

## Supporting Information

### **Octahedron-shaped three-shell Ln<sub>14</sub>-substituted polyoxotungstogermanates encapsulating a W<sub>4</sub>O<sub>15</sub> cluster: luminescence and frequency dependent magnetic properties**

Yong-Jiang Wang, Shi-Yu Wu, Yan-Qiong Sun\*, Xin-Xiong Li, Shou-Tian Zheng\*

College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, China.

\*E-mail: sunyq@fzu.edu.cn; stzheng@fzu.edu.cn

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#### **1. Materials and Methods**

All other starting materials were of analytical grade and obtained from commercial sources without further purification<sup>1</sup>. Elemental analyses of C, H, N and O were carried out with a Vario EL Cube elemental analyzer. Infrared (IR) spectra (KBr pellet) were recorded on an Opus Vertex 70 FT-IR infrared spectrophotometer in the range of 400–4000 cm<sup>-1</sup>. Powder X-ray diffraction (PXRD) patterns were measured using a Rigaku DMAX 2500 diffractometer with CuK $\alpha$  radiation ( $\lambda$  = 1.54056 Å). Thermogravimetric analyses were performed on a Mettler Toledo TGA/SDTA 851<sup>e</sup> analyzer under an N<sub>2</sub>-flow atmosphere with a heating rate of 10 °C/min in the temperature of 25–800 °C. Variable-temperature susceptibility measurements were performed in the temperature range of 2–300 K at a magnetic field of 0.1 T on the polycrystalline samples with a Quantum Design PPMS-9T magnetometer. The experimental susceptibilities were corrected for Pascal's constants.

#### **2. Synthesis and Synthetic discussion**

**Preparation of aqueous solutions of Ln(ClO<sub>4</sub>)<sub>3</sub> (1.0 mol L<sup>-1</sup>):** lanthanide oxides (0.125 mol, Ln=Eu (44.00g), Gd (45.31g), Tb (45.73g), Dy (46.63g), Ho (47.23g), Er (47.82g)) adding

perchloric acid aqueous solution(70.0% -72.0%, 60.0 ml) at about 70 °C. Aqueous solution of  $\text{Ln}(\text{ClO}_4)_3$ , 1.0 mol  $\text{L}^{-1}$ , Ln=Eu, Gd, Tb, Dy, Ho, Er) was obtained by diluting the concentrated solution to 250.00 ml with deionized water.

**Synthesis of 1-Tb:** A mixture of solid  $\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$  (0.329g, 1mmol),  $\text{GeO}_2$  (0.016g, 0.15mmol), 1,2,4-Triazole(0.075g, 1.085mmol), was dissolved in 2 mL of distilled water, add 0.15mL 1M  $\text{Tb}(\text{ClO}_4)_3$  with vigorous stirring, after stirring for another 1h. The mixture was sealed in a 23 mL Teflon-lined autoclave and heated at 150°C for 72 h. After cooling to room temperature and place for another 24 hours, colorless crystals were obtained. Yield: 11.5 % based on  $\text{Tb}(\text{ClO}_4)_3$ . IR: 3346.53(s), 1628.18(s), 900.76(s), 856.20(s), 741.58(w), 613.78(w), 500.04(w), 429.08(w). Elemental analysis was performed.

**Synthesis of 1-Eu:** The reaction process of **1-Eu** is similar to **1-Tb** except that  $\text{Eu}(\text{ClO}_4)_3$  (1.0 mol  $\text{L}^{-1}$ ) was used to replace  $\text{Tb}(\text{ClO}_4)_3$  (1.0 mol  $\text{L}^{-1}$ ). Yield: 12.3% IR: 3346.53(s), 1628.18(s), 900.76(s), 856.20(s), 741.58(w), 613.78(w), 500.04(w), 429.08(w).

**Synthesis of 1-Gd:** The reaction process of **1-Gd** is similar to **1-Tb** except that  $\text{Gd}(\text{ClO}_4)_3$  (1.0 mol  $\text{L}^{-1}$ ) was used to replace  $\text{Tb}(\text{ClO}_4)_3$  (1.0 mol  $\text{L}^{-1}$ ) Yield: 12% IR: 3346.53(s), 1628.18(s), 900.76(s), 856.20(s), 741.58(w), 613.78(w), 500.04(w), 429.08(w).

**Synthesis of 1-Dy:** The reaction process of **1-Dy** is similar to **1-Tb** except that  $\text{Dy}(\text{ClO}_4)_3$  (1.0 mol  $\text{L}^{-1}$ ) was used to replace  $\text{Tb}(\text{ClO}_4)_3$  (1.0 mol  $\text{L}^{-1}$ ) Yield: 15.2% IR: 3346.53(s), 1628.18(s), 900.76(s), 856.20(s), 741.58(w), 613.78(w), 500.04(w), 429.08(w).

