Journal of Alloys and Compounds 323–324 (2001) 820–823
www.elsevier.com/locate/jallcom

Lanthanide complexes dispersed in enamel: a promising new material for photonic devices

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Abstract

A lanthanide-thin-film based dosimeter with high sensitivity and selectivity to UV cumulative measurements was developed. The dosimeter is based on nitrocellulose–enamel and has been designed in order to present useful responses covering the three main UV regions related to skin damage effects: UV-A (365 nm), UV-B (315 nm), UV-C (290 nm).The active part of the system is a thin layer of commercial nitrocellulose enamel ultrasound-mixed with lanthanide complex powder. We have monitored the Eu (III) emission ($^5D_0 \rightarrow {}^7F_2$) and the Tb (III) emission ($^5D_4 \rightarrow {}^7F_5$) as a function of UV exposure time and a luminescence decrease of the Eu (III) emission was observed. Since this effect is irreversible, a memory effect is associated to the system allowing dosimetry measurements. For the red (600 nm), green (540 nm) and blue (430 nm) excitation the luminescence remained the same, which reinforces the UV selectivity of the dosimeter proposed. We may also adjust the dosimeter sensitivity by controlling the amount of powder mixed with the enamel.

Keywords: UV dosimetry; Lanthanide complexes; Enamel film; LCMD; Photonic devices

1. Introduction

The past years have raised the search towards the design, synthesis and characterization of new lanthanide complexes for the production of advanced Light Conversion Molecular Devices (LCMD) [1–7]. Their use range from radiation sensors to a variety of photonic and integrated optoelectronic device applications [4], such as sensors for bioinorganic systems [5–7] and luminescent labels in fluoroimmunoessays [5,6]. However, in order to obtain a high luminescent complex we have to consider several aspects [8–10]: (i) molar absorptivity (ϵ) of the ligand, (ii) a high energy transfer from ligand to metal, (iii) efficient luminescence of the ion related to non-radioactive decay processes due to OH and CH oscillators. In this way, we have worked with fluoride β-diketones [11], namely btfa (4,4,4-trifluoro-1-phenyl-2,4-butanedione) and hfc (6,7,7,8,8,8-heptafluoro-2,2′-dimethy-l,3,5-hydroxymethylene (+) camphore) and water was replaced by heterobiaryl ligands (1,10-phenanthroline (phen), 2,2′-bipyridine (bipy)) to avoid non-radioactive decays due to C–H (replaced to C–F) and O–H oscillators, since the luminescence could be quenched by a multiphonon process.

Several complexes were synthesized in this work, $Eu(btfa)_3bipy$, $Tb(btfa)_3phen$, $Eu(btfa)_3phen$, $Eu(hfc)_3bipy$. These complexes are very efficient light converters under UV excitation, where the ligands act as high absorbing UV antennae [11] and efficiently transferring energy to the Ln (III) emitters.

The chemical and physical properties of these materials [11] allow us to mix them in an enamel-like medium without any loss in the luminescence efficiency. As a result, a highly uniform and stable layer of complex powder dispersed in enamel is obtained with strong luminescence comparable to their powder giving it a potential technological applicability.

We have monitored Eu (III) red ($^5D_0 \rightarrow {}^7F_2$) and Tb (III) green ($^5D_4 \rightarrow {}^7F_5$) emissions as a function of UV excitation/exposure time. We have also observed their behavior regarding three main light colors, red, green and blue. For the europium red luminescence, a continuous decrease under UV radiation exposure was observed, which is associated to the complex photofragmentation, since it is related to the absorption of the ligands. For the Tb (III)$^5D_4 \rightarrow {}^7F_5$ emission, the behavior is opposite for several minutes. A luminescence raise is observed for this green

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0925-8388/01/$ – see front matter
PII: S0925-8388(01)01152-5

emission, diminishing afterwards. Meanwhile, for visible light exposition, no luminescence decrease was observed confirming the dosimeter selectivity for the UV region.

This system may work as an UV dosimeter previously described [1–3], which features high selectivity and sensitivity to UV radiation. Moreover, it may be controlled by varying the amount of powder mixed with the enamel depending on the application (needs and aims), the source to be measured or, the exposed material.

