

Article



# **Composites Based on Polylactide Doped with Amorphous Europium(III) Complex as Perspective Thermosensitive Luminescent Materials**

Andrey A. Knyazev <sup>1,\*</sup>, Aleksandr S. Krupin <sup>1</sup> and Yuriy G. Galyametdinov <sup>1,2</sup>

- <sup>1</sup> Department of Physical and Colloid Chemistry, Kazan National Research Technological University, 68 Karl Marx, Kazan 420015, Russia
- <sup>2</sup> Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS, 10/7 Sibirsky Tract, Kazan 420029, Russia
- \* Correspondence: knjazev2001@mail.ru

**Abstract:** This work reports fabrication of polylactide (PLA) films doped with various additives of an amorphous Eu(III) complex. We study the temperature behavior of the luminescence intensity and lifetime of the PLA-Eu(III) composites in the range of 298–353 K and investigate the mechanism of luminescence temperature quenching. The peak relative sensitivity of the films reaches  $20.1 \% \times K^{-1}$  and exceeds the respective characteristics of all known lanthanide-containing thermosensors designed for the range of physiological temperatures. The produced films can be potential novel materials for luminescent thermosensors.

Keywords: amorphous Ln(III) complexes; polylactide; photoluminescence; thermosensors



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# 1. Introduction

Lanthanide compounds attract sustainable attention of scientists for their unique luminescent characteristics such as monochromatic luminescence bands, long emission lifetimes, and a theoretically possible 100% internal quantum efficiency [1–6]. Trivalent Ln<sup>3+</sup> ions generate narrow and intensive emission bands because of *f*-*f* electron transitions in the 4*f* layer. These ions provide a broad range of luminescence lifetimes that can be suitable for a variety of applications [7]. The ions themselves, however, have low adsorption coefficients  $\varepsilon$  (1–10 L·mol<sup>-1</sup>·cm<sup>-1</sup>). Their luminescence properties are limited by parity-forbidden *f*-*f* transitions [8]. According to the literature data, a solution to this problem is to synthesize Ln(III) complexes with organic ligands that have considerably higher adsorption coefficients ( $\varepsilon \approx 10^3-10^4$  L·mol<sup>-1</sup>·cm<sup>-1</sup>) [7]. Such ligands play the role of an antenna, which adsorbs an excitation quantum of light and transfers it to the emission levels of the metal ion through the mechanism of internal conversion [1,5]. Efficient transfer and adsorption of energy is not the only function of such a ligand environment. The ligands encapsulate the central metal ion and isolate it from a possible impact of solvent or salt hydrate water [9,10].

Derivatives of  $\beta$ -diketones are promising chromophores with highly efficient energy transfer capabilities [11–16]. In such compounds, the ligand environment exerts a negligible impact on the electron energy levels of the metal ions because their 4*f* electrons are shielded by complete 5*s* and 5*p* shells. The resulting intraconfigurational transitions of 4*f*-*f* electrons in Ln<sup>3+</sup> ions do not change. Therefore, luminescent substances based on Ln(III) compounds can be promising components of functional materials for a variety of applications such as optoelectronic instruments, biological fluorescent markers, light emitting devices, light transforming coatings, pigments, or luminescent thermometers [5,17–21]. In this respect, amorphous Ln(III) compounds are in the focus of recent research and development attention because they can be processed into nanoscale films, which are highly demanded in modern technological applications [22]. Amorphous materials are represented by condensed phases,

which do not exhibit long-range translational (or orientational) order or periodicity, which are typical for crystals [23]. Transparency of such materials, therefore, cannot be high. They can be applied to fabrication of optical systems without photon scattering, such as luminescent materials, solar cells, or electroluminescent materials [24,25].