**Synthesis of 1-Ho:** The reaction process of **1-Ho** is similar to **1-Tb** except that  $\text{Ho}(\text{ClO}_4)_3$  (1.0 mol  $\text{L}^{-1}$ ) was used to replace  $\text{Tb}(\text{ClO}_4)_3$  (1.0 mol  $\text{L}^{-1}$ ) Yield: 13% IR: 3346.53(s), 1628.18(s), 900.76(s), 856.20(s), 741.58(w), 613.78(w), 500.04(w), 429.08(w).

**Synthesis of 1-Er:** The reaction process of **1-Er** is similar to **1-Tb** except that  $\text{Er}(\text{ClO}_4)_3$  (1.0 mol  $\text{L}^{-1}$ ) was used to replace  $\text{Tb}(\text{ClO}_4)_3$  (1.0 mol  $\text{L}^{-1}$ ) Yield: 8% IR: 3346.53(s), 1628.18(s), 900.76(s), 856.20(s), 741.58(w), 613.78(w), 500.04(w), 429.08(w).

**Synthetic discussion:** The alkaline environment ( $\text{pH}=10$ ) provided by organic small molecule 1,2,4-triazole is one of the important factors for the synthesis of **1-Ln**, but there is no 1,2,4-triazole molecules in the structure. (We use X-ray single crystal diffraction and elemental analysis for detection). At the same time, we tried to replace 1,2,4-triazole with other similar organic molecules such as imidazole and melamine, and we can also get the compound **1-Ln**, but the crystal yield is relatively low and the quality is not good. If  $\text{LnCl}_3$  or  $\text{Ln}(\text{NO}_3)_3$  was chosen instead of  $\text{Ln}(\text{ClO}_4)_3$ ,

compound **1-Ln** cannot be obtained, the reason may be that perchlorate acts as an anionic template, we guess that  $\text{ClO}_4^-$  anion promote the formation of the center  $\{\text{W}_4\text{O}_{15}\}$  unit. When  $\text{Co}(\text{NO}_3)_2$  (0.0291g 0.1mmol) was added extra, the yield can be greatly improved, transition metals salt may play a role as a mineralizer in the reaction. So we come to the conclusion that the alkaline environment (pH=10) and the  $\text{Ln}(\text{ClO}_4)_3$  is necessary for the self-assembly of **1-Ln**, and  $\text{Co}(\text{NO}_3)_2$  is also important for a higher yield.

### 3. Single-crystal X-ray Crystallography

Structures were solved by direct methods followed by successive difference Fourier methods. Computations were performed using SHELXTL and final full-matrix refinements were against  $F^2$ . The structures were solved by direct methods and refined by the full-matrix least-squares method on  $F^2$ , with all non-hydrogen atoms refined with anisotropic thermal parameters. All of the hydrogen atoms attached to carbon atoms were placed in calculated positions and refined using N the riding model. All calculations were carried out with the SHELXTL and OLEX crystallographic software. Crystallographic data for the structures reported have been deposited at the Cambridge Crystallographic Data Center with CCDC reference numbers 1867006 for compounds **1-Tb**†. The selected crystal parameters, data collection, and refinements are summarized in **Table S1**.

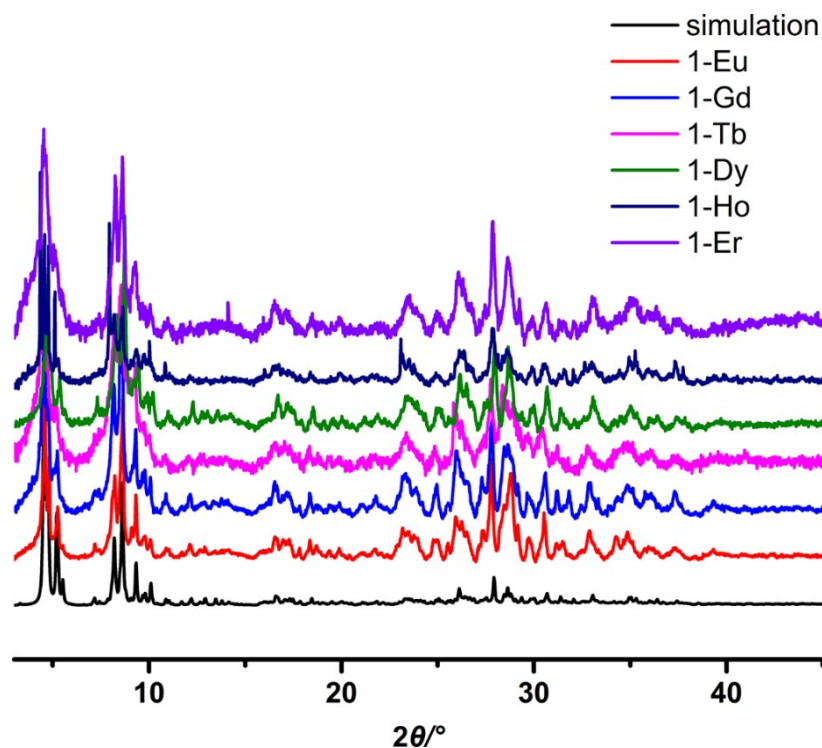
**Table S1.** Crystallographic data collection and refinement results for **1-Tb**.