2. Experimental

We have prepared the compounds $Ln(L)_3L'$ (Ln=Eu (III) and Tb (III), L=btfa (4,4,4-trifluoro-1-phenyl-2,4-butanedione) and hfc (6,7,7,8,8,8-heptafluoro-2,2′-dimethyl-l,3,5-hydroxymethylene (+)camphore) and L′=1,10-phenanthroline, 2,2′-bipyridine) essentially in the same way as reported elsewhere [8,12]. The powder was purified twice and dried at 80°C over P_2O_5 under low pressure (<1 mmHg). The Ln content was determined by a complexometric titration with EDTA (0.01 M), where the powder was dissolved in ethanol and xylenol orange was used as the indicator. The carbon and hydrogen were determined by elemental analysis.

A glass support was cleaned and degreased appropriately to assure uniformity and adhesion. The complex powder (~ 0.8–8 mg) is then ultrasoundly mixed with enamel until complete dispersion is reached. For the mixed complex, the two compounds ($Eu(btfa)_3bipy/Tb(btfa)_3phen$ 5:95) were vigorously blended in order to obtain homogeneity. In the same way, the complex was mixed with enamel in an ultrasound equipment until total dispersion of the powder in the medium.

The spectroscopic measurements were obtained at room temperature using a double 2.0 m Jobin-Yvon Ramanor U-1000 monochromator, coupled to a photomultiplier tube RCAC31034-RF. The excitation source was an Xe–Hg lamp of 150 W with a Corning 7-54 filter for UV-A and a H-10 excitation monochromator. Registering and processing of the signals and data were accomplished by an interface Spectralink connected to a microcomputer. For the measurements with red, green and blue light colors, we have exposed the sample to the corresponding wavelengths and measured the relative luminescence at 365 nm, while for UV exposure, the measurement was performed during that exposure.

3. Results and discussion

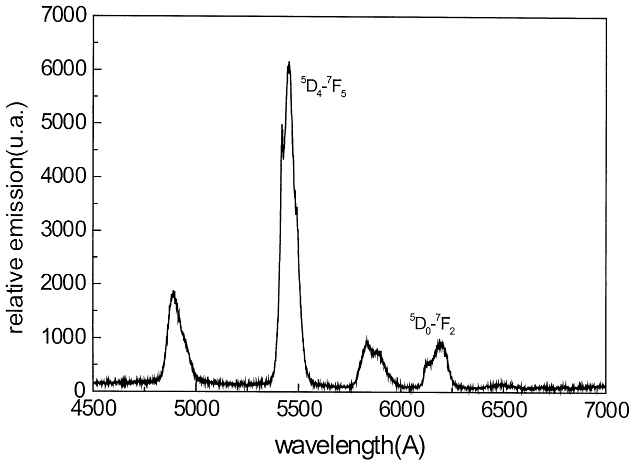

Fig. 1. Emission spectrum for ($Eu(btfa)_3bipy/Tb(btfa)_3phen$ 5:95) in enamel host at room temperature under 365 nm excitation.

Fig. 1 illustrates an emission spectrum for a ($Eu(btfa)_3bipy/Tb(btfa)_3phen$ 5:95) under 365 nm excitation. We may notice well defined peaks corresponding to the transitions associated to the Eu (III) and Tb (III) ions remarking the negligible influence of the enamel medium in the luminescence behavior. The transitions $^5D_0 \rightarrow {}^7F_2$ of Eu (III) and $^5D_4 \rightarrow {}^7F_5$ of Tb (III) were monitored as a function of time of UV excitation/exposure owing to their high relative emission intensity.

The Tb (III) green emission ($^5D_4 \rightarrow {}^7F_5$) and Eu (III) red emission ($^5D_0 \rightarrow {}^7F_2$) were monitored in real time under UV-A (365 nm), UV-B (315 nm), and UV-C (290 nm) excitation/exposure.

Fig. 2(a) shows the Eu (III) emission intensity as a function of the UV exposure time for 0.8 mg of the complex $Eu(btfa)_3bipy$. Its emission decreases in an exponential regime with time constants $\tau=2.2$; 1.9 h and 0.68 h for UV-A, UV-B and UV-C exposure respectively. In Fig. 2 (b) the same behavior is observed for 8 mg of the complex $Eu(btfa)_3bipy$ with $\tau=2.7$ and 1.3 h for UV-B and UV-C respectively.

