A lanthanide-titanium oxo cluster-polymer composite: From clusters to fluorescent ink

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Fluorescent ink has become an effective anti-counterfeiting material to prevent counterfeiters from making and selling fake products [1–4]. From its practical application, an ideal fluorescent ink should be environmentally friendly, have high stability and good viscosity, and exhibit excellent luminescent performance. To obtain such fluorescent inks, different fluorescent materials, such as carbon dots [5–7], lanthanide-doped compounds [8–10], inorganic semiconductor complexes [11–13], organic dyes [14–16], metal-organic frameworks [17–19], lanthanide coordination compounds [20,21] and cluster compounds [22,23], have been used to prepare fluorescent inks. Although these fluorescent materials have their own advantages as fluorescent inks, they also have their own disadvantages. For example, organic dyes used as fluorescent inks often encounter the problems of aggregation-induced quenching and small Stokes shifts [14–16], while carbon dots suffer from unclear structures, and concerns about the reproducibility of carbon dots have affected their widespread use [5,6]. Therefore, it is necessary to develop fluorescent ink with excellent performance.

Lanthanide-titanium oxo clusters (LTOCs) are regarded as promising luminescent materials. The formation of Ln–Ti–O species can not only effectively increase the rigidity of LTOCs, but also greatly reduce the energy required for Ln³⁺ photoluminescence sensitization [24–26]. Additionally, their structural stability and luminescence performance can be greatly improved by introducing strongly electron-donating carboxylic acid ligands into LTOCs [27,28]. However, the poor solubility and film-forming properties of LTOCs make them difficult to use directly as fluorescent inks. In previous work, we have demonstrated that the preparation of LTOC-polymer composites (LTOCPs) through covalently

linking LTOCs to polymers can effectively improve the mechanical properties of the LTOCs, without noticeably changing their luminescent performance [29]. Distinctly, if the LTOCs in the LTOCPs display excellent luminescent properties, the LTOCPs as fluorescent ink exhibit excellent performance. Along this line, we use amino-containing LTOCs of Eu₂Ti₄-NH₂ (Eu₂Ti₄-NH₂ = [Eu₂Ti₄(μ₂-O)₂(μ₃-O)₄(phen)₂(tbza)₉(paza)]·8H₂O (1), Htbza = 4-*tert*-butylbenzoic acid, Hpaza = 4-amino-benzoate acid, phen = 1,10-phenanthroline) and PEG (PEG = methoxy-poly(ethylene glycol) succinimidyl carbonate, 2000 g mol^{−1}) to prepare the LTOCP of Eu₂Ti₄-NH₂@PEG (2) through an amidation reaction activated by *N*-hydroxy succinimide (NHS). Significantly, 2 not only exhibits excellent fluorescent properties, but also has good solubility in a wider range of solvents and excellent film-forming properties.

Cluster 1 was prepared through solvothermal reaction of 4-*tert*-butylbenzoate (Htbza, 0.36 mmol, 64 mg), 4-aminobenzoic acid (Hpaza, 0.04 mmol, 6 mg), Eu(OAc)₃·4H₂O (0.065 mmol, 26 mg), 1,10-phenanthroline monohydrate (phen, 0.1 mmol, 20 mg) and Ti(O^{*i*}Pr)₄ (0.08 mmol, 24 μL). The purity of bulk sample 1 was demonstrated by the similarity between experimental powder X-ray diffraction (PXRD) patterns and simulated patterns (Fig. S1). Single-crystal XRD shows that the Eu₂Ti₄-NH₂ cluster belongs to the monoclinic crystal *P*2₁/*c* space group and consists of two Eu³⁺, four Ti⁴⁺, two μ₂-O, four μ₃-O, two phen, nine tbza[−], one paza[−] and four CH₃CN (Table S1). Structurally, the cluster core of the [Eu₂Ti₄O₆]¹⁰⁺ in 1 is the same as that reported previously in the cluster of Eu₂Ti₄(μ₂-O)₂(μ₃-O)₄(phen)₂(tbza)₁₀·4CH₃CN [30], that is, each Eu³⁺ connects to two Ti⁴⁺ ions through one μ₃-O, forming a triangular [EuTi₂(μ₃-O)]⁹⁺ unit, which is further connected by a pair of μ₂-O and μ₃-