Name code	<b>1-Tb</b>
Empirical formula	$\text{Ge}_6\text{Na}_{15.7}\text{O}_{297.1}\text{Tb}_{13.9}\text{W}_{68}$
Formula weight (g/mol)	20263.29
Temperature / K	175(2)
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	24.294(2)
<i>b</i> / Å	25.167(2)
<i>c</i> / Å	27.200(3)
$\alpha$ / °	97.093(2)
$\beta$ / °	96.008(2)
$\gamma$ / °	97.663(2)
<i>V</i> / Å <sup>3</sup>	16231(3)
<i>Z</i>	2
$\rho_{\text{calcd}}$ / g.cm <sup>-3</sup>	4.146
$\mu$ / mm <sup>-1</sup>	27.636
F(000)	17356.0
Crystal size / mm <sup>3</sup>	0.3 × 0.2 × 0.1
$\theta$ range / °	3.04 to 49.92
Limiting indices	-28 ≤ <i>h</i> ≤ 28, -29 ≤ <i>k</i> ≤ 29, -32 ≤ <i>l</i> ≤ 32
<i>R</i> <sub>int</sub>	0.0349
GooF	1.019
<i>R</i> [ <i>I</i> > 2σ]	<i>R</i> <sub>1</sub> <sup>a</sup> = 0.0639, <i>wR</i> <sub>2</sub> <sup>b</sup> = 0.1557

$R(\text{all data})$	$R_I^a = 0.0929,$ $wR_2^b = 0.1766$
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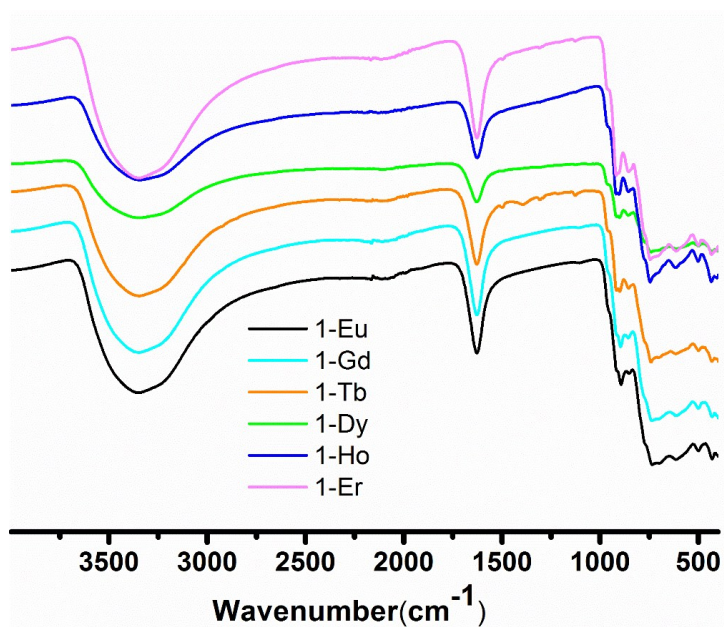
<sup>a</sup> $R_I = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ , <sup>b</sup> $wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2/w(F_o^2)]^{1/2}}{w}$ ,  $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ ,  $P = (F_o^2 + 2F_c^2)/3$ , where  $x = 0.025500$ ,  $y = 5.539400$  for **1-Tb**.

#### 4. Additional Figures



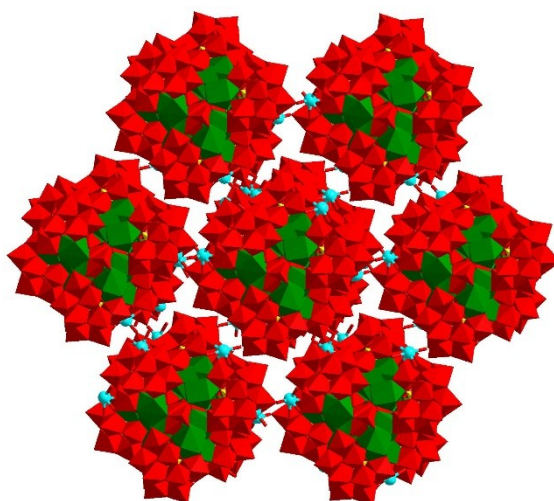
**Fig. S1** The simulated and experimental PXRD patterns of **1-Ln**.

