

# Photosensitivity of nanoporous glasses and polymers doped with $\text{Eu}(\text{fod})_3$ molecules

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**Abstract.** The decay kinetics of photoluminescence (PL) of  $\text{Eu}^{3+}$  ions (the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  transition) excited by UV radiation (in particular, by a laser) is studied in a Vycor nanoporous glass and transparent polymers doped with  $\text{Eu}(\text{fod})_3$  molecules (where fod stands for 6,6,7,7,8,8,8-heptafluor-2,2-dimethyl-3,5-octadionate) using a solution of supercritical  $\text{CO}_2$ . It is found that the decrease in the PL intensity is caused by the photoinduced transformation of the ligand component of the complex (fod), while the decay rate depends significantly on the type of the matrix. Models of mechanisms of photodissociation of the original complex related to excitation to the singlet absorption band of the ligand ( $\text{S}_0 \rightarrow \text{S}_1$  transition) in one case and to the ligand–metal charge transfer band in the other case are proposed.

**Keywords:** photochemistry, photoluminescence, polymers, nanoporous glass, supercritical impregnation, photodissociation.

## 1. Introduction

Chelates of rare-earth elements, including  $\text{Eu}(\text{fod})_3$  molecules (where fod stands for 6,6,7,7,8,8,8-heptafluor-2,2-dimethyl-3,5-octadionate) are introduced quite frequently into transparent dielectrics like silica glass [1, 2], glasses obtained by the sol–gel method [3–5], as well as various polymer materials [6–8]. It is well known (see, for example, [5–8]) that favourable luminescence parameters of  $\text{Eu}^{3+}$  ions at the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition in the red spectral region are used for practical application of such materials. Such Eu-activated materials can be used as laser media [9], and in various luminescence sensors [10] or matrices for efficient high-density data storage [11]. It was shown in [8] that an optical fibre based on  $\text{Eu}(\text{fod})_3$ -doped polymethylmethacrylate can be used as an optical amplifier. In all these cases, it becomes necessary to carry out separate inves-

tigations of photochemical processes initiated by near-UV radiation and occurring in the chelate molecules surrounded by a matrix of a certain composition. Thus, the analysis of a specific mechanism of photoinduced decay of europium chelate molecules in various transparent dielectrics should lead to the development of methods for enhancing or lowering the photosensitivity of such media, depending on the specific purposes for which these matrices are intended.

A rather prospective method of modification of optical properties of samples is the doping of metalloorganic compounds (MOCs) into the free inner volume of a sample by using supercritical media (SCM), e.g., supercritical carbon dioxide [12, 13].

At present, the most efficient method for exciting red luminescence in europium chelates is the  $\text{S}_0 \rightarrow \text{S}_1$  singlet excitation of organic ligands in the near UV spectral region [8, 14, 15]. In this case, the excitation energy is resonantly transferred through the singlet–triplet system of the ligand to the  ${}^5\text{D}_j$  levels of  $\text{Eu}^{3+}$  ions. Therefore, it should be interesting to find the excitation conditions (composition of the material, excitation wavelength, chelate concentration) which can cause photoinduced decay of chelate molecules, leading to the decay of the red PL of  $\text{Eu}^{3+}$  ions. It is also necessary to find out whether such a decay is connected (at least partially) with the photoinduced change in the valence of europium. The aim of this paper is to study experimentally these problems.

## 2. Experimental

We used in our experiments 1.7-mm-thick plates of porous Vycor silica glass (Bioanalytic Systems, Inc., USA) with an average pore size of 4 nm, 1-mm-thick plates of polymethylmethacrylate (PMMA), and 300- $\mu\text{m}$ -thick films of polydimethylsiloxane (PDMS) and polypropylene (PP). Polycrystalline  $\text{Eu}(\text{fod})_3$  powder (ALDRICH Chemical Company) was doped into matrices through a solution of supercritical  $\text{CO}_2$ . The experimental setup for impregnation of supercritical  $\text{CO}_2$  is shown in [12]. Table 1 shows the data about the conditions of impregnation of supercritical  $\text{CO}_2$  and concentrations in various samples.

Optical absorption spectra were recorded in the range 200–650 nm using a DDS-30 deuterium lamp and an incandescent lamp, an MDR-6 monochromator (a spectral resolution of 0.2 nm), and a FEU-100 photomultiplier.

Photochemical processes were studied by irradiating samples simultaneously by the 312.6-nm and 313.2-nm lines from a DRSh-500 high-pressure mercury-arc lamp or simultaneously by the 351.1-nm and 363.8-nm lines from

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**Table 1.** Concentrations and conditions of supercritical impregnation in investigated samples.

