Supporting Information for *Acta Phys. -Chim. Sin.* doi: 10.3866/PKU.WHXB201912007

稀土-钛氧簇合物 $EuTi_6$，$EuTi_7$ 和 La_2Ti_{14} 的可控合成

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Controlled Synthesis of Lanthanide-titanium Oxo Clusters $EuTi_6$, $EuTi_7$ and La_2Ti_{14}

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Computational details.

1. The valence states of metal ions in **1**–**4** are analyzed by means of bond valance sum (BVS) calculations.

Table S1 The valence states of metal ions in compounds 1–4.

1		2		3		4	
Metal ions	Valence	Metal ions	Valence	Metal ions	Valence	Metal ions	Valence
Eu1	3.13	Eu1	3.09	Eu1	2.99	La1	2.93
Ti1	4.17	Ti1	3.72	Ti1	4.14	Ti1	4.24
Ti2	4.19	Ti2	3.72	Ti2	4.18	Ti2	4.39
Ti3	4.19	Ti3	4.19	Ti3	4.19	Ti3	4.15
Ti4	4.15	Ti4	4.09	Ti4	4.20	Ti4	4.18
Ti5	4.18	Ti5	4.07	Ti5	4.18	Ti5	4.14
Ti6	4.16	Ti6	4.13	Ti6	4.22	Ti6	4.13
		Ti7	3.75	Ti7	4.21	Ti7	4.04

$$\text{Valence} = \sum \exp((R_0 - R)/B_0)$$

2. Band gap value is calculated by UV-Vis diffuse reflectance spectra.

Plot $E = h\nu$ ($h\nu = 1240.824/\lambda$) as the X-axis, $(\alpha h\nu)^2$ ($\alpha = 2.303A \times 10^9$) as the Y-axis, and then draw two tangent lines to that curve. The intersection of these two tangent lines is the forbidden band width value.

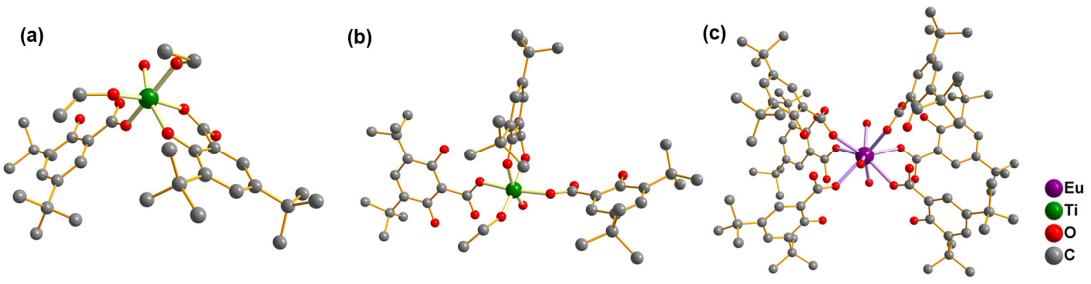

Fig. S1 The coordination configurations of Ti^{4+} and Eu^{3+} for compound 1.

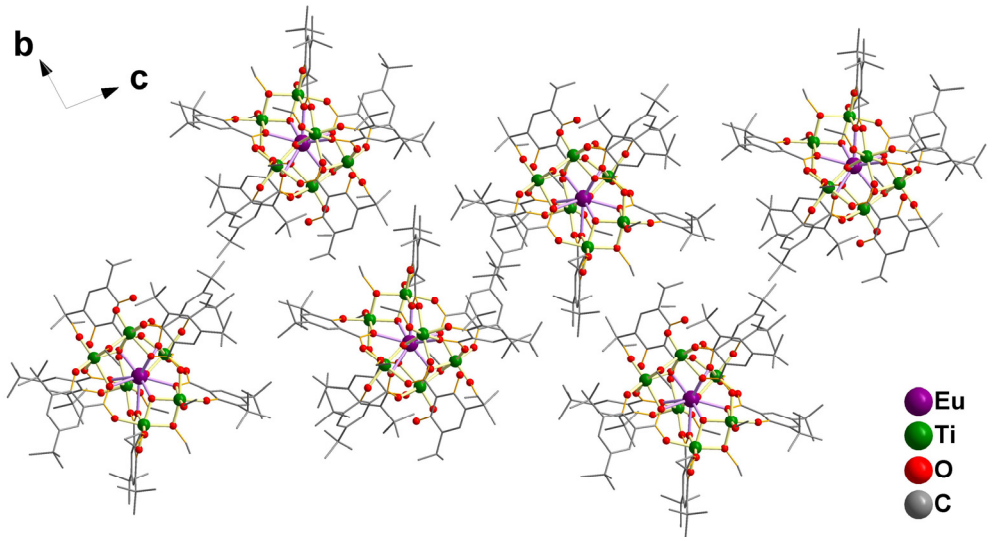

Fig. S2 The packing structure of compound 1 in *a*-axis.