Luminescent thermometry [26–30] is among the most rapidly developing applications of coordination Ln(III) compounds. A variety of luminophores are known to possess temperature sensing capabilities such as organic compounds, quantum dots, metal clusters, nanoparticles doped with dyes, metal-ligand complexes, and lanthanide-containing materials [31,32]. They are potential thermosensors for applications in microelectronics, microfluidics, photonics, biology, and medicine. The working principle of the related thermometry devices is to track the temperature behavior of the following luminescence parameters: quenching time, intensity, area or position of the emission peak, the intensity ratio of the emission bands, etc. [33]. Characteristic narrow emission bands of Ln(III) ions allow a high-precision detection of temperature changes. In addition to the useful properties listed above, Ln(III) compounds possess long luminescence lifetime characteristics, so it is possible to use time-gated methods to increase their signal-to-noise ratio [34].

Applications of the majority of Ln(III) complexes in optoelectronic technologies are, however, limited by their low thermal stability and photostability. To address this issue, Ln(III) complexes are doped into various matrices: organic (polymers, liquid crystals), inorganic (glass, silicates), or sol-gel organic-inorganic hybrids [7,35]. Doping polymers with rare earth metal complexes results in a uniform distribution of dopants among polymer chains. The resulting composites demonstrate higher luminescence efficiencies, greater chemical and thermal stabilities, and enhanced mechanical properties. Such composites are, therefore, more suitable materials for producing transparent films [36–42].

In this respect, such polymers as ABS, PLA, SBS, PET, PVA, etc. are particularly attractive due to their 3D printing potential. The proposed method allows the easy deposit of luminescent composites on various surfaces. Therefore, this work discusses fabrication of thermally sensitive films based on PLA polymer and an amorphous Eu(III) complex. Polylactide (PLA) was selected as a model matrix due to its optical properties, processability, and relative cheapness. The review of literature, however, reveals only a few reports on doping polylactide with Ln(III) ions [43–45] because of its low photostability. It should be noted, however, that PLA is a non-toxic, biodegradable, and biocompatible polymer. PLA-based materials are, therefore, promising model systems for studying immobilization of lanthanide(III) compounds to further introduce them into living organisms and perform in vivo diagnostics of cancer. This work, therefore, focuses on fabrication of thermally sensitive films that consist of PLA and an amorphous Eu(III) complex. In the previous work, we demonstrated that amorphous Ln(III) compounds dissolve well in organic solvents, mix with various polymers, and distribute uniformly in a polymer matrix due to their unique structural features (anisotropy of geometry and long hydrocarbon substituents on molecular edges) [46]. It allows to avoid formation of crystalline defects, neutralize the effect of luminescence self-quenching, and obtain a more efficient mechanism of intermolecular energy transfer as compared with known analogues [47]. Such complexes are efficient light absorbers in a broad spectral range of 250–400 nm, so it is not necessary to use hard UV radiation for their excitation [48,49]. High UV absorption capacity of the complexes will also contribute to increased photostability of the PLA matrix. In addition, their melting temperatures are low and similar to the melting temperature of PLA. Therefore, the resulting composites can be easily deposited on various surfaces by conventional 3D-printing tools.

#### 2. Results and Discussion

To synthesize Eu(III) complexes, we used original  $\beta$ -diketones and 1,10-phenanthroline as the antenna ligands. Their triplet levels are known to provide an efficient energy transfer to the emitting levels of Eu<sup>3+</sup> ions [50]. The adduct of Eu(III) tris( $\beta$ -diketonate) with 1,10-phenanthroline was synthesized by the reaction shown in Figure 1. The composition and structure of the synthesized complex were confirmed by elemental analysis, mass spectrometry and IR spectroscopy. Absence of water in the first coordination sphere was confirmed by the FTIR data (Figure S1).



**Figure 1.** Synthesis of tris( $\beta$ -diketonate) Eu(III) complexes with 1,10-phenanthroline.

The synthesized compound is an amorphous powder that dissolves well in nonpolar and low-polar organic solvents due to its structural features (anisotropy of geometry and long hydrocarbon substituents on molecular edges) (Figure S2) [51]. The amorphous structure of the Eu(III) complex was confirmed by the presence of the amorphous halo in the XRD diffractogram.