As shown, The observed peaks match with the simulated peaks very well, which suggests that **1-Ln** is pure phase and **1-Eu**, **1-Gd**, **1-Tb**, **1-Dy**, **1-Ho**, and **1-Er** are isomorphous crystals.

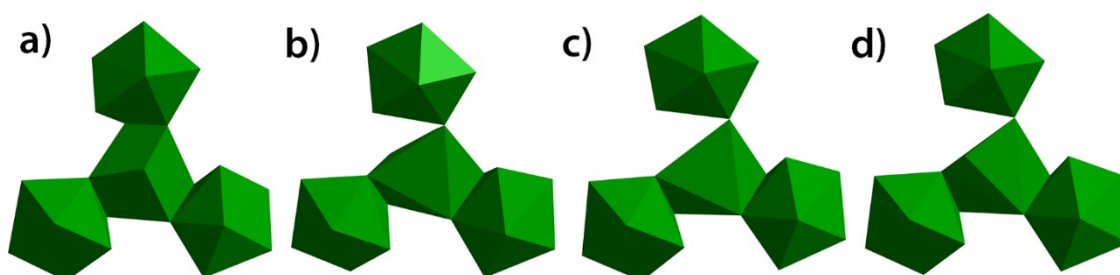


**Fig. S2** The IR spectra of **1-Ln**.

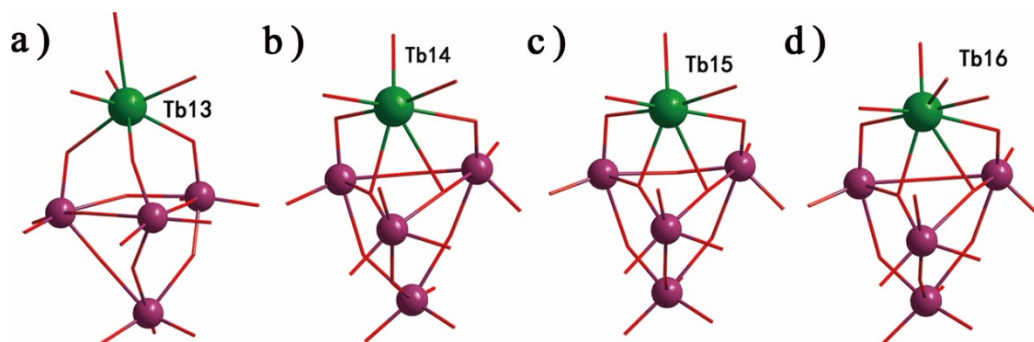
The absorption peak of compound **1-Ln** at  $3346.53\text{ cm}^{-1}$  is attributed to the stretching vibration peak of the O-H group of the water and the O-H of the coordinating hydroxyl group. The absorption peak of  $1628.18\text{ cm}^{-1}$  corresponds to the H-O-H bending vibration of crystal water. Characteristic absorption peaks in the range of  $600 - 1000\text{ cm}^{-1}$  may be attributed to  $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W})$ ,  $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$ ,  $\nu_{\text{as}}(\text{Ge}-\text{O}_a)$ ,  $\nu_{\text{as}}(\text{W}-\text{O}_i)$  stretching vibration peak. The characteristic absorption peak at  $429\text{ cm}^{-1}$  belongs to  $\nu_{\text{as}}(\text{Ln}-\text{O}_l)$ . No characteristic absorption peak of 1, 2, 4-Triazole was found in the spectrum which is consistent with the results of X-ray single crystal diffraction of **1-Ln**.



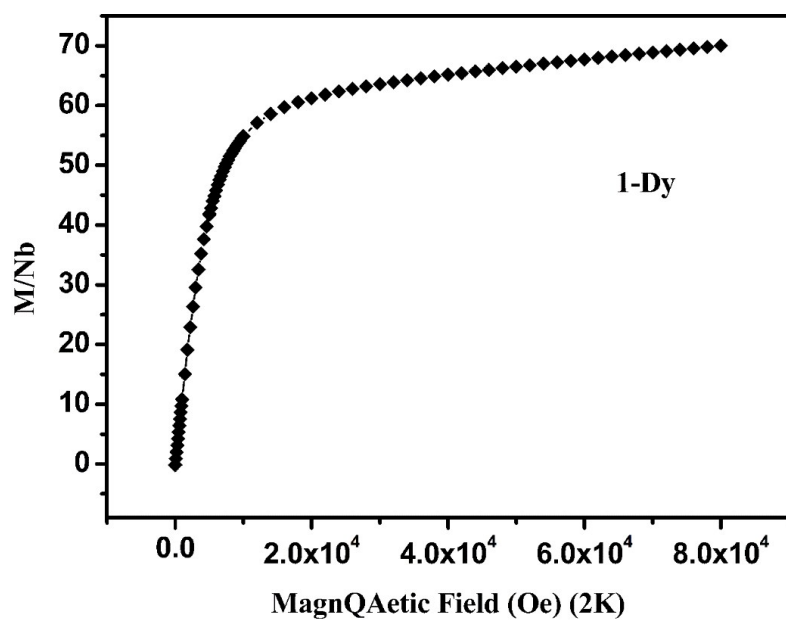
**Fig. S3** 3D extended inorganic POM framework of **1-Tb** constructed from 14-Ln-containing  $[(\text{Tb}_{14}(\text{H}_2\text{O})\text{W}_4(\text{OH})\text{O}_{14})(\text{WO}_4)_4(\text{GeW}_{10}\text{O}_{38})_6]^{43-}$  polyanions linked by  $\text{Na}^+$  cations. Polyhedron color: LnOx (x=7-9), green; WO6 and WO4, red; GeO4, yellow. Atom color:  $\text{Na}^+$ , cyan.