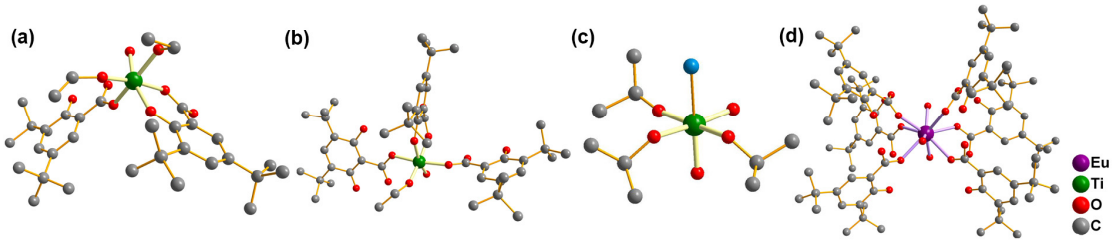

Fig. S3 The coordination configurations of Ti^{4+} and Eu^{3+} for compound 2.

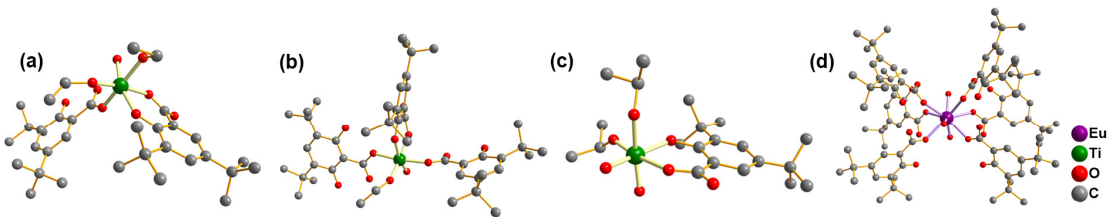

Fig. S4 The coordination configurations of Ti^{4+} and Eu^{3+} for compound 3.

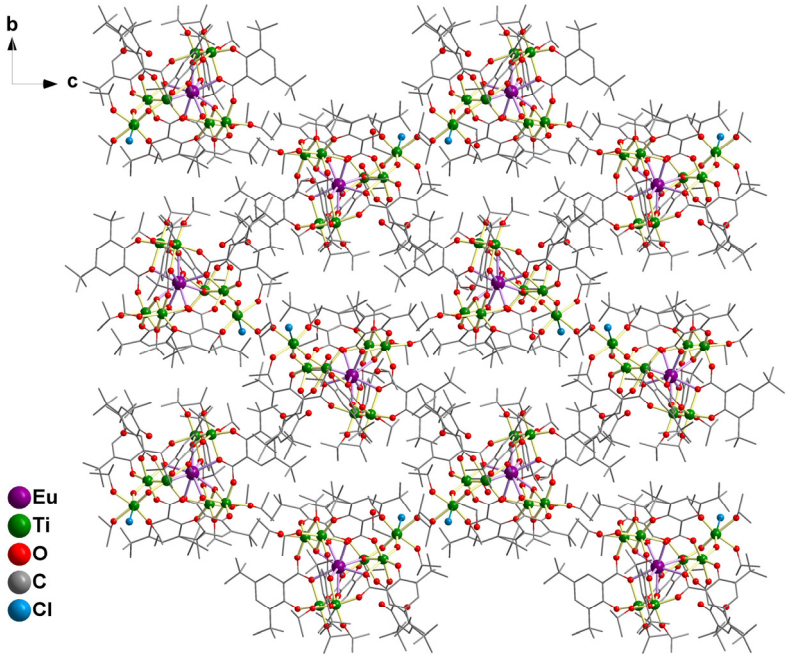

Fig. S5 The packing structure of compound 2 in *a*-axis.