The synthesized Eu(III) complex and PLA polymer were used to produce composite films with various luminophore content by the *spin-coating* method. The thickness of the films was 500 nm ( $\pm 10\%$ ). The films were virtually transparent in the visible and IR ranges (transmission over 90%) and absorbed UV light with high efficiency (Figure S3).

The absorption spectra contain peaks, which are similar to those observed in the spectra of the Eu(III) complex dissolved in hexane (Figure S4). These peaks are displaced due to the presence of PLA and the resulting change in dielectric permittivity. No absorption peaks of the complexes were identified in the 200–300 nm range because of relatively high extinction coefficients of PLA polymer. The concentration dependences of absorption can be adequately described by Bouguer–Lambert–Beer law (Figure S5).

The luminescence spectra of the films (Figure 2) contain the excitation peaks similar to the absorption ones. It may indicate that the energy absorbed by the complexes doped into the PLA matrix is predominantly consumed by emission processes. UV irradiation of the PLA film doped with the individual Eu(III) complex initiates luminescence that is typical for this Eu(III) ion.



**Figure 2.** Synthesis of tris( $\beta$ -diketonate) Eu(III) complexes with 1,10-phenanthroline.

Comparison of the emission spectra of the films with different Eu(III) content revealed that an increase in the luminophore concentration results in a nonlinear growth of its luminescence intensity, which reaches maximum at 17.5 wt% of the doped complex (Figure 3a). This effect is associated with the concentration quenching of luminescence. In turn, concentration quenching of analogous known film materials occurs at 3–10% of doped complexes [52,53]. Long hydrocarbon substituents at the edges of the synthesized complex do not favor its crystallization and allow to broadly vary the content of luminophore in polymer to achieve the maximum emission efficiency at high concentrations. As the authors demonstrated previously by studying a similar system with PMMA [47] and conjugated polymer (PVK) [46], higher content of the amorphous component in a polymer matrix does not lead to formation of larger aggregates and crystalline defects and the resulting self-quenching of luminescence as compared with analogous crystalline systems.



**Figure 3.** Concentration dependence of luminescence intensity (**a**), lifetime (**b**) and quantum efficiency  $\Phi^{\text{Ln}}$  (**c**) of PLA composite films doped with the Eu(III) complex at  $\lambda_{\text{ex}} = 340$  nm and  $\lambda_{\text{em}} = 613$  nm (marker symbols—experimental data, dashed line—approximation).

Figure 3b shows the concentration dependence of the luminescence lifetime. The luminescence quenching curve of the composites can be adequately described by a monoexponential approximation (the coefficient of determination  $R^2 > 0.995$ ). The authors suggest that this complex exhibits a single type of coordination sphere luminescence. An increase in the Eu(III) complex content results in both longer lifetime and higher intensity of luminescence that agrees with the literature data [21,54]. The authors suggest that an increased lifetime at higher luminophore concentration can be associated with changes in the symmetry of the emission of the Eu<sup>3+</sup> ion. Characterizing the mechanism of this interesting phenomenon, however, will require additional and deeper research activities.

The luminescence spectra were used to calculate the luminescence quantum efficiency of individual Eu(III) complexes and PLA films doped with Eu(III) complexes at the excita-

tion wavelength of 330 nm (Table S1 and Figure 3c), which corresponds to the excitation maximum of the  $Eu^{3+}$  ion [55,56].

A twofold increase in the relative quantum yield of luminescence was found for the composite film with 17.5 wt% of the Eu(III) complex, as compared with the solution of the individual complex. This effect is associated with a reduced non-radiative relaxation in the polymer matrix initiated by vibrational modes of solvent molecules, and an increased contribution of emission processes due to a uniform distribution of the Eu(III) complex in the composite film. Figure 3c demonstrates the concentration dependence of the quantum efficiency and the relative quantum yield of luminescence found for the PLA films doped with the Eu(III) complexes. The films containing 17.5 wt% of the Eu(III) complex demonstrate the maximum quantum efficiency of luminescence ( $\varphi^{Ln}$ ).