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O bridges to generate a cluster core of $[\text{Eu}_2\text{Ti}_4\text{O}_6]^{10+}$. Among the six metal atoms in the cluster core of $[\text{Eu}_2\text{Ti}_4\text{O}_6]^{10+}$, four Ti^{4+} ions form a parallelogram, and two Eu^{3+} are located on either side of the parallelogram (Fig. 1a). Solidifying the cluster core of $[\text{Eu}_2\text{Ti}_4\text{O}_6]^{10+}$ by two phen ligands, nine tbza[−] ligands and one paza[−] ligand generates **1** (Fig. 1b). Each Eu^{3+} ion is coordinated by two N atoms from one *o*-phenanthroline ligand, four O atoms from four benzoic acid ligands and two μ_3 -O atoms in a distorted triangular dodecahedral geometry. Each Ti^{4+} ion is coordinated by two μ_3 -O, one μ_2 -O, and three O from three different benzoic acid ligands in a distorted octahedral geometry. Guest acetonitrile molecules are within the gaps of the cluster molecules through C–H···O interactions (Fig. 1c). The Ti–O and Eu–O bond distances are 1.817(3)–2.114(3) Å and 2.334(2)–2.426(3) Å, respectively. The Eu–N bond distances are 2.540(3)–2.635(4) Å (Table S2). The bond distances of Ti–O, Eu–O and Eu–N are comparable to those reported in $\text{Eu}_2\text{Ti}_4(\mu_2\text{-O})_2(\mu_3\text{-O})_4(\text{phen})_2(\text{tbza})_{10}4\text{CH}_3\text{CN}$ [30]. Although single-crystal structural analysis reveals that there are four guest acetonitrile molecules in **1**, both the elemental (Supplementary information) and thermogravimetric (TG) analyses (Fig. S2) indicate that there are eight guest H_2O molecules in **1**. This discrepancy is due to the guest acetonitrile molecules between the clusters being easily lost at room temperature.

Because **1** contains a paza[−] ligand, an amidation reaction activated by *N*-hydroxysuccinimide (NHS) was performed through the reaction of **1** with PEG in toluene solution. Finishing the crosslink reaction between the amine group of **1** and succinimidyl carbonate group of PEG generates the powder of **2**. Fig. 2 illustrates the ^1H nuclear magnetic resonance (^1H NMR) spectra of **1**, **2**, and PEG. The chemical shift peaks of the aromatic group (7–9 ppm) and *tert*-butyl (1.3 ppm) in the spectrum of **1** and the chemical shift signals of the $\text{CH}_2\text{--CH}_2\text{--O}$ (3.6 ppm) in PEG appeared in the spectrum of **2**; in particular, the chemical signal for the proton of the NH_2 group (4.7 ppm) in **1** completely disappeared in the spectrum of **2**, distinctly indicating that the amino group in paza[−] in **1** completely reacted with PEG through NHS activation.

To demonstrate the integrity of **1** in **2**, energy dispersive X-ray spectroscopy (EDS) and element mapping were conducted in **2** (Fig. S3). The element mapping of **2** indicates that both the europium and titanium in **2** are uniformly distributed. The EDS result reveals that the Eu/Ti atomic ratio in **2** is 1/1.94. This value is very close to the 2/4 ratio obtained from the crystal structure of **1**.

Figure 1 The metal core structure of **1** (a) and its coordination structure (b); the schematic diagram of the acetonitrile molecules in the single crystal structure in **1** (c). Color code: purple for Eu, green for Ti, red for O, gray for C, blue for N. Hydrogen atoms are omitted for clarity.

Figure 2 ^1H NMR (500 MHz, CDCl_3) spectra for PEG, **1** and **2**.

These results imply that **1** is intact in **2**. According to the elemental analysis of **2**, the molecular weight of **2** is approximately 4400 g mol^{-1} . Thus, the average ratio of **1** to PEG in **2** is 1/1, consistent with the TG analysis of **2** (Fig. S2) and the crystal structure of **1**.

Figure 3 The excitation and emission spectra of **1** (a) and **2** (b) in the solid state. The insets are photographs of **1** and **2** under 312 nm UV irradiation (top) and in daylight (bottom). (c) Luminescence spectra of **2** in different solutions. (d) SEM images of **1** (left) and **2** (right) on the silicon substrate when the toluene solution was evaporated. (e) Images of **2** dissolved in different solvents under 312-nm UV irradiation. MeCN: methyl cyanide, PhMe: toluene, THF: tetrahydrofuran, AcOEt: ethyl acetate, MeOH: methanol, DMF: *N,N*-dimethylformamide, EtOH: ethanol.

Fig. 3 shows the excitation and emission spectra of **1** and **2** in the solid-state. The peaks mainly appear in the ultraviolet (UV) region from 240 to 400 nm, and the most intense signals in the excitation spectra for **1** and **2** are at 294 and 299 nm, respectively. As shown in Fig. 3a, b, both **1** and **2** display five Eu³⁺ emission peaks. The five Eu³⁺ emission peaks are at 577–581 nm ($^5D_0 \rightarrow ^7F_0$), 585–602 nm ($^5D_0 \rightarrow ^7F_1$), 609–629 nm ($^5D_0 \rightarrow ^7F_2$), 649–658 nm ($^5D_0 \rightarrow ^7F_3$), and 685–708 nm ($^5D_0 \rightarrow ^7F_4$), while those for **2** are at 577–581 nm ($^5D_0 \rightarrow ^7F_0$), 586–601 nm ($^5D_0 \rightarrow ^7F_1$), 608–628 nm ($^5D_0 \rightarrow ^7F_2$),

647–658 nm ($^5D_0 \rightarrow ^7F_3$), and 680–708 nm ($^5D_0 \rightarrow ^7F_4$). The similarity between **1** and **2** in the excitation and emission spectra further suggests that **1** maintains its structural integrity in **2**.