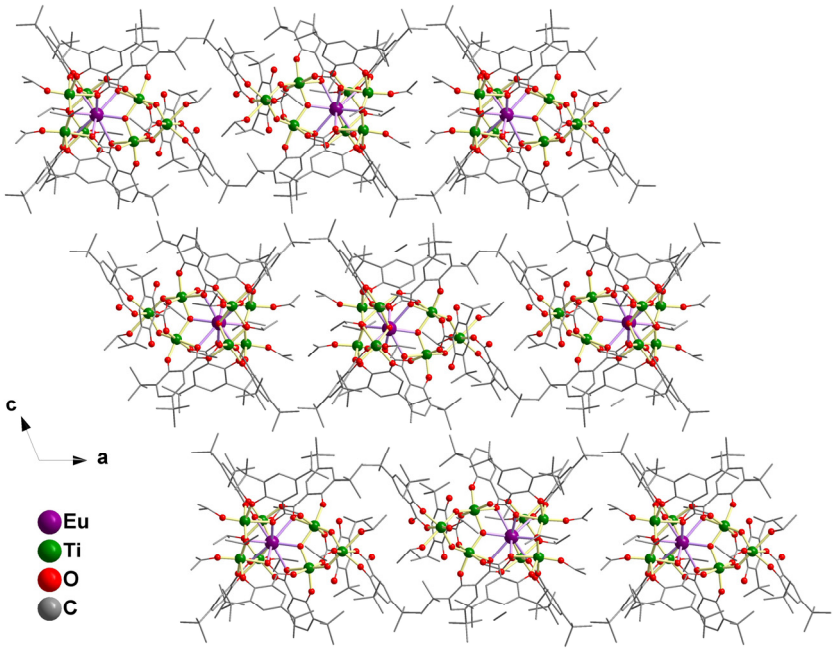

Fig. S6 The packing structure of compound 3 in *b*-axis.

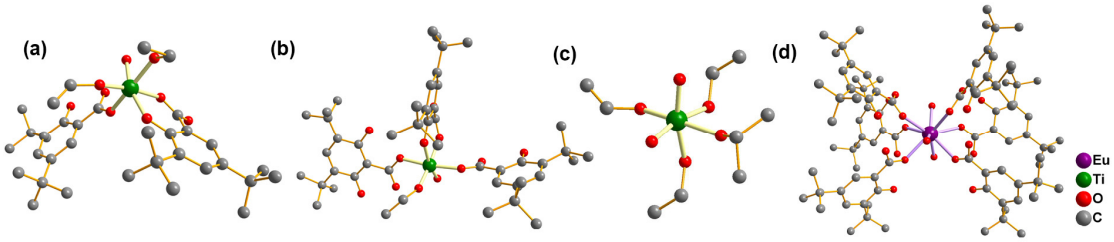

Fig. S7 The coordination configurations of Ti^{4+} and La^{3+} for compound 4.

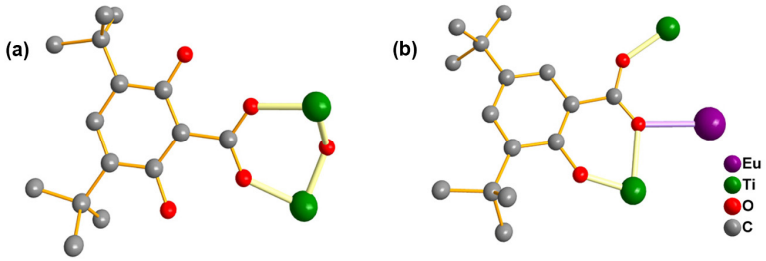

Fig. S8 The coordination configurations of ligand.