In comparison with other known analogues, the studied compounds were shown to undergo concentration quenching of luminescence at higher concentrations of the doped complex. For example, individual Eu(bzac)<sub>3</sub>phen [54] has a larger relative quantum yield of luminescence. In the PLA matrix, however, the Eu17.5 film shows a 1.4 times better performance due to a reduced quenching of luminescence.

PLA films doped with the Eu(III) complexes demonstrate good luminescence. They allowed us to evaluate applicability of these materials as thermosensors. We studied the impact of temperature on the luminescence intensity and lifetime. Figure 4a demonstrates the influence of temperature on the normalized luminescence intensity of the films in the 298–353 K range at  $\lambda_{ex} = 340$  nm and  $\lambda_{em} = 613$  nm.



**Figure 4.** Temperature dependences of the normalized luminescence intensity (**a**), sensitivity of the normalized intensity ( $S_r^I$ ) (**b**), lifetime (**c**) and the luminescence lifetime ( $S_r^\tau$ ) (**d**) obtained for the PLA composite films doped with a different content of the Eu(III) complex at  $\lambda_{ex} = 340$  nm and  $\lambda_{em} = 613$  nm (marker symbols—experimental data, dashed lines—approximations).

Temperature dependences of the normalized luminescence intensity of composite films decrease non-linearly and can be described by exponential functions with  $R^2 > 0.99$  correlation coefficients. Temperature exerts a strong influence on the luminescence intensity by decreasing it more than 30 times. In the range of 298–333 K, an increase in luminophore concentration does not lead to intensive changes in the sensitivity of the luminescence intensity (Figure 4b). A sharp increase in the sensitivity is observed at higher temperatures up to 353 K. At higher temperatures, the signal from the sample drops to an unclear noise level.

The maximum relative intensity sensitivity (Equation (5)) varies from 11.7 to  $20.1 \% \times K^{-1}$ . This value exceeds those of all other known  $\beta$ -diketonate lanthanide-containing thermosensors (Table 1). An increase in the luminophore content results in a nearly linear growth in the luminescence intensity sensitivity. Its temperature range includes the physiological temperatures of a human body. Such materials, therefore, can find potential applications in medicine.

#	Material	$\begin{array}{l} Maximum \ Relative \\ Sensitivity \ S_m, \ \% \times K^{-1} \end{array}$	Range, K	T <sub>m</sub> , K	Optical Parameter	Reference
1	Eu(keto) <sub>3</sub> (H <sub>2</sub> O)	$7.0 imes10^{-2}$	12-300	50	Bandwidth	[57]
2	PDMS-eddpo- Ln(bzac)3 (Ln = Eu,Tb)	11	158–248	203	Two intensities	[58]
3	$Ln(tfac)_3 \cdot 2H_2O$ (Ln = Eu, Tb)	7.1	293-343	293	Two intensities	[59]
4	Ln-DPA ( $Ln = Eu$ , $Tb$ )	1.5	293-333	293	Two intensities	[60]
5	$Eu(bzac)_3(H_2O)_2$	1.4	188-303	293	Lifetime	[61]
6	$Ln(btfa)_3(H2O)_2$ (Ln = Eu, Tb)	5.8	295-315	296	Two intensities	[62]
7	Eu <sup>3+</sup> /RhB-based polymer	3.6	300-310	302	Two intensities	[63]
8	Eu <sup>3+</sup> /RhB-based polymer	3.8	300-310	302	Two intensities	[64]
9	$Eu(bzac)_3(H_2O)_2$	5.3	188-303	303	Single intensity	[61]
10	Eu(tta) <sub>3</sub> (pyphen)	1.7	283-323	323	Lifetime	[65]
11	Eu(CPDK <sub>3-5</sub> ) <sub>3</sub> phen	2.2	298-348	298	Lifetime	[66]
12	Eu(CPDk <sub>3-C3F7</sub> ) <sub>3</sub> Phen	0.87	298–363	343	Single intensity	[67]

Table 1. Examples of existing thermosensors based on Ln(III) complexes.