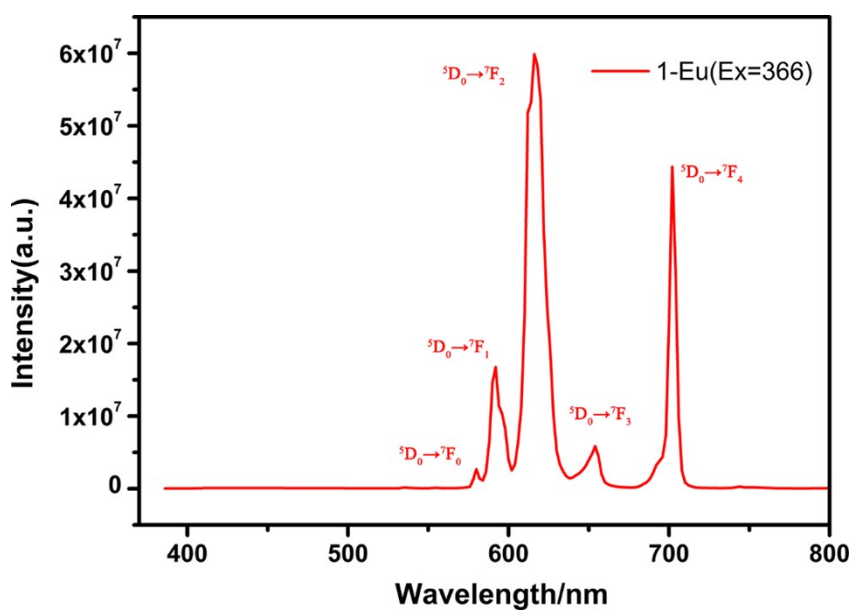
**Fig. S4** Coordination modes of Tb13(a), Tb14(b), Tb15(c), Tb16(d). The occupancy rates: 1 for Tb13; 0.246 for Tb14; 0.299 for Tb15 and 0.371 for Tb16. O atoms connect with Tb14: 0.333 for O260; 0.536 for O252. O atoms connect with Tb15: 0.5 for O259; 0.75 for O258. O atoms connect with Tb16: 0.5 for O266; 0.676 for O229.



**Fig. S5** Polyhedron presentation of four  $\{Ln_4\}$  clusters in **1-Tb**. The central atoms are Tb13(a), Tb14(b), Tb15(c), Tb16(d) separately.



**Fig. S6** The field dependence of magnetization at 2.0K for **1-Dy**



**Fig. S7** The Emission spectrum of **1-Eu**.

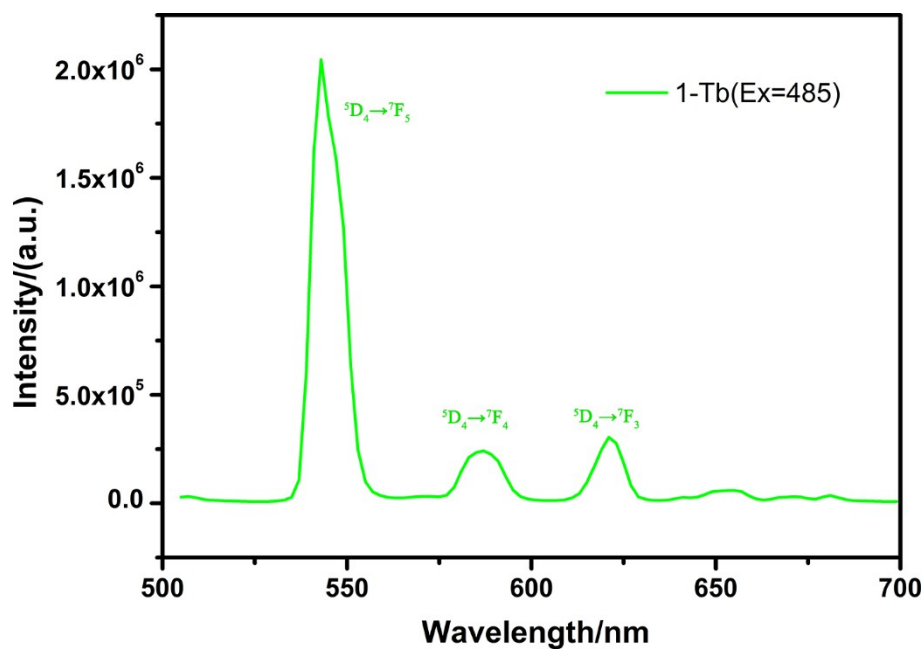


Fig. S8 The Emission spectrum of 1-Tb.