Table S3 shows the luminescence lifetime and quantum yield (QY) of **1** and **2** in the solid-state and solution, respectively. The solid-state lifetime and QY for **1** are 1643 μs and 50.91%, respectively, while those for **2** are 1370 μs and 30.69%, respectively (Figs S4 and S5). The difference in luminescence performance between **1** and **2** is attributed to the nonradiative vibration from PEG in **2**

Figure 4 Images of the logos inkjet printed by **2**. The top images show input patterns. The middle images show the printed output patterns under daylight. The bottom images show printed output patterns under 312 nm UV light. (a) College of Chemistry and Chemical Engineering, Xiamen University logo; (b) Fuzhou University logo; (c) Xiamen University logo; (d) Xiamen University 100 centenary celebration logo.

[31]. Significantly, in comparison with **1**, not only the solubility of **2** in polar solvents but also its adhesion to the substrate is obviously improved. As shown in Fig. 3, **2** can be dissolved in toluene, CH_2Cl_2 , ethanol, ethyl acetate, etc., although the QYs of **2** in different solutions change on a case-by-case basis due to the solvent effects (Fig. 3c and Table S3). Moreover, scanning electron microscopy (SEM) images show that **1** exhibits obvious agglomerations and cracks, while **2** displays good film forming characteristics and adhesion to the substrate upon evaporation of the toluene solution (Fig. 3d).

Because **2** is stable in solution and has excellent film forming characteristics and strong fluorescence intensity, it was used to prepare the precursor ink for inkjet printing in a mixed solution of ethanol and ethylene glycol ($v/v = 4/1$). Such an ink is transparent and stable in the ambient environment, and the solvents have low toxicity, which is of great importance for industrialization. As shown in Fig. 4, when ink of **2** was used to print computer-designed logos on indium tin oxide (ITO) glass through a high-precision printer, the printed logos were transparent and invisible under ambient conditions

(middle) due to the excellent film forming properties of **2**. Upon irradiation with UV light, the printed logos exhibited bright red photoluminescence observed by the naked eye (bottom). It was mentioned that the anti-counterfeiting labels printed by **2** remain bright after being exposed to the air for six months, which is comparable to that observed in CdS quantum dots (QDs) [11] and indicates that **2** has high light stability [5,17] (Fig. S6). Therefore, **2**, as a fluorescent ink, has both good concealment and effectiveness. These results indicate that the prepared materials hold promising potential in applications such as anticounterfeiting labels.

In summary, a lanthanide-polymer composite of **2** was, for the first time, prepared through the NHS-activated amidation reaction of **1** with PEG. Analysis of the ^1H NMR and SEM of **1** and **2** indicate that **1** is intact within **2**. Significantly, when **2** was used to prepare the precursor ink for inkjet printing in a mixed solution of ethanol and ethylene glycol ($v/v = 4/1$), the printed logos displayed good concealment and effectiveness due to their excellent solubility in polar solvents, film formation and luminescent performance. Thus, **2**, as a fluorescent ink, has the

advantages of environmental friendliness, stability, good viscosity and excellent luminescent performance.

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Author contributions Long L initiated and coordinated the research. Deng Y synthesized the materials, conducted the measurements and wrote the manuscript draft. Zheng X printed the anticounterfeiting labels. Zheng H conducted the fluorescence test. Xu H conducted the SCXRD characterization and solved the crystallographic structure. Li F, Long L, Zheng L participated in the discussion and analysis of the data.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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稀土钛氧簇-高分子复合材料: 从簇合物到荧光油墨

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摘要 要将荧光油墨应用于实际, 通常要求该油墨对环境友好且稳定, 并且具有良好的黏度和优异的发光性能. 本文中, 我们通过含有氨基的稀土钛氧簇 $\text{Eu}_2\text{Ti}_4\text{-NH}_2$ (**1**)与PEG (PEG = 甲氧基聚乙二醇琥珀酰亚胺碳酸酯, 2000 g mol^{-1})反应合成了稀土钛氧簇-高分子复合材料 $\text{Eu}_2\text{Ti}_4\text{-NH}_2\text{@PEG}$ (**2**). 对**2**的相关表征表明, **1**的结构在**2**之内是完整的. **1**和**2**的发光性质表明其固态量子产率分别为50.91%和30.69%. 与化合物**1**相比, **2**在极性溶剂中的溶解度和成膜性能大大提高. 当使用**2**的乙醇/乙二醇($v/v = 4/1$)混合溶液用于喷墨打印的墨水时, 喷墨打印的标签显示出良好的隐蔽性和有效性.