It is well known [26,28] that the luminescence intensity of thermosensitive materials can be strongly influenced by the sample characteristics and measurement conditions. Moreover, it is rather difficult to consider the factor of film degradation under prolonged irradiation to avoid considerable errors in temperature measurements [68–70]. Thermosensors can also experience changes in their emission intensity when the medium's refractive index changes (for instance, when water or other liquid is absorbed onto the sensor's surface) or when measurements are performed in complex biological or chemical media. The luminescence quenching time, in its turn, does not depend on the above factors [26,28]. Therefore, this parameter is often used for more reliable and accurate temperature measurements.

Figure 4c illustrates the temperature dependence of the luminescence lifetime obtained for the composite film samples. The temperature has a significant impact on the luminescence lifetime and reduces it by nearly 15 times (for the 20 wt% Eu(III) film). The more Eu(III) complex we add into the composite film, the stronger is the temperature impact on the lifetime. At 311K, the curves cross and the impact of the Eu(III) complex concentration inverses. In the range of 308–343 K, the luminescence lifetime decreases almost linearly (correlation coefficients R<sup>2</sup> > 0.94) as temperature increases. The slope of the temperature line in the range of 308–343 K was 11.3–13.3  $\mu$ s/K (Figure 4c). Thus, the produced film materials can be used for high-precision temperature measurements including the range of physiological human temperatures.

The maximum value of the relative sensitivity lifetime (Figure 4d) (Equation (5)) varies in the range of 5.4–7.3  $\% \times K^{-1}$  at the median temperature of 333K. An increase in the luminophore content leads to a nearly linear growth in the luminescence lifetime

sensitivity, the same as for the luminescence intensity sensitivity. The sensitivity decreases at temperatures higher than 333 K.

The absolute sensitivity of the luminescence lifetime (Equation (4) varies in the range of 14.1–19.1  $\% \times K^{-1}$ . For all the samples, it has a minimum at different temperatures and gradually shifts to the lower temperature range (Figure 5). This effect may be associated with a growing influence of temperature at higher concentrations of the doped Eu(III) complex.



**Figure 5.** The absolute sensitivity of the luminescence intensity in PLA composite films doped with a different content of the Eu(III) complex as a function of temperature at  $\lambda_{ex} = 340$  nm and  $\lambda_{em} = 613$  nm (marker symbols—experimental data, dashed lines—approximations).

According to the literature data, the temperature-induced luminescence quenching of mononuclear  $\beta$ -diketonate Europium(III) compounds may occur via vibrational relaxation quenching or energy transfer quenching by the LMCT band [32]. The authors have previously shown in [66] that the temperature-induced quenching in anisometric Europium(III) compounds occurs through the second mechanism that involves the LCMT state. To reveal the mechanism of quenching in the PLA composite films, we evaluated the rate constants ( $k_{ET}$ ) by the kinetic analysis. The dependence of  $k_{ET}$  on temperature was calculated by the Arrhenius Equation [71–74] (Figure 6a):

$$ln\left(\frac{1}{\tau_{obs}}-\frac{1}{\tau_{77K}}\right) = ln k_{ET} = ln k_0 - \frac{E_a}{k} \times T^{-1}$$

The dependences of the luminescence lifetimes of the composites were calculated by the following Equation [66] (Figure 6b):

$$\theta(T) = \left(\frac{1}{\tau_{77K}} + k_0 \times exp\left(\frac{-E_a}{kT}\right)\right)^{-1}$$

where  $\theta(T)$  is the temperature function of the lifetime,  $\tau_{obs}$  is the observed luminescence lifetime,  $\tau_{77K}$  is the lifetime at 77 K that is the temperature of zero luminescence quenching,  $k_0$  is the frequency factor,  $E_a$  is the activation energy, and k is the Boltzmann constant.

