd 2.18%). Meanwhile, the weight loss of 3.10% in the range of 124-283 °C corresponds to the removal of coordinated H_2O and free HIN molecules (Calcd 3.02%). After 283 °C, IN^- and CH_3COO^- ligands are removed and the skeleton collapses.

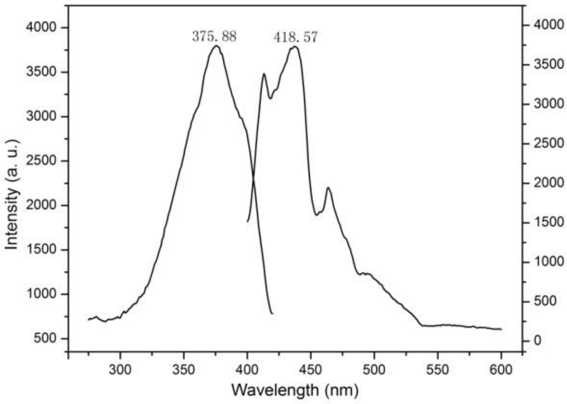

Fig. S5 The excitation (left) and emission (right) spectra of compound **1**.