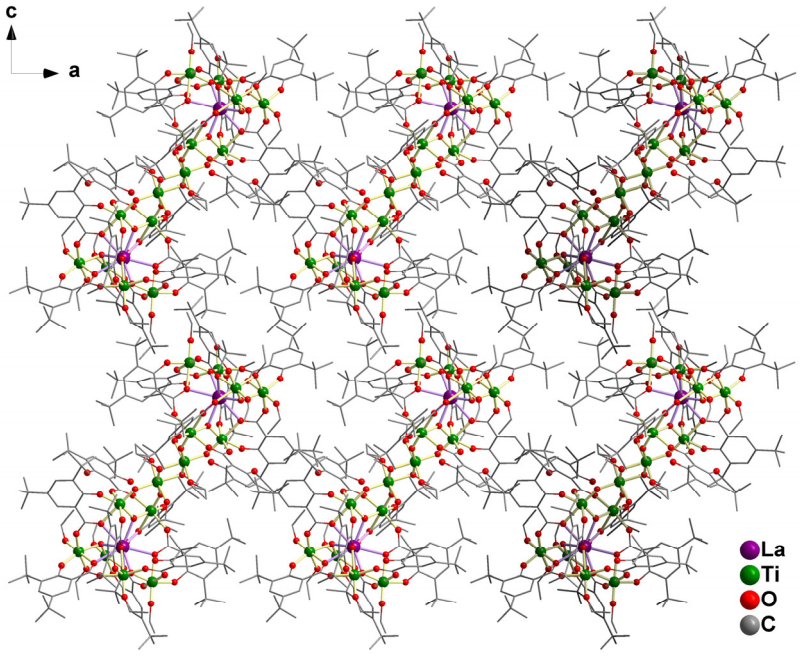

Fig. S9 The packing structure of compound 4 in *b*-axis.

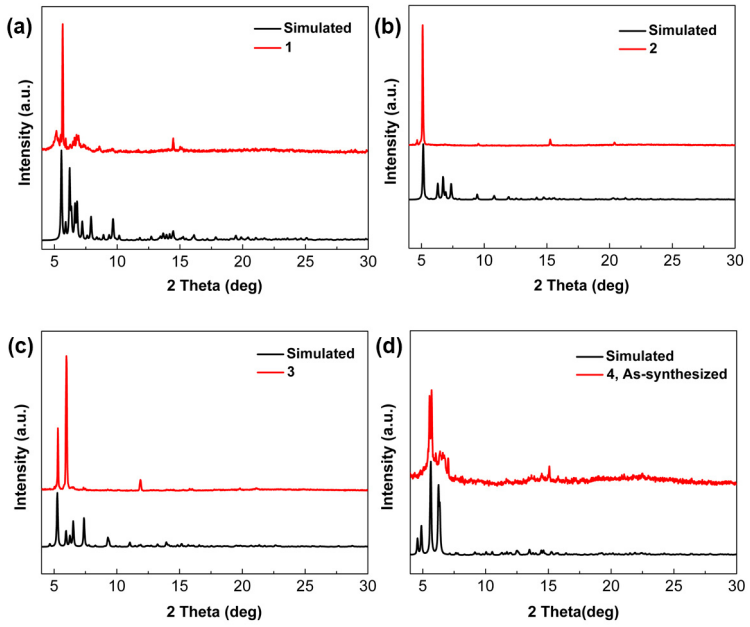

Fig. S10 PXRD curves of compounds 1-4 as-synthesized (red) and simulated (black).

Photocatalytic H_2 generation

Photocatalytic hydrogen production tests were carried out in a quartz reaction cell connected to a closed gas circulation and evacuation system. 20 mg photocatalyst was dispersed into an aqueous methanol solution (20 mL, 10%) in a closed gas circulation system. The suspension was degassed thoroughly and then irradiated by a 300 W Xe lamp (300–800 nm). The gas products were detected by online GC with a thermal conductivity detector (TCD) to quantify the amount of H_2 produced.

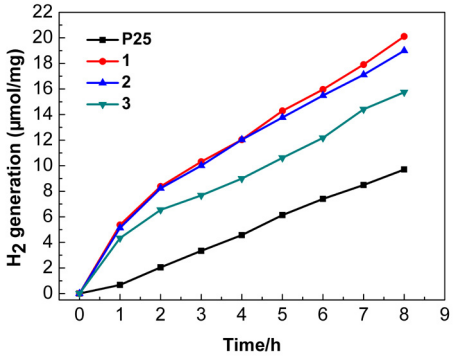

Fig. S11 The amount of hydrogen evolution of compounds 1, 2, 3 and P25 at different times.