The Arrhenius plots of all the composites were approximated by linear equations with the  $R^2 > 0.99$  correlation coefficients (Figure 6a). These approximations allowed for calculating the frequency factors  $k_0$  and activation energies for various amounts of the Eu(III) complex in the PLA films (Table 2). The values of these parameters agree with those found for similar Eu(III) compounds.



**Figure 6.** Arrhenius plot of the lifetime (**a**) and the simulated lifetime (**b**) as the functions of temperature obtained for PLA composite films doped with different amounts of the Eu(III) complex at  $\lambda_{ex} = 340$  nm and  $\lambda_{em} = 613$  nm (marker symbols—experimental data, dashed lines—approximations).

**Table 2.** The frequency factor and activation energies of the PLA composite films doped with different amounts of the Eu(III) complex and similar compounds.

Sample	The Frequency Factor $k_0$ , s <sup>-1</sup>	Activation Energy $E_a$ , cm <sup>-1</sup>	Reference
5 wt% Eu(III)	$8.78 imes10^{15}$	6661	This paper
10 wt% Eu(III)	$4.65 imes10^{16}$	6982	This paper
15 wt% Eu(III)	$1.45 imes10^{17}$	7197	This paper
20 wt% Eu(III)	$1.96 imes10^{17}$	7228	This paper
Eu(NTA) <sub>3</sub> ·H <sub>2</sub> O in PMMA	$1.8 imes 10^{14}$	6300	[75]
Eu(thd) <sub>3</sub>	$1.2 imes10^{13}$	4120	[76]
Eu(tta) <sub>3</sub> dapm in cellulose triacetate matrix	$7 imes 10^{16}$	7070	[77]
Eu(hfa) <sub>3</sub> (DPCO) <sub>2</sub>	$1.1  imes 10^7$	3120	[74]

An increase in the luminophore content in the PLA polymer matrix was found (Table 2) to increase the activation energy and frequency factor  $k_0$ . This effect can be explained by analyzing the Arrhenius equation: a higher activation energy results in a larger impact of temperature on  $k_{ET}$  and the lifetime and, thus, the value of  $S_r^{\tau}$  increases.

$$\frac{dln \, k_{ET}}{dT} = \frac{E_a}{kT^2}$$

A significant disadvantage of film materials produced from classic  $\beta$ -diketonate Ln(III) complexes is an irreversible decrease in their luminescence intensity after UV radiation exposure [21,78–80]. This process is particularly intensive in the presence of atmospheric oxygen. Therefore, we studied the impact of a prolonged UV exposure on the luminescence intensity and lifetime of the composite films with 5 wt% Eu(III), 10 wt% Eu(III), 15 wt% Eu(III), and 20 wt% Eu(III) (Figure S6).

An increase in luminophore content in the PLA matrix is found to significantly improve the photostability of the films. Under continuous UV irradiation, composite films containing 20 wt% luminophore show the 50% reduction in luminescence intensity after 6 h, while the films containing only 5 wt% of the Eu(III) complex demonstrate the 80% reduction. The film that contains the largest amount of the luminophore (20 wt% Eu(III)) demonstrates a highly stable luminescence lifetime, which decreases by just 5% after exposure to UV radiation. A cyclic study of the luminescence intensity during heating and cooling of the 20 wt% Eu(III) composite film was performed to confirm the thermal stability of the samples (Figure S7). The produced samples withstand 5 cycles of heating and cooling under irradiation at 340 nm and show only a small reduction in intensity (less than 5%) and virtually no changes in the luminescence lifetime.

Thus, we can conclude that the produced composites can make promising materials for luminescent thermometers capable of measuring temperatures in the range of 303–353 K, including the physiological temperature range of the human body.