From Fig. 2 we observe that the luminescence quenching is faster for 290 nm excitation in both cases and that, as expected, the more complex powder dispersed in the enamel, the slower the luminescence decrease, allowing us to prepare a device for each kind of sensitivity we need: for low doses we may use low concentrations to attain faster responses.

Fig. 3 presents real time measurements for the mixed powder ($Eu(btfa)_3bipy/Tb(btfa)_3phen$ 5:95) in the enamel host. Immediately after painting the glass support with enamel, we have observed an orange-yellow luminescence of the mixed complex film, resulted from the additive synthesis of green and red emission. Afterwards it becomes visibly green, i.e., there is no contribution from the europium complex anymore. Therefore we monitored the Tb (III) green emission ($^5D_4 \rightarrow {}^7F_5$) as a function of UV excitation/exposure. The time constants measured were $\tau=3.5$; 30 and 50 h for UV-A, UV-B and UV-C exposure respectively. The results for this system differed from the previous one ($Eu(btfa)_3bipy$)-the order is inverted regarding UV-A, UV-B and UV-C photofragmentation power and

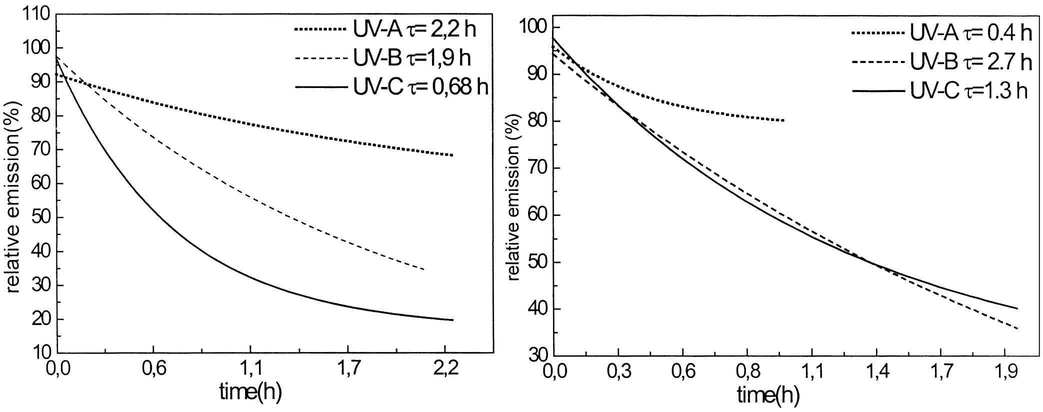

Fig. 2. (a-left)-Eu (III)$^5D_0 \rightarrow {}^7F_2$ emission intensity as a function of UV exposure time for 0.8 mg of Eu(btfa)$_3$bipy in enamel. (b-right) The corresponding curve for 8 mg of Eu(btfa)$_3$bipy in enamel.

also time constants measured for the mixed-complex system is twice greater. For this last reason, we might infer that Tb luminescence decrease is negligible when compared to Eu behavior.

We have also obtained similar curves for Eu(hfc)$_3$bipy, a very high volatile complex for thin film applications. In this case, the time constants were considerably high and rather negligible for UV-A and UV-C regions (60 h). On the other hand, for UV-B, in which the higher luminescence is observed, $\tau=1.5$ h.

On the whole, we may say that the luminescence decrease behavior for each kind of complex vary and therefore we can choose the compound accordingly depending on the kind of source to be dosed like artificial ones or even the sunlight itself. The Tolerance Limit Value (TLV) for UV-A for human skin, for instance, is 28 mJ/cm^2 for 8 h of exposition per day. We have used an excitation source for UV-A that gives this dose in about 2 h. The most important feature is that we can measure doses below TLV, even for attenuated sources. This wide range of sensitivity is one of the greatest advantages of this dosimeter allowing us to adjust it to our aims.