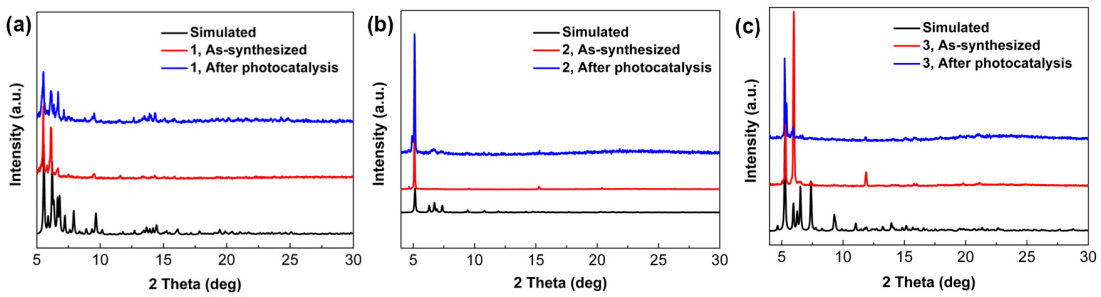

Fig. S12 PXRD of compounds 1–3 as-synthesized (red), simulated (black) and after 8h illumination by UV light (blue).

Photoelectrochemistry Studies

Preparations of ITO electrodes.

The working electrodes were prepared as follows: 2 mg catalyst, 650 μL of ultra-pure water, 250 μL of HO^{i}Pr (isopropanol) and 100 μL of Nafion were added to a 5 mL bottle. The mixture was stirred by ultrasonic machine for 20 min. 40 μL of the mixture was coated on half of an ITO glass slice (1 cm × 2 cm) and dried at room temperature.

Charge-separation efficiency.

The catalyst photoanode, a platinum foil cathode, and silver chloride electrode as reference electrode were placed in a single-compartment cell filled with 20 mL of aqueous solution containing 0.5 M NaOAc/HOAc electrolyte at pH 5.0. The transient short circuit photocurrents of **1**−**3** were carried out with the on-off cycle's illumination with a mercury lamp (350–450 nm), with applying an external bias of +0.6 V (*vs*. NHE).

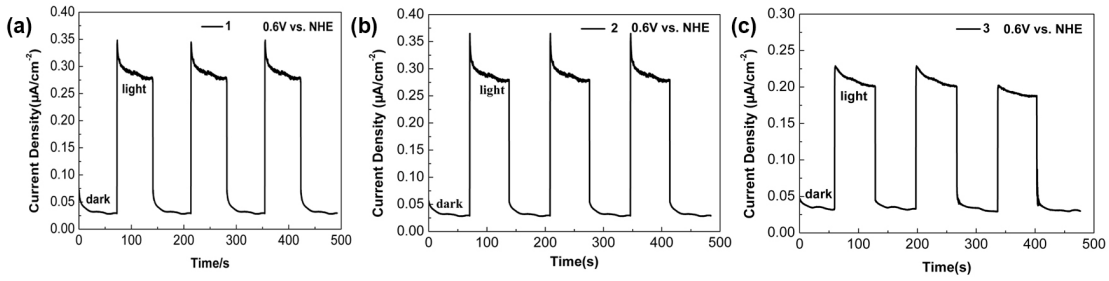

Fig. S13 Transient short-circuits photocurrent of compounds 1, 2 and 3 with light or no light in 0.5 mol·L^{-1} NaAc/HAc buffer at pH 5.0.

Table S2 Crystal data for compounds 1-4.

Complex	$EuTi_6$ (**1**)	$EuTi_7$ (**2**)	$EuTi_7$ (**3**)	La_2Ti_{14} (**4**)
formula	$C_{123}H_{187}EuO_{33}Ti_6$	$C_{141}H_{230}ClEuO_{38}Ti_7$	$C_{150}H_{235}EuO_{39}Ti_7$	$C_{280}H_{430}La_2O_{78}Ti_{14}$
FM	2633.07	3055.95	3149.63	5992.63
T/K	173	100	100	100
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	14.3095(6)	19.7031(4)	31.8797(7)	18.8577 (11)
b/Å	15.4662(5)	30.6200 (4)	15.4388(3)	20.3186 (11)
c/Å	32.2330(9)	26.0850(4)	36.0246(10)	20.8614 (12)
α/°	95.492(2)	90	90	83.085(4)
β/°	95.271(3)	102.088(2)	112.229(3)	87.178(4)
γ/°	99.469(3)	90	90	72.223(5)
V/Å^3	6961.9(4)	15388.3(5)	16413.0(7)	8280.0(8)
Z	2	4	4	1
*D*c/g cm^{-3}	1.256	1.319	1.275	1.194
μ/mm^{-1}	6.51	6.55	6.02	5.19
θ/°	2.9–54.8	3.7–70.1	3.8–55.5	3.6–63.4
obsd reflns	13396	15981	14624	18174
$R_1[I>2\sigma(I)]$[a]	0.082	0.092	0.082	0.092
wR_2(All data)[b]	0.240	0.281	0.248	0.300

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$. 1 Å = 0.1 nm.

