Elastic changes in luminescence intensity of vitrified film of europium(III) β-diketonate complex

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Abstract. We have observed an elastic change in luminescent properties of a 20 µm thick vitrified film (prepared from an amorphous powder of an anisometric europium(III) β-diketonate complex through a melt-processing technique and sandwiched between two quartz plates) caused by the prolonged UV irradiation. The film under UV light irradiation exhibits a typical Eu³⁺ ion emission peaked at 611 nm. The irradiation of the film by a 337 nm pulsed nitrogen laser with 0.2 mW average output power for 80 min leads to 1.5-fold decrease in the luminescence intensity at 611 nm. Despite the fact that in the case of traditional film-type materials based on lanthanide(III) β-diketonate complexes such effect is attributed to irreversible ligand photofragmentation, we have observed no photodecomposition of the anisometric complexes in the vitrified film. Moreover, we detected full reversibility of the luminescence intensity by keeping the film in the dark for 21 h. It is worth noting that this feature can be used for the design of new reusable luminescent dosimeters for UV light.

1. Introduction
Lanthanide(III) complexes with β-diketonate ligands combine unique photophysical properties (narrow-band luminescence with a large Stokes' shift, high quantum yield, long decay time from tens to hundreds of microseconds) [1] and attractive chemical characteristics (relatively easy synthesis, good solubility in many basic solvents and a possibility of incorporation into different host matrices) [2]. These properties make them very promising for the fabrication of film-type luminescent photonic materials and devices such as monochromatic light sources, optical oxygen sensors, luminescent thermometers, light-conversion materials, OLED devices [2-6].

A serious drawback of applying film materials based on lanthanide(III) β-diketonate complexes is quick decrease in their luminescence intensity under prolonged UV irradiation. The process is irreversible and often attributed to photofragmentation of β-diketone ligands [7-9]. This effect had been utilized to developed single-use thin-film luminescent UV dosimeters based on europium(III) and terbium(III) β-diketonate complexes [7, 9, 10].

We had proposed an alternative approach to design luminescent materials based on mesogenic lanthanide(III) β-diketonate complexes having an anisometric geometry in contradistinction to non-mesogenic analogues [11-14]. Our materials are vitrified films fabricated from powders of the
complexes by a melt-processing technique and sandwiched between two quartz plates. Their technological advantages are the simplicity in design, intense luminescence, high transparency in the visible region and full resistance to UV radiation [15-21]. In addition, the absorption/excitation bandwidth and the luminescence intensity of the films can be adjusted by varying their local structure in the preparation process [16-19, 21] and by using external factors such as prolonged UV laser irradiation [15, 16, 20] or temperature exposure [15, 17-19, 21].

In our previous work we had studied the photophysical properties of the vitrified film prepared from the anisometric europium(III) β-diketonate complex, [Eu(DK$_{12-14}$)$_3$phen] ($\text{DK}_{12-14} = 1$-(4-(dodecyloxy) phenyl)-3-(4-(tetradecyloxy) phenyl) propane-1,3-dione, phen = 1,10-phenanthroline) (see figure 1). We found that the strong Eu$^{3+}$ emission of the film efficiently excited by irradiation in the wavelength range of 280-425 nm. The film was photostable under prolonged irradiation by a 337 nm pulsed nitrogen laser with 0.05 mW average output power, insensitive to atmospheric oxygen and fully reversible relative to dependence of the luminescence decay time at 611 nm on temperature ranging in 270-370 K. These facts allowed considering the film as a promising probe for reusable luminescent thermometers, suitable for long-term temperature monitoring [21].

In this work we found elastic changes in the luminescence intensity at 611 nm of the Eu(DK$_{12-14}$)$_3$phen film caused by the nitrogen laser irradiation at room temperature when its average output power much exceeds 0.05 mW. Despite the fact that in the case of non-anisometric lanthanide(III) β-diketonate complexes the decrease of the luminescence intensity under laser irradiation usually is irreversible (because of ligand photofragmentation), we had observed that the initial luminescence intensity of the vitrified film was fully restored after being in the dark.

![Figure 1. The chemical structure of the Eu(DK$_{12-14}$)$_3$phen complex.](image)

2. Experimental
The powder of the Eu(DK$_{12-14}$)$_3$phen complex was synthesized according to the procedure described in a previous report [11]. An alcoholic solution of EuCl$_3$·6H$_2$O (1 equiv.) was slowly added dropwise to a stirred hot alcoholic solution of β-diketone (3 equiv.), 1,10-phenanthroline (1 equiv.), and KOH (3 equiv.). The formed light yellow precipitate was isolated by hot filtration, washed with hot alcohol, and dried in vacuum. Further, the product was dissolved in toluene, and the obtained solution was filtered off and evaporated to dryness in vacuum. The yield, the mass spectra and the elemental analysis data of the DK$_{12-14}$ β-diketone ligand and the Eu(DK$_{12-14}$)$_3$phen complex have been published previously [21].