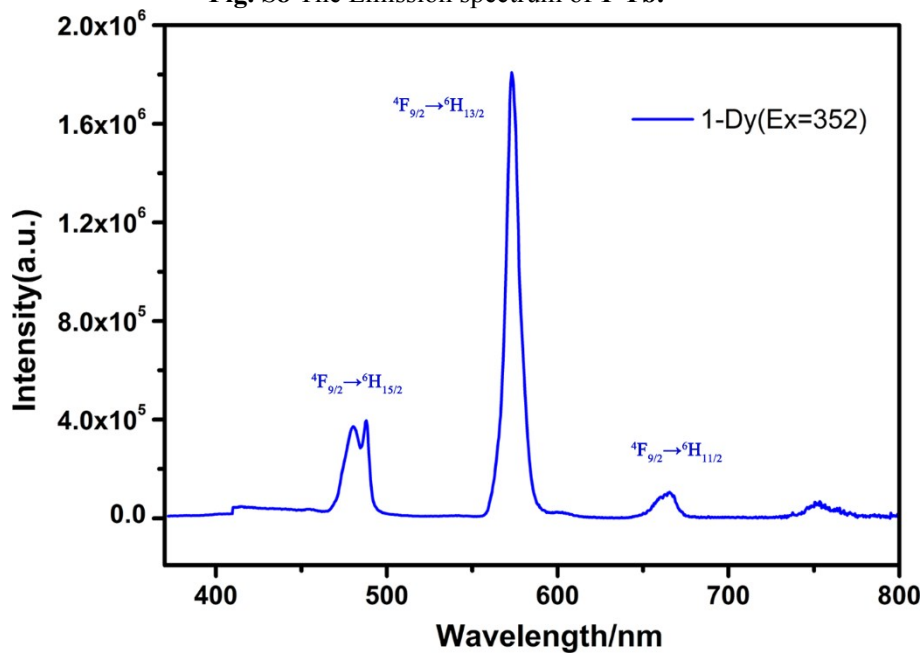


Fig. S9 The Emission spectra of 1-Dy.

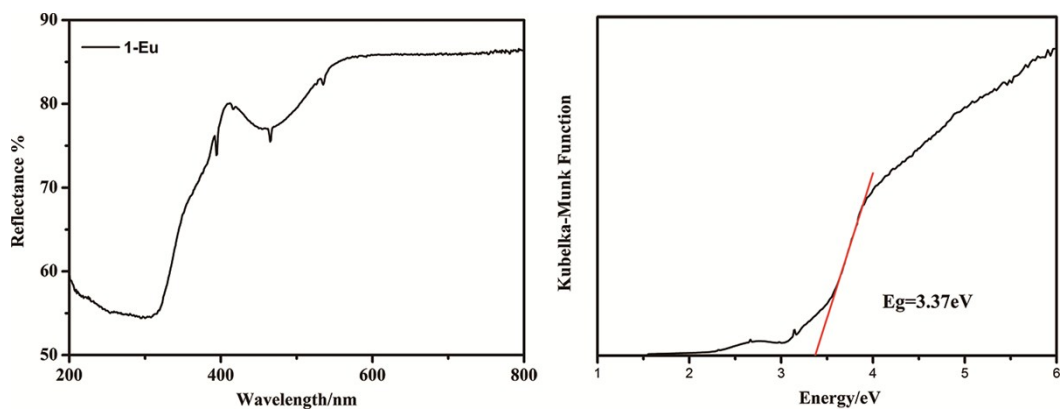


Fig. S10 The UV spectra of 1-Eu.