Table S3 Selected bond distances and bond angles of compound 1.

Bond	Dis (Å)	Bond	Angle (°)
Eu1—O3	2.313 (5)	Ti2—O1—Ti1	104.5 (2)
Eu1—O2	2.338 (5)	Ti2—O1—Eu1	114.9 (3)
Eu1—O1	2.352 (5)	Ti1—O1—Eu1	114.8 (2)
Eu1—O13	2.540 (5)	Ti4—O2—Ti3	125.4 (3)
Eu1—O7	2.541 (5)	Ti4—O2—Eu1	116.0 (3)
Eu1—O16	2.551 (5)	Ti3—O2—Eu1	114.6 (2)
Eu1—O10	2.553 (5)	Ti5—O3—Ti6	102.4 (2)
Eu1—O22	2.573 (5)	Ti5—O3—Eu1	114.1 (3)
Eu1—O4	2.577 (5)	Ti6—O3—Eu1	115.0 (2)
Ti1—O27	1.769 (6)	Ti2—O4—Eu1	97.2 (2)
Ti1—O9	1.869 (5)	Ti1—O7—Eu1	98.9 (2)
Ti1—O1	1.903 (5)	Ti6—O10—Eu1	99.05 (18)
Ti1—O25	2.000 (5)	Ti5—O13—Eu1	97.1 (2)
Ti1—O14	2.011 (5)	Ti3—O16—Eu1	99.2 (2)
Ti1—O7	2.175 (6)	Ti4—O22—Eu1	98.44 (19)
Ti2—O26	1.766 (7)	Ti2—O25—Ti1	97.4 (2)
Ti2—O6	1.871 (6)	Ti6—O30—Ti5	97.2 (2)
Ti2—O1	1.888 (5)	Ti4—O19	2.042 (6)
Ti2—O25	1.991 (6)	Ti4—O22	2.159 (6)
Ti2—O11	2.010 (6)	Ti5—O31	1.761 (5)
Ti2—O4	2.189 (6)	Ti5—O15	1.873 (6)
Ti3—O28	1.736 (6)	Ti5—O3	1.912 (5)
Ti3—O18	1.903 (6)	Ti5—O23	2.001 (6)
Ti3—O2	1.910 (6)	Ti5—O30	2.004 (5)
Ti3—O5	1.978 (5)	Ti5—O13	2.187 (5)
Ti3—O20	2.049 (6)	Ti6—O32	1.757 (6)
Ti3—O16	2.141 (6)	Ti6—O12	1.897 (6)
Ti4—O29	1.775 (6)	Ti6—O3	1.919 (5)
Ti4—O24	1.884 (5)	Ti6—O30	1.975 (6)
Ti4—O2	1.890 (5)	Ti6—O17	2.026 (6)
Ti4—O8	1.997 (6)	Ti6—O10	2.133 (5)

Table S4 Selected bond distances and bond angles of compound 2.

