

Luminescent Tetra-nuclear Lanthanide-titanium-organic Compound Obtained by the Mixed-ligand^①

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ABSTRACT A new heterometallic lanthanide-titanium-organic compound: $[\text{Eu}_2\text{Ti}_2(\text{dip})_6(\text{dig})_2(\text{H}_3\text{O})_2]$ solvent (**1**, dip = diphenylglycolic acid, dig = diglycolic acid) has been synthesized under solvothermal conditions. Compound **1** contains a tetra-nuclear $\{\text{Eu}_2\text{Ti}_2\}$ unit with the mixed ligands of dip and dig. Compound **1** displays intense red luminescence. Furthermore, the IR, PXRD, UV-vis and TGA spectra were also studied.

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1 INTRODUCTION

Crystalline polyoxo-titanium clusters have attracted growing interest in recent years due to their rich structural chemistry and broad applications^[1–8]. To date, functional ligands such as amino alcohol, oxime, phosphonate, carboxylate, and derivatives have been successfully used in the synthesis of a large number of polyoxo-titanium clusters. Two notable examples are $\{\text{Ti}_{42}\}$ and $\{\text{Ti}_{52}\}$ clusters. The former shows a fullerene-like polyoxotitanium cage, which is constructed from platonic $\{\text{Ti}_{12}\}$ icosahedron and an Archimedean $\{\text{Ti}_{30}\}$ icosidodecahedron^[9], while the latter contains a 3.6 nm oxo cluster with a boat-like interlayer structure. $\{\text{Ti}_{52}\}$ shows the largest size and highest efficiency for photocatalytic H_2 production in the family of titanium-oxo clusters^[10]. In a comprehensive review, Fang et al. summarized the synthetic strategies, diverse structures and tunable properties of reported polyoxo-titanium clusters^[11].

The incorporation of other metal ions and Ti^{4+} ion into the same framework leads to new types of heterometallic coordination metal cluster. To date, Ti-Cu, Ti-Mn, Ti-Co, Ti-Zn and Ti-Ag clusters with different nuclearity and topology have been reported^[12–18]. For example, in the heterometal-oxo $\{\text{Ag}_2\text{Ti}_{10}\}$ and $\{\text{Ag}_4\text{Ti}_8\}$ clusters, the doped Ag atoms are surrounded by the Ti–O core and exposed to the cluster surface, and displayed good photocurrent response in the visible region^[19]. Wright and co-workers reported a

heterometallic $\{\text{Ti}_{18}\text{Mn}\}$ cage, which has a C_3 symmetric core structure containing an interstitial tetrahedral Mn ion and can be used as a single-source precursor to such a composite material of $\alpha\text{-Mn}_2\text{O}_3/\text{TiO}_2$ ^[20].

The family for heterometallic Ti-Ln clusters is also known. For example, Long and co-workers reported a luminescent lanthanide-titanium oxo cluster of $\{\text{Eu}_2\text{Ti}_4\}$. This compound can be used as the luminescence sensor for nitrobenzene detection^[21]. In the past decades, we have focused on the hydro/solvothermal synthesis of new heterometallic clusters. Recently, we successfully synthesized a luminescent Ti-Ln-organic compound constructed by tetra-nuclear Ti-Ln building units and diphenylglycolic acid^[22]. If two different types of ligands of diphenylglycolic and diglycolic acids are involved in the same reaction system, the cooperativity of mixed ligands can be used to understand the effect of ligands on the frameworks and may provide new opportunities to obtain interesting Ti-Ln compound. Herein, we report the syntheses, structures and properties of a new Ti-Ln coordination compound: $[\text{Eu}_2\text{Ti}_2(\text{dip})_6(\text{dig})_2(\text{H}_3\text{O})_2]$ solvent (dip = diphenylglycolic acid, dig = diglycolic acid) (**1**). Colorless prismatic crystals of **1** were obtained by solvothermal reactions of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, TiOSO_4 , diphenylglycolic acid, diglycolic acid, NaBr and NaOH in the mixed solvents of $\text{C}_2\text{H}_5\text{OH}$ and H_2O at 170 °C for 6 days. Compound **1** contains tetra-nuclear Ti-Eu building units.

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2 EXPERIMENTAL

2.1 Materials and measurements

All chemicals were purchased commercially and used without further purification. Powder X-ray diffraction (PXRD) data were obtained by placing the picked crystals onto the flat sample holders using a Philips PW3040/60 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The Fourier transform infrared (FT-IR) spectra (KBr pellets) were recorded on a Nicolet NEXUS670 spectrometer. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C analyzer at a heating rate of $10 \text{ }^\circ\text{C/min}$ under an air atmosphere. UV-vis spectra on solid samples were recorded using a Cary 5000 UV-vis spectrometer. Photoluminescence analyses were performed on an Edinburgh Instrument FLS920 fluorescence spectrometer.