Matrix	$t_{im}/h$	$T_{im}/^{\circ}C$	$P_{im}/atm$	$N_{im}/cm^{-3}$	$N/cm^{-3}$
Vycor	2	50	130	$10^{16}$	$2 \times 10^{17}$
PMMA	1	80	250	$1.4 \times 10^{18}$	$3.8 \times 10^{18}$
PDMS	1	80	250	$10^{16}$	$10^{17}$
PP	1	80	250	$1.4 \times 10^{18}$	$9 \times 10^{17}$
PDMS	1	80	215	$2.6 \times 10^{18}$	$4 \times 10^{19}$

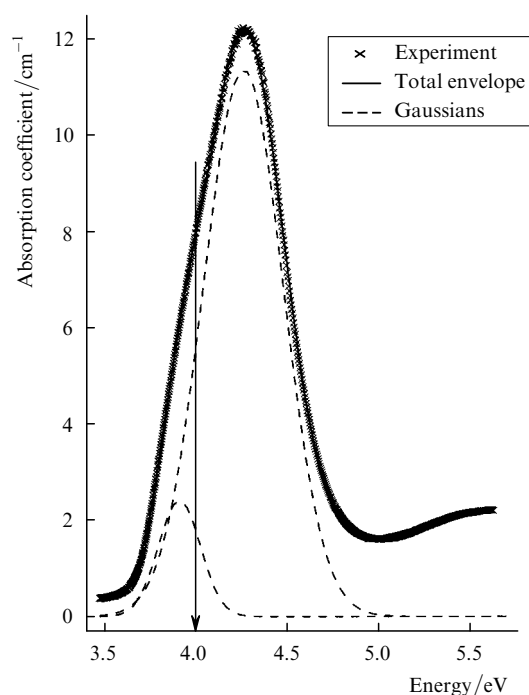
Note:  $t_{im}$  is the impregnation time;  $T_{im}$  and  $P_{im}$  are the temperature and pressure of  $CO_2$  in the chamber;  $N_{im}$  and  $N$  are the  $Eu(fod)_3$  concentration in  $CO_2$  solution and in the samples after impregnation.

a Beam Lock 2080 argon laser (Spectra Physics). The power densities and irradiation times are presented in Table 2. In addition, irradiation was performed by an NSHU590 LED at 380 nm (the FWHM 0.1 eV, power density  $0.1 \text{ W cm}^{-2}$ ). Red PL from  $Eu^{3+}$  ions ( $^5D_0 \rightarrow ^7F_j$  transitions) was detected with an R300 photomultiplier (Hamamatsu), a BPX-65 silicon photodiode was used as the reference photodetector, while the reference signal was provided by a phosphor having a constant quantum yield of luminescence in the range 350–650 nm. The luminescence signals and signals from the reference photodetector were recorded with a Tektroniks TDS-1012 digital storage oscilloscope, and the PL signal was normalised to the reference signal at each time point.

### 3. Experimental results and discussion

#### 3.1 Mercury lamp irradiation

As mentioned above, red PL can be excited in  $Eu(fod)_3$  molecules doped into various matrices most efficiently through the singlet absorption band of the ligand. For this reason, the first experiments aimed at studying the mechanism of photoinduced decay of these molecules were performed by exciting the ligand of a complex by lines from a mercury lamp. Figure 1 shows the corresponding absorption band at 4.28 eV (292 nm) for the solution of  $Eu(fod)_3$  molecules in ethyl alcohol (concentration  $10^{17} \text{ cm}^{-3}$ ) which can be decomposed into two components at 3.91 eV (320 nm) and 4.25 eV (295 nm). In our opinion [14, 16], this band is related to two forms of  $Eu(fod)_3$  molecules: the basic form (absorbing at 295 nm) and the hydrolysed form (absorbing at 320 nm). Investigations of absorption spectra in this region for various matrices containing  $Eu(fod)_3$  molecules show that the position of the singlet absorption band does not change significantly depending on the matrix [14]. Therefore, the wavelength of the exciting radiation from the mercury lamp used in each case falls within this absorption band. One can see

**Figure 1.** Absorption spectrum of the  $Eu(fod)_3$  solution in ethyl alcohol (concentration  $10^{17} \text{ cm}^{-3}$ ). The arrow corresponds to  $\lambda = 313 \text{ nm}$ .

from the example of PP (Fig. 2) that the action of such radiation results in a considerable lowering of the singlet band intensity and hence to a decrease in the intensity of red luminescence.