Bond	Dis (Å)	Bond	Angle (°)
Eu1—O2	2.316 (3)	Ti2—O1—Ti1	104.24 (17)
Eu1—O3	2.334 (3)	Ti2—O1—Eu1	115.18 (19)
Eu1—O1	2.362 (4)	Ti1—O1—Eu1	116.4 (2)
Eu1—O16	2.525 (4)	Ti3—O2—Ti4	102.26 (16)
Eu1—O22	2.525 (4)	Ti3—O2—Eu1	114.08 (15)
Eu1—O13	2.544 (4)	Ti4—O2—Eu1	115.00 (16)
Eu1—O7	2.558 (3)	Ti6—O3— Ti5	124.00 (19)
Eu1—O19	2.594 (3)	Ti6 —O3— Eu1	117.30 (18)
Eu1—O10	2.616 (4)	Ti5 —O3 —Eu1	115.03 (17)
Ti1—O9	1.890 (5)	Ti6— O4— Ti7	136.3 (2)
Ti1—O1	1.913 (4)	Ti5— O5— Ti7	136.9 (3)
Ti1—O15	2.001 (4)	Ti2 —O7 —Eu1	97.78 (13)
Ti1—O27	2.003 (5)	Ti1 —O10 —Eu1	99.26 (15)
Ti1—O29	2.058 (4)	Ti4 —O13— Eu1	99.10 (14)
Ti1—O10	2.147 (4)	Ti3—O16—Eu1	98.33 (14)
Ti2—O8	1.849 (5)	Ti6—O19—Eu1	98.06(13)
Ti2—O1	1.881 (5)	Ti5—O22—Eu1	98.86 (14)
Ti2—O12	2.000 (4)	Ti2—O27—Ti1	96.77 (18)
Ti2—O27	2.003 (5)	Ti3—O30—Ti4	96.40 (16)
Ti2—O28	2.157 (4)	Ti5—O3	1.922 (4)
Ti2—O7	2.198 (4)	Ti5—O11	1.976 (4)
Ti3—O32	1.786 (4)	Ti5—O24	2.032 (4)
Ti3—O17	1.889 (4)	Ti5—O22	2.202 (4)
Ti3—O2	1.918 (3)	Ti6—O4	1.760 (4)
Ti3—O30	2.011 (4)	Ti6—O20	1.883 (4)
Ti3—O21	2.014 (4)	Ti6—O3	1.892 (4)
Ti3—O16	2.168 (4)	Ti6—O6	1.992 (4)
Ti4—O31	1.787 (4)	Ti6—O25	2.066 (4)
Ti4—O14	1.901 (4)	Ti6—O19	2.182 (4)
Ti4—O2	1.941 (4)	Ti7—O5	1.827 (4)
Ti4—O30	2.019 (4)	Ti7—O33	1.831 (6)
Ti4—O18	2.027 (4)	Ti7—O4	1.883 (5)
Ti4—O13	2.171 (4)	Ti7—O34	2.133 (5)
Ti5—O5	1.786 (4)	Ti7—O35	2.161 (5)
Ti5—O23	1.871 (4)	Ti7—Cl1	2.467 (2)

Table S5 Selected bond distances and bond angles of compound 3.

Bond	Dis (Å)	Bond	Angle (º)
Eu1—O1	2.320 (4)	Ti2—O1—Ti1	102.95 (18)
Eu1—O3	2.358 (4)	Ti2—O1—Eu1	115.04 (16)
Eu1—O2	2.359 (4)	Ti1—O1—Eu1	114.43 (18)
Eu1—O10	2.550 (4)	Ti4—O2—Ti3	104.6 (2)
Eu1—O7	2.557 (3)	Ti4—O2—Eu1	116.04 (18)
Eu1—O16	2.576 (4)	Ti3—O2—Eu1	115.46 (15)
Eu1—O19	2.577 (4)	Ti6—O3—Ti5	124.4 (2)
Eu1—O22	2.584 (4)	Ti6—O3—Eu1	116.60 (16)
Eu1—O13	2.591 (3)	Ti5—O3—Eu1	115.87 (19)
Ti1—O31	1.775 (4)	Ti5—O4—Ti7	143.5 (2)
Ti1—O11	1.884 (4)	Ti6—O5—Ti7	142.3 (2)
Ti1—O1	1.916 (4)	Ti2—O7—Eu1	98.52 (13)
Ti1—O30	1.997 (4)	Ti1—O10—Eu1	98.36 (14)
Ti1—O14	1.999 (4)	Ti5—O13—Eu1	97.97 (14)
Ti1—O10	2.153 (4)	Ti6—O16—Eu1	98.00 (13)
Ti2—O32	1.761 (4)	Ti3—O19—Eu1	98.00 (13)
Ti2—O8	1.869 (4)	Ti3—O33—Ti4	96.41 (18)
Ti2—O1	1.915 (3)	Ti1—O30—Ti2	96.83 (17)
Ti2—O17	2.009 (4)	Ti4—O22—Eu1	98.13 (15)
Ti2—O30	2.010 (4)	Ti5—O3	1.893 (3)
Ti2—O7	2.155 (4)	Ti5—O20	1.990 (4)
Ti3—O34	1.762 (4)	Ti5—O27	2.068 (4)
Ti3—O18	1.870 (4)	Ti5—O13	2.182 (4)
Ti3—O2	1.894 (4)	Ti6—O5	1.787 (4)
Ti3—O33	1.997 (4)	Ti6—O15	1.865 (4)
Ti3—O9	2.018 (4)	Ti6—O3	1.874 (4)
Ti3—O19	2.188 (4)	Ti6—O21	1.962 (4)
Ti4—O35	1.768 (4)	Ti6—O28	2.027 (4)
Ti4—O2	1.875 (4)	Ti6—O16	2.196 (4)
Ti4—O23	1.877 (4)	Ti7—O36	1.758 (5)
Ti4—O33	2.002 (4)	Ti7—O5	1.831 (4)
Ti4—O6	2.008 (4)	Ti7—O4	1.888 (4)
Ti4—O22	2.169 (4)	Ti7—O24	1.912 (5)
Ti5—O4	1.750 (4)	Ti7—O37	2.181 (5)
Ti5—O12	1.872 (4)	Ti7—O25	2.223 (5)