2.2 Synthesis of **1**

A mixture of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1 mmol, 0.44 g), TiOSO_4 (0.5 mmol, 0.08 g), diphenylglycolic acid (1 mmol, 0.23 g), diglycolic acid (1 mmol, 0.13 g), and NaBr (1 mmol, 0.10 g) was added to the mixed solvents of $\text{C}_2\text{H}_5\text{OH}$ (6 mL) and H_2O

(3 mL). The resulting mixture was stirred and slowly added with NaOH (pHs = 4~5), and sealed in a 30 mL Teflon-lined stainless-steel autoclave, heated at $100 \text{ }^\circ\text{C}$ for 6 days, and then cooled to room temperature. Colorless block crystals of **1** (10% yield based on Ti) were obtained. The IR bands (cm^{-1}) for **1**: 3418 (vs), 3055 (w), 1638 (vs), 1491 (w), 1442 (m), 1316 (vs), 1219 (w), 1177 (w), 1079 (w), 1044 (vs), 1002 (w), 912 (w), 828 (s), 780 (s), 716 (m), 688 (w), 605 (w) (Fig. S1).

2.3 Crystal structure determination

The intensity data were collected on a Bruker APEX II with graphite-monochromatic $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. All absorption corrections were performed using the multiscan program. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with the SHELXS-97 and SHELXL-97 programs^[23]. All atoms except H were refined anisotropically. Some ambiguous solvent molecules reside in those regions of diffuse electron density, and they were treated by the PLATON/SQUEEZE procedure. Selected bond lengths of compounds **1** are listed in Table 1.

Table 1. Selected Bond Lengths (\AA) for **1**

Bond	Dist.	Bond	Dist.
Eu(1)–O(2)	2.318(4)	Eu(2)–O(8)	2.506(4)
Eu(1)–O(3)	2.403(4)	Eu(2)–O(21)	2.525(4)
Eu(1)–O(W2)	2.425(4)	Eu(2)–O(15)	2.577(4)
Eu(1)–O(8)	2.429(4)	Ti(1)–O(12)	1.836(4)
Eu(1)–O(28)	2.439(4)	Ti(1)–O(11)	1.837(4)
Eu(1)–O(5)	2.495(4)	Ti(1)–O(10)	1.846(4)
Eu(1)–O(6)	2.524(4)	Ti(1)–O(5)	2.062(4)
Eu(1)–O(9)	2.539(4)	Ti(1)–O(6)	2.082(4)
Eu(1)–O(7)	2.555(4)	Ti(1)–O(7)	2.098(4)
Eu(2)–O(16)	2.325(4)	Ti(2)–O(20)	1.835(4)
Eu(2)–O(W1)	2.407(4)	Ti(2)–O(18)	1.843(4)
Eu(2)–O(9)	2.416(4)	Ti(2)–O(17)	1.851(4)
Eu(2)–O(14)	2.421(4)	Ti(2)–O(21)	2.079(4)
Eu(2)–O(25)	2.448(4)	Ti(2)–O(19)	2.082(4)
Eu(2)–O(19)	2.485(4)	Ti(2)–O(15)	2.088(4)

3 RESULTS AND DISCUSSION

3.1 Crystal structure of the title complex

Single-crystal X-ray analysis reveals that compound **1** crystallizes in the monoclinic space group $P2_1/c$ ^[24]. The asymmetric unit of **1** contains two Eu^{3+} ions, two Ti^{4+} ions, six dip ligands, two dig ligands and two coordinated water molecules. Two Eu^{3+} ions are nine-coordinated with a tri-capped trigonal-prism coordination geometry: four O

atoms from four dip ligands, four O atoms from two dig ligands and one coordinated water molecule. Two Ti^{4+} ions are six-coordinated with distorted octahedral coordination environment: six oxygen atoms from three dip ligands. The Eu–O distances range from 2.318(4) to 2.577(4) \AA , and the Ti–O distances from 1.835(4) to 2.098(4) \AA (Table 1). The distances are similar to the reported compounds^[21]. Two Eu^{3+} and Ti^{4+} ions are linked by six dip and two dig ligands to give a tetra-nuclear $[\text{Eu}_2\text{Ti}_2(\text{dip})_6(\text{dig})_2][\text{Eu}_2\text{Ti}_2]$ unit (Fig. 1). The

dip and dig ligands show two and one coordination modes, respectively. The dip ligand shows a “V” shaped configuration. Remarkably, compound **1** is different to the recently

reported tetra-nuclear $[\text{Tb}_2\text{Ti}_2(\mu_3\text{-O})_2]$ cluster core constructed by $\mu_3\text{-O}$ ions and dip ligands^[22].