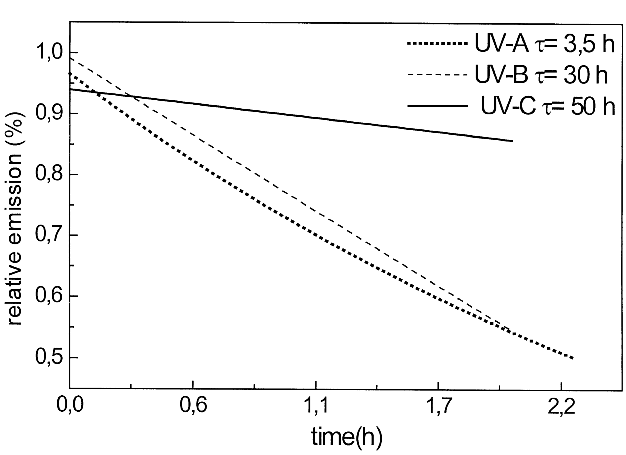

Fig. 3. Tb (III) green emission ($^5D_4 \rightarrow {}^7F_5$) intensity as a function of UV exposure time for 0.8 mg of Eu(btfa)$_3$bipy/Tb(btfa)$_3$phen 5:95 in enamel.

Fig. 4 shows in 3D the behavior of 0.8 mg Eu(btfa)phen enamel system under UV-A excitation with $\tau=4.8$ h. As it can be seen, the emission spectrum outline does not change after 15 scans (~2 h) of UV exposure. This suggests no interference of the enamel medium in the complex luminescence emission.

4. Conclusions

We have developed a dosimeter based on lanthanide complexes dispersed in enamel system [13], in which the luminescence decrease of the complexes is monitored and correlated to the amount of UV exposure. The effect of the Eu (III) luminescence quenching is irreversible, giving it a memory effect, allowing highly reliable dosimetric mea-

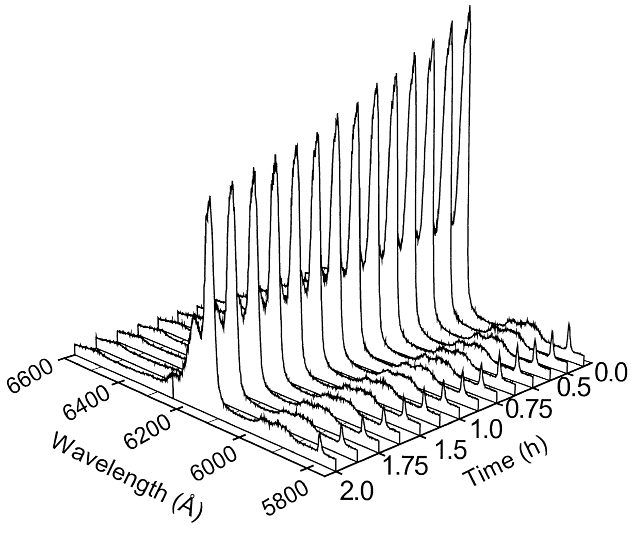

Fig. 4. A 3D view of Eu (III) emission intensity as a function of UV-A exposure for 0.8 mg of Eu(btfa)phen.

surements. The system response is also reproducible, and it could be accurately associated to the amount of UV energy per unit area, since it is possible to obtain a calibration curve using an integration sphere for absolute measurements [1,2].

The dosimeter sensitivity may be adjusted by varying the amount of powder used or the type of complex in order to suit our needs and goals. The system response could also provide a parameter that indicates an overall effect on human skin, for instance. We could also design as a simple radiation index, which is related to the permanent skin damage. It may also be produced by controlling its sensitivity, to establish a final point of a process involving UV radiation.

A quick visual analysis of the film provides a fast UV time of exposure indicator and also the ratio intensity of $(^5D_4 \rightarrow {}^7F_5)/(^5D_0 \rightarrow {}^7F_2)$ transitions gives a high accuracy for the dosimeter.

Acknowledgements

The authors would like to thank the Brazilian agencies CNPq, CAPES, FACEPE, FINEP and PADCT program for financial support. Thanks for the helpful comments from Prof. Larry Thompson, from University of Minnesota, Duluth Campus. We also would like to thank the technical support from Blenio J. P. da Silva and João Carlos de Albuquerque from the Physics Department of UFPE.

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