The luminescence excitation spectrum was registered on a Varian Cary Eclipse spectrofluorimeter. The luminescence spectrum was recorded on an optical spectrometer based on an MDR-23 grating
monochromator (LOMO, Saint Petersburg, Russia) coupled to an FEU-100 photomultiplier tube [22]. The luminescence was excited by an LGI-21 pulsed nitrogen laser (337 nm wavelength, 2.1 mW average output power, 10 ns pulse duration, 100 Hz repetition rate). The laser beam power of 0.05 mW resulted in no change in the luminescent properties of the 3 mm² exposed surface area of the film. The photostability was studied by monitoring the dependence of the mean luminescence intensity at 611 nm on irradiation time by the 337 nm LGI-21 pulsed nitrogen laser with 0.05 mW average output power. All experiments were carried out at room temperature.

3. Results and discussion

The luminescence excitation spectrum of the Eu(DK$_{12-14}$)$_3$phen film exhibits a broad band with the maximum at 335 nm (see figure 2). This band corresponds to the ligand-centered singlet-singlet transitions and reveals the coordination of the organic ligands to the Eu$^{3+}$ ion.

A narrow-band luminescence of the film under irradiation by the 337 nm pulsed nitrogen laser caused by the $^5$D$_{0}$$rightarrow$F$_0$ (579.5 nm), $^5$D$_{0}$$rightarrow$F$_1$ (588 nm), $^5$D$_{0}$$rightarrow$F$_2$ (611 nm), $^5$D$_{0}$$rightarrow$F$_3$ (651.5 nm) and $^5$D$_{0}$$rightarrow$F$_4$ (704.5 nm) intraconfigurational transitions of the Eu$^{3+}$ ion (see figure 2) [22]. No observed emission from the ligands expected in the wavelength range of 450-720 nm suggests that the ligand-to-metal energy transfer in the film is quite efficient [21].

![Figure 2. Luminescence spectrum (solid line) under the exposure to a 337 nm pulsed nitrogen laser with 0.05 mW average output power and excitation luminescence spectrum (dashed line) with the emission monitored at 611 nm of the Eu(DK$_{12-14}$)$_3$phen film.](image)

In our previous work we showed that the irradiation of the Eu(DK$_{12-14}$)$_3$phen film by the 337 nm pulsed nitrogen laser with 0.05 mW average power for 4 h resulted in no change in the mean luminescence intensity at 611 nm [21]. In this work we have found, that the irradiation of the film by the nitrogen laser with 0.2 mW average power for 80 min leads to the 1.5-fold decrease in the mean luminescence intensity (see figure 3a). As already noted, traditional film materials based on lanthanide(III) β-diketonate complexes have a propensity for irreversible luminescence decrease under prolonged UV irradiation. As a rule, this effect is attributed to the photofragmentation of β-diketone ligands [7-9]. However, figure 3b shows that in the case of the Eu(DK$_{12-14}$)$_3$phen film, the initial luminescence intensity is completely recovered by storing the film in the dark for 21 h. For the best of our knowledge, this observation has been made for the first time, and according to the literature data such behavior is highly unusual for known traditional lanthanide(III) β-diketonate film. At this moment, we offer no proper explanation for mechanism responsible for the observed phenomena.
Although it is reasonable to assume that some elastic structural changes of the film induced by UV laser irradiation are playing crucial role in the photophysical properties of the film, additional experimental and theoretical studies are needed to reveal the details of mechanisms responsible for observed luminescence data.

**Figure 3.** Dependence of the mean luminescence intensity of 3 mm$^2$ surface area of the Eu(DK$_{12}$-$14$)$_3$phen film monitored at 611 nm on the irradiation time using a 337 nm pulsed nitrogen laser with 0.2 mW average output power (a). Dependence of the mean luminescence intensity of the UV modified film on the time spent in darkness (b).

4. **Conclusion**
For the first time we report on the elastic changes in the luminescent properties of a 20 μm thick vitrified film of an anisometric europium(III) β-diketonate complex. A prolonged nitrogen laser irradiation of the film led to the 1.5-fold decrease in luminescence intensity and followed keeping the film in the dark for about 21 h fully restored initial luminescence intensity. It should be noted, that the observed luminescence behavior is in contradiction with literature data reported for luminescence intensity decrease caused by photodegradation under UV light exposure in in the case of traditional film materials based on lanthanide(III) β-diketonate complexes. Although the explanation of the observed phenomena requires additional research investigations, it is clear, that the elastic changes in the luminescent properties open promising opportunities in designing novel reusable probes based on anisometric lanthanide(III) β-diketonate complexes for UV dosimetry.

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