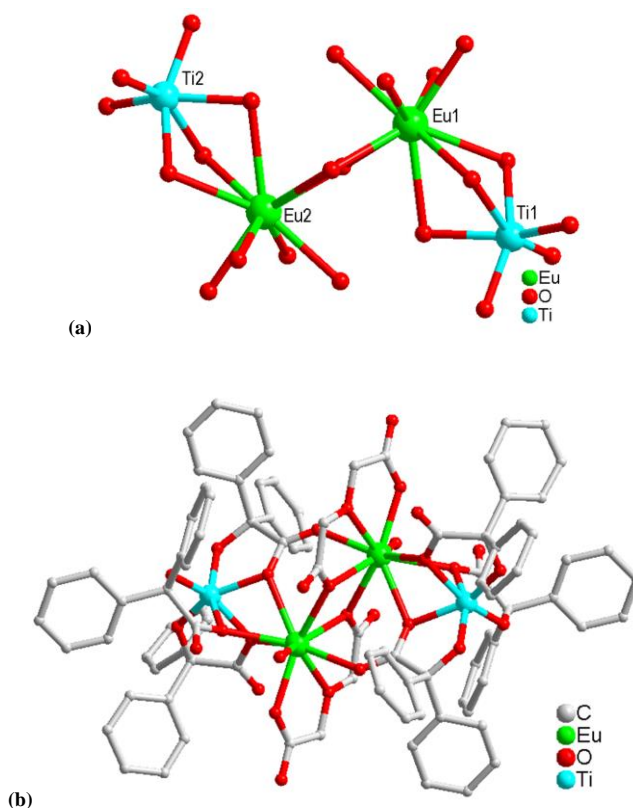


Fig. 1. (a) Tetra-nuclear $\{\text{Eu}_2\text{Ti}_2\}$ core in **1**. (b) Coordination environment of $\{\text{Eu}_2\text{Ti}_2\}$ core in **1**

3.2 Physical characterization

The experimental PXRD patterns of compound **1** match well with the simulated PXRD patterns of **1**, and the difference in reflection intensities between the simulated and experimental patterns was due to the variation in the preferred orientation of the powder sample during collection of the experimental PXRD data (Fig. S2). The thermal behavior of **1** was examined by TGA in a dry air atmosphere from 30 to 800 °C. These compounds show a similar thermal behavior and undergo two steps of weight loss. The lattice-water molecules were gradually lost in the temperature range of 30–240 °C for **1**. Above this temperature, the weight loss is due to the decomposition of organic ligands (Fig. S3). The UV-vis absorption spectra of compound **1** show strong absorption bands at about 270 nm (Fig. 2). Compound **1** displays strong red luminescence when excited at 396 nm. Four emission bands at 579, 592, 618, 649 and 693 nm correspond to the characteristic $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 0\sim 4$) transition of the Eu^{3+} ion (Fig. 3, S4, S5). The absence of any ligand fluorescence in the emission spectra of **1** indicates that the

intramolecular energy transfer from the coordinated ligand to the Eu^{3+} ions is efficient. The lifetime for $^5\text{D}_0 \rightarrow ^7\text{F}_2$ is 3.58 ns (Fig. S6).

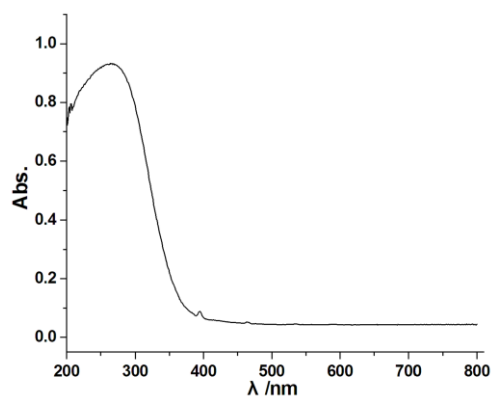


Fig. 2. UV-Vis spectra of compound **1**

4 CONCLUSION

In summary, a new luminescent tetra-nuclear lanthanide-titanium-organic compound has been successfully obtained under solvothermal conditions based on the mixed ligands of

diphenylglycolic and diglycolic acids. Compound **1** emits red light. The successful isolation of compound **1** demonstrates that the mixed-ligand approach is effective to synthesize

versatile heterometallic Ti-Ln cluster with different structures and interesting properties.

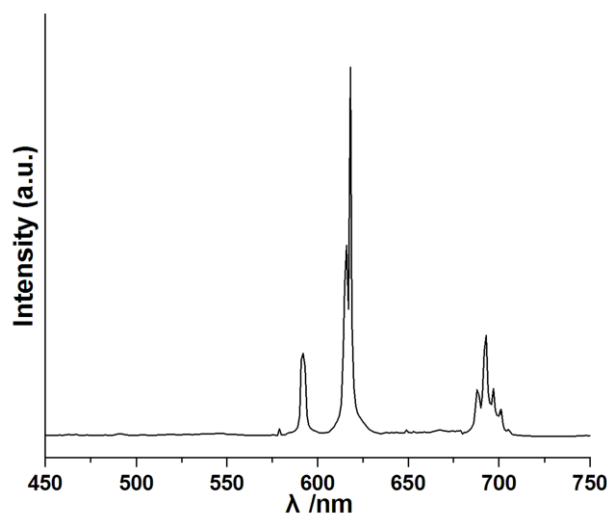


Fig. 3. Emission spectra of **1** in the solid state at room temperature

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