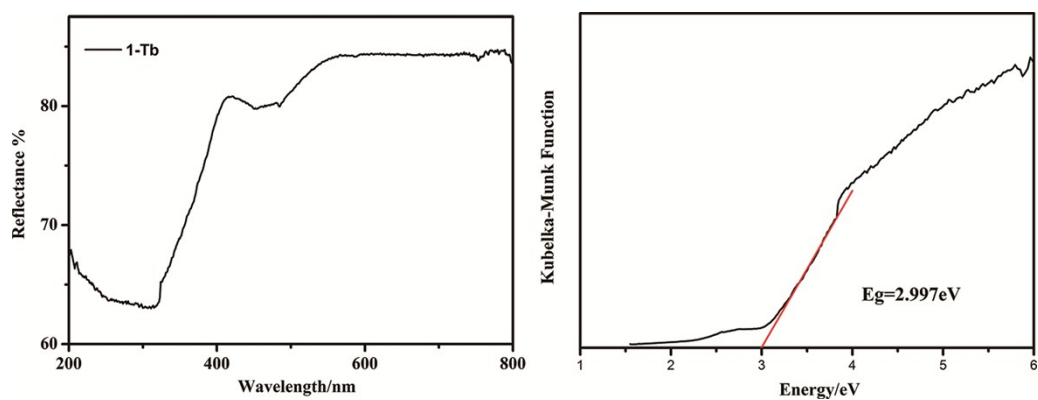


Fig. S11 The UV spectra of 1-Tb.

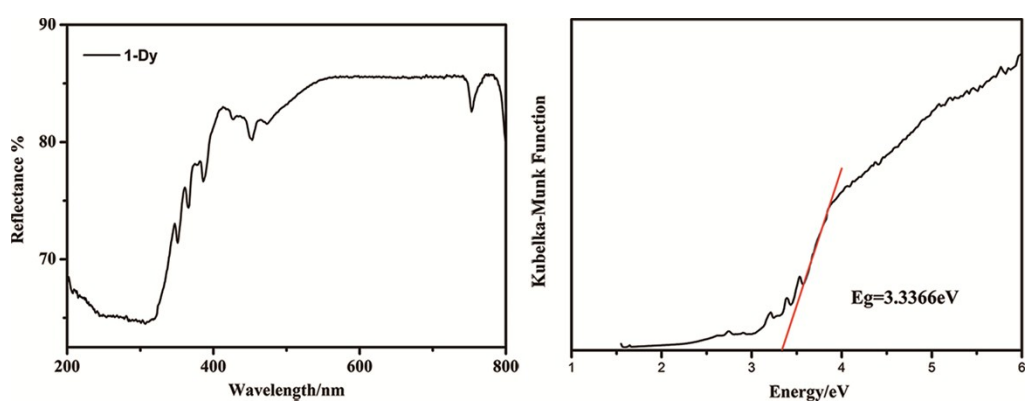


Fig. S12 The UV spectra of 1-Dy.

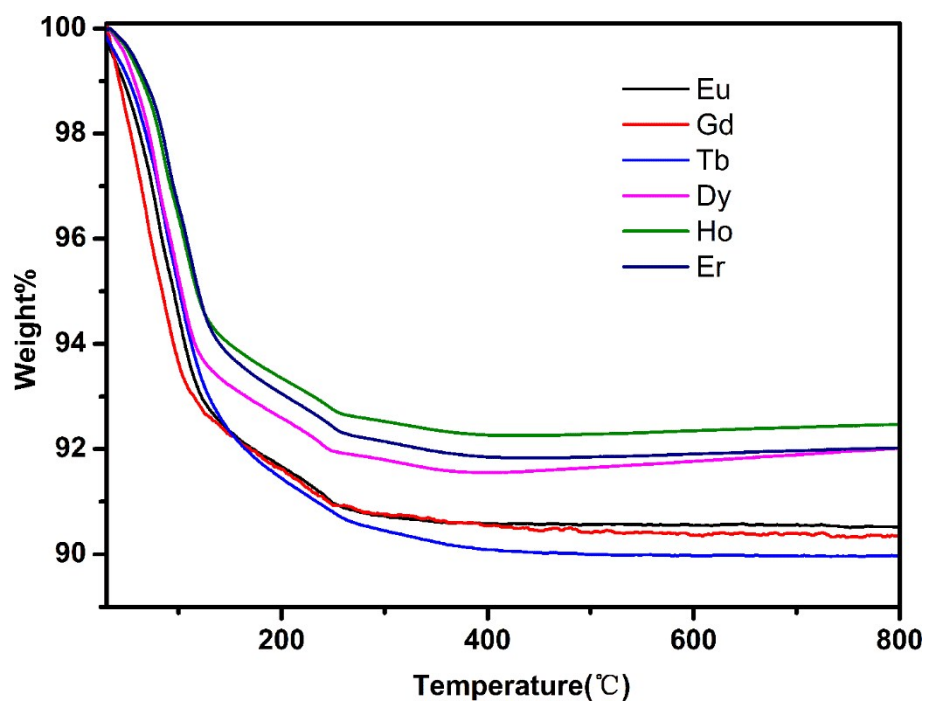


Fig. S13 TG curves of 1-Ln(Ln= Eu, Gd, Tb, Dy, Ho, Er).