Table S6 Selected bond distances and bond angles of compound 4.

Bond	Dis (Å)	Bond	Angle (°)
La1—O2	2.408 (5)	Ti1—O1—Ti2	122.8 (3)
La1—O3	2.424 (5)	Ti1—O1—La1	114.4 (2)
La1—O1	2.468 (5)	Ti2—O1—La1	114.8 (2)
La1—O16	2.596 (5)	Ti3—O2—Ti4	103.9 (3)
La1—O25	2.609 (5)	Ti3—O2—La1	114.5 (2)
La1—O22	2.611 (5)	Ti4—O2—La1	114.5 (2)
La1—O10	2.612 (5)	Ti6—O3—Ti5	127.2 (3)
La1—O19	2.618 (5)	Ti6—O3—La1	115.0 (2)
La1—O7	2.637 (5)	Ti5—O3—La1	114.0 (2)
Ti1—O30	1.764 (6)	Ti5—O4—Ti7	141.5 (3)
Ti1—O1	1.871 (6)	Ti6—O5—Ti7	141.4 (3)
Ti1—O11	1.880 (8)	Ti2—O7—La1	98.9 (2)
Ti1—O13	1.998 (9)	Ti1—O10—La1	98.9 (2)
Ti1—O20	1.999 (7)	Ti4—O16—La1	98.7 (2)
Ti1—O10	2.195 (5)	Ti3—O32—Ti4	98.0 (3)
Ti2—O31	1.739 (6)	Ti5—O25—La1	98.49 (17)
Ti2—O8	1.869 (7)	Ti6—O22—La1	98.76 (19)
Ti2—O1	1.873 (6)	Ti3—O19—La1	98.3 (2)
Ti2—O17	1.966 (8)	Ti7—O37—Ti7^{i}	104.8 (2)
Ti2—O12	1.982 (10)	Ti2—O7	2.180 (5)
Ti3—O33	1.763 (7)	Ti5—O9	1.990 (5)
Ti3—O18	1.884 (6)	Ti5—O29	2.053 (5)
Ti3—O2	1.912 (5)	Ti5—O25	2.188 (5)
Ti3—O32	1.996 (6)	Ti6—O5	1.764 (5)
Ti3—O24	2.017 (6)	Ti6—O23	1.885 (5)
Ti3—O19	2.181 (6)	Ti6—O3	1.891 (5)
Ti4—O34	1.752 (7)	Ti6—O6	1.995 (5)
Ti4—O15	1.874 (6)	Ti6—O28	2.056 (5)
Ti4—O2	1.914 (5)	Ti6—O22	2.186 (5)
Ti4—O32	1.997 (6)	Ti7—O4	1.860 (5)
Ti4—O21	2.022 (5)	Ti7—O5	1.871 (5)
Ti4—O16	2.193 (6)	Ti7—O36	1.893 (6)
Ti5—O4	1.752 (5)	Ti7—O37	1.997 (5)
Ti5—O26	1.878 (5)	Ti7—O37^{i}	2.015 (6)
Ti5—O3	1.908 (5)	Ti7—O35	2.121 (6)

References

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