PLA is a polymer material, which is used for 3D-printing applications. The composites produced in this work (PLA + 2.5 wt% Eu(III) complex) were successfully tested for their compatibility with a 3D-pen (Figure S8).

## 3. Materials and Methods

## 3.1. Materials

Europium(III) chloride hexahydrate, 1,10-phenanthroline, toluene, chloroform, hexane and polylactide (PLA) (Ecogenius PLA 3D printing filament, natural, diam. 1.75 mm) were purchased from Sigma-Aldrich (Burlington, NJ, USA).

## 3.2. Characterization Techniques

CHN elemental microanalysis was performed by Delta V Plus isotope mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). X-ray Fluorescence analysis was performed with Bruker M4 «Tornado» spectrometer. FT-IR spectra were recorded on an IR Fourier spectrometer IFS-66v/s Bruker. The mass spectra data were obtained using a Bruker Esquire LC-Ion Trap Mass Spectrometer. Thermal stability was studied by thermogravimetry-differential scanning calorimetry method on NETZSCH STA 449 C Jupiter. The thickness of the films was measured by the "Proton" profilometer model 130. Absorption and transmission spectra were measured by Perkin–Elmer Lambda-35 UV/Vis spectrophotometer. Excitation and luminescence spectra, luminescence decay curves were measured by Varian Cary Eclipse spectrofluorometer. A UVGL-58 Handheld UV Lamp (6 W, 365 nm) was used as a source of UV light to study the photostability of the samples. To demonstrate 3D printing capabilities, we used 3D pen NOVEX NPEN-88GN.

## 3.3. Synthesis

Ligand 1-[4-(4-propylcyclohexyl)phenyl]-octane-1,3-dione was prepared according to modified literature procedures [81,82]. The complex tris[1-[4-(4-propylcyclohexyl)phenyl]-octane-1,3-diono]-[1,10-phenantroline]europium (Eu(CPDk<sub>3-5</sub>)<sub>3</sub>Phen) was prepared according to [83].

Tris[1-[4-(4-propylcyclohexyl)phenyl]-octane-1,3-diono]-[1,10-phenanthro1ine]europium. Yield: 70% (0.095 g).  $C_{81}H_{107}N_2O_6Eu$ : calcd. C, 71.60; H, 7.99; N, 2.04; O, 7.22; Eu, 11.05; Found C, 71.11; H, 8.25; N, 2.00; O, 7.38; Eu, 11.20. FTIR (PE pellet) (cm<sup>-1</sup>): v(Eu–N) 431 and 178 cm<sup>-1</sup>; v(Eu–O) 479 and 471 cm<sup>-1</sup>. FTIR (CCl<sub>4</sub> solution) (cm<sup>-1</sup>): v(C=N, Phen) 2249, 1582, 1490 cm<sup>-1</sup>; v(C=O); 1465, 1437 cm<sup>-1</sup>; v(CH Alk) 2868, 1349, 1220, 1021, 708 cm<sup>-1</sup>; v(C=C) 980 cm<sup>-1</sup>; v(CH Arom) 3146, 1074, 623 cm<sup>-1</sup>; v(Eu–O) 477, 439 cm<sup>-1</sup>. ESI-MS (m/z): 1380 (M + Na)<sup>+</sup>.

## 3.4. Preparation of PLA—Eu(III) Complex Hybrid Films

The films were prepared as described in [47].

## 3.5. Calculation of the Quantum Efficiency

The emission quantum efficiency ( $\varphi^{Ln}$ ) of the <sup>5</sup>D<sub>0</sub> emitting level of the Eu<sup>3+</sup> ion, according to Equation (1) [84]:

$$\varphi^{Ln} = \frac{A_{rad}}{A_{rad} + A_{nrad}} = \frac{A_{rad}}{A_{tot}} \tag{1}$$

where  $A_{rad}$  and  $A_{nrad}$  are the radiative and non-radiative rates, respectively.