Thermal gravimetric analyses (TGA) of **1-Tb 1-Eu, 1-Dy, 1-Ho, 1-Gd** and **1-Er** were performed under nitrogen atmosphere in the range 25–800 °C to determine their thermal stabilities. There are two-step weight loss for **1-Tb 1-Eu, 1-Dy, 1-Ho, 1-Gd** and **1-Er**, The first weight loss of 7.40% for **1-Tb** from 30-143 °C (Calcd 7.27% for **1-Tb**), 7.45% for **1-Eu** from 30-140 °C(Calcd 7.30 for **1-Eu**), 7.43% for **1-Dy** from 30-195 °C(Calcd 7.25 for **1-Dy**), 7.33% for **1-Ho** from 30-260 °C(Calcd 7.24 for **1-Ho**), 7.60% for **1-Gd** from 30 to 145 °C(Calcd 7.24 for **1-Ho**) and 7.69% for **1-Er** from 30 to 255 °C(Calcd 7.23 for **1-Er**), corresponding to the release of the 86 free water molecules.

## 5. Bond Valence Sum (BVS) Calculations

**Table S2. The bond valence sum calculations of the Ge W and Tb atoms.**

Tb1	3.22537	3	W61	6.15062	6	W25	6.23589	6
Tb2	2.91926	3	W39	6.173288	6	W6	6.14155	6
Tb3	3.16726	3	W45	6.046399	6	W50	6.17552	6
Tb4	2.85644	3	W29	6.298684	6	W28	6.22644	6
Tb5	3.28569	3	W32	6.177681	6	W5	6.20738	6
Tb6	3.02822	3	W38	6.016474	6	W7	5.95575	6
Tb7	2.86858	3	W30	6.054441	6	W36	6.16004	6
Tb8	3.07293	3	W9	6.328659	6	W14	6.22466	6
Tb9	3.07699	3	W19	6.201339	6	W2	6.03393	6
Tb10	3.17791	3	W26	6.234096	6	W47	6.05541	6
Tb11	3.29753	3	W44	6.047284	6	W1	6.43806	6
Tb12	2.96728	3	W42	6.307285	6	W17	6.38583	6
W52	6.06452	6	W48	6.117444	6	W62	6.09920	6
W3	6.24671	6	W51	6.000363	6	W60	5.98674	6
W56	6.08454	6	W53	6.161695	6	W24	6.16702	6
W7	5.97925	6	W55	6.295501	6	W15	6.03913	6
W13	6.33741	6	W31	6.40835	6	W40	6.32341	6
Ge1	3.90751	4	W23	6.164773	6	W12	6.12705	6
Ge2	3.98425	4	W27	5.989095	6	W22	6.11682	6
Ge3	3.77117	4	W35	5.946711	6	W10	6.14384	6
Ge4	3.89958	4	W68	5.994846	6	W18	6.19059	6
Ge5	3.92682	4	W67	6.44767	6	W58	6.00264	6
Ge6	3.85143	4	W65	6.23065	6	W37	6.14612	6
W47	5.922005	6	W54	6.422254	6	W43	6.14007	6
W21	6.106503	6	W20	6.268944	6	W34	5.99548	6
W8	6.01731	6	W59	6.319434	6	W33	6.09833	6
W46	6.18505	6	W64	6.314052	6	W11	6.28735	6
W66	6.38806	6	W57	6.11954	6			

**Table S3. The bond valence sum calculations of the O in W<sub>4</sub>O<sub>15</sub> unit.**

Atom Code	Bond Valence	Valence state	Atom Code	Bond Valence	Valence state	Atom Code	Bond Valence	Valence state
O229	2.02308	2	O170	2.06891	2	O234	2.12200	2
O251	1.89416	2	O259	1.31644	1	O218	2.15372	2
O252	2.18363	2	O219	2.1032	2	O263	2.08857	2
O260	1.23193	1	O258	2.23258	2	O254	2.16927	2
O266	1.00001	1	O236	2.19046	2	O264	1.92936	2
O262	2.13082	2	O212	2.10367	2	O248	2.14212	2

**Table S4. The bond valence sum calculations of the O in 4 WO<sub>4</sub> units and the atom O255 connect with Tb13.**

O183	1.940658	2	O246	1.90727	2	O232	2.09264	2
O109	1.932778	2	O197	1.61345	2	O244	1.61345	2
O242	2.05877	2	O216	2.00336	2	O240	1.95952	2
O150	1.70307	2	O194	2.08200	2	O155	1.94694	2
O113	2.01734	2	O250	1.93470	2			
O251	1.89416	2	O123	1.91985	2	O255	0.19335	0

1. J. B. Peng, X. J. Kong, Q. C. Zhang, M. Orendac, J. Prokleska, Y. P. Ren, L. S. Long, Z. Zheng and L. S. Zheng, *J. Am. Chem. Soc.*, 2014, **136**, 17938-17941.