Contributions to  $A_{nrad}$  include back-energy transfer to the sensitizer [85–87], electron transfer quenching (mainly for Eu<sup>3+</sup>) [87,88], and most importantly quenching by matrix vibrations. O–H vibrations are effective quenchers of lanthanide luminescence [89–92]. Moreover, other vibrations commonly found in organic molecules can have important contributions to  $A_{nrad}$  [92].

Non-radiative processes influence the observed luminescence lifetime  $(\tau_{obs} = (A_{rad} + A_{nrad})^{-1})$ . In turn, the radiative lifetime is not affected by these processes, by definition  $(\tau_{rad} = A_{rad}^{-1})$ .

If the radiative lifetime,  $\tau_{rad}$ , is known,  $\varphi^{Ln}$  can be calculated using the observed luminescence lifetime  $\tau_{obs}$  (Equation (2)).

$$\varphi^{Ln} = \frac{\tau_{obs}}{\tau_{rad}} \tag{2}$$

If we assume that both the energy of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition and its dipole strength are constant, we get Equation (3), which relates the shape of the emission spectrum of Eu<sup>3+</sup> to its radiative lifetime.

$$\frac{1}{I_{rad}} = A_{MD,0} \cdot n^3 \cdot \left(\frac{I_{tot}}{I_{MD}}\right) \tag{3}$$

In this formula, *n* is the refractive index of the medium (the solvent),  $A_{MD,0}$  is the spontaneous emission probability for the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition in vacuum, and  $I_{tot}/I_{MD}$  is the ratio of the total area of the corrected Eu<sup>3+</sup> emission spectrum to the area of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  band. From the theoretically calculated dipole strength, we can find that  $A_{MD,0}$  has a value of 14.65 s<sup>-1</sup> [84].

## 3.6. Calculation of the Thermal Sensitivity

The absolute thermal sensitivity  $(S_a)$  is calculated by Equation (4) [93]:

$$S_a = \frac{\partial \Delta}{\partial T} \tag{4}$$

where  $\Delta$  is the luminescence lifetime or intensity.

The relative thermal sensitivity  $(S_r)$  is calculated by Equation (5) [93]:

$$S_r = \frac{|\partial \Delta|}{\partial T \times \Delta} \times 100\%$$
<sup>(5)</sup>

### 4. Conclusions

In this study, PLA polymer and the synthesized amorphous Eu(III) complex were used to prepare composite materials with varying percentages of the doped luminophore. The quantum efficiency, photostability, and temperature sensitivity of the thermosensor luminescence were shown to increase when the luminophore is introduced in amounts up to 20 wt%. The maximum relative intensity sensitivity varies from 11.7 to 20.1 %×K<sup>-1</sup>. This value exceeds those of all other known  $\beta$ -diketonate lanthanide-containing thermosensors. The maximum value of the relative lifetime sensitivity various in the range of 5.4–7.3 %×K<sup>-1</sup> at the median temperature of 333 K. The composites developed in this work can be promising thermosensors for measuring temperatures between 303 K and 353 K, including the human physiological temperature range.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www. mdpi.com/article/10.3390/inorganics10120232/s1. Figure S1: FTIR spectrum of the Eu(III) complex; Figure S2. 3D structure of the Eu(III) complex;. Figure S3: Absorption spectra of PLA composite films doped with different content of the Eu(III) complex; Figure S4: Absorption spectra of the ligands and synthesized complexes dissolved in hexane; Figure S5: Concentration dependence of the absorption spectra of PLA composite films doped with different content of the Eu(III) complex; Figure S6: Normalized intensity and lifetime of luminescence plotted for the composite films doped with different content of the Eu(III) complex as the functions of UV irradiation time; Figure S7: Cyclic dependences of luminescence intensity and lifetime of the composite film doped with 20 wt% Eu(III); Figure S8: Photos of the 3D-printed PLA composites doped with 2.5 wt% of the Eu(III) complex in visible and UV light; Table S1: Quantum efficiency of luminescence ( $\Phi^{Ln}$ ) of samples and analogues.

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