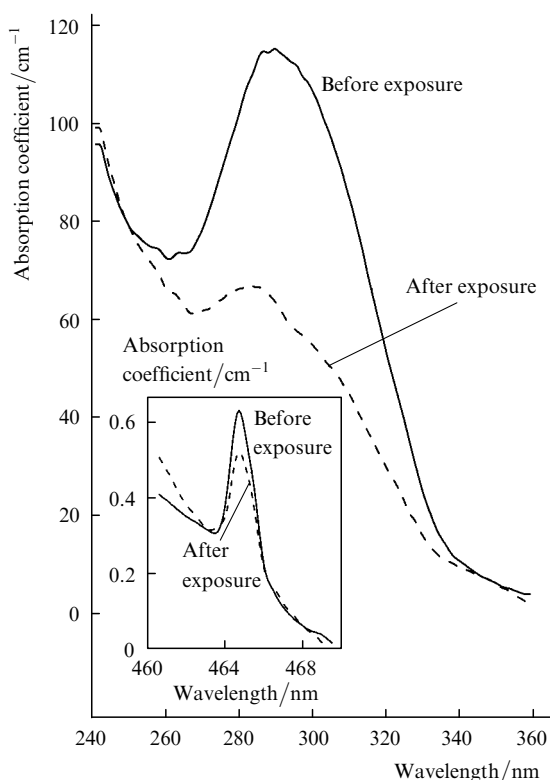
The results of investigations of the decay kinetics of red luminescence upon such excitation are shown in Fig. 3 for various doped matrices. An analysis of the decay kinetic curves (see Table 2) obtained by excitation of Vycor glass, PMMA, PDMS and PP by a mercury lamp shows that the slowest decrease in the PL intensity occurs in PP, while the decrease of the PL intensity in Vycor glass is the fastest. In all the cases considered by us, the observed kinetics corresponds to the same process of photodissociation of  $Eu(fod)_3$  molecules. In all probability, the high efficiency of decay of  $Eu(fod)_3$  molecules in Vycor glass is due to a larger free volume [12, 13] in this material as compared to other materials, which increases the possibility of relaxation of  $Eu(fod)_3$  molecules transformed into new states as a result of irradiation.

It was found by the example of PDMS (Table 1) that such a method of irradiation (see inset to Fig. 2) simultaneously with the efficient decay of red PL ( $^5D_0 \rightarrow ^7F_j$  transitions in  $Eu^{3+}$  ions) leads to a considerable decrease

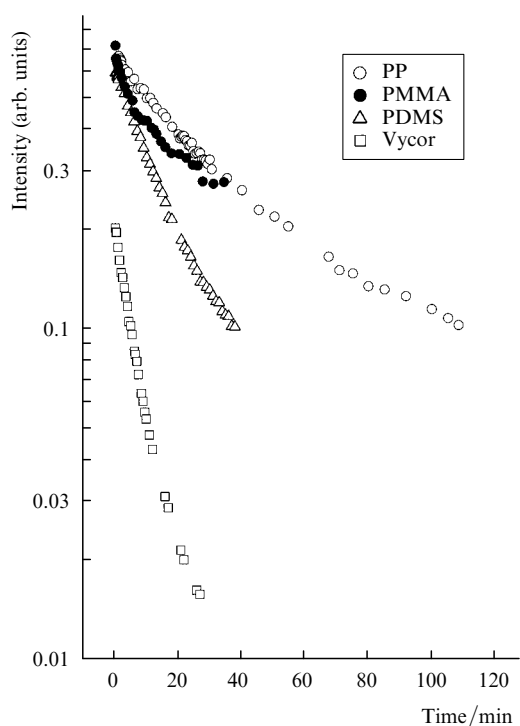
**Table 2.** Data on the kinetics of the PL intensity decay for  $Eu^{3+}$  ions ( $^5D_0 \rightarrow ^7F_j$  transition) during UV irradiation in various matrices.

Matrix	$N/cm^{-3}$	$\alpha L$	DRSh-500		Ar laser			
			$0.1 \text{ W cm}^{-2}$		$1.5 \text{ W cm}^{-2}$		$8 \text{ W cm}^{-2}$	
			$t/\text{min}$		$t_1/\text{min}$	$t_2/\text{min}$	$t_1/\text{min}$	$t_2/\text{min}$
Vycor	$2 \times 10^{17}$	2.3	$6.3 \pm 0.1$	–	–	–	–	–
PMMA	$3.8 \times 10^{18}$	1.8	$9.0 \pm 0.7$	–	–	–	–	–
PDMS	$10^{17}$	0.6	$14.3 \pm 0.2$	–	–	–	–	–
PP	$9 \times 10^{17}$	1.5	$30.6 \pm 0.6$	$0.3 \pm 0.01$	$8.0 \pm 0.8$	$0.1 \pm 0.01$	$4.0 \pm 0.4$	

Note:  $N$  is the  $Eu(fod)_3$  concentration,  $\alpha$  (in  $\text{cm}^{-1}$ ) is the absorption coefficient at  $\lambda = 313 \text{ nm}$ ;  $L$  (in cm) is the optical layer thickness;  $t_{1,2}$  is the time in which the PL intensity decreases by a factor of e; and  $t$  is the 'rapid' PL intensity decay time (the 'slow' decay time was not measured in the case of irradiation by a DRSh-500 lamp).



**Figure 2.** Absorption spectrum of PP before and after irradiation by a DRSh-500 lamp at 313 nm (exposure time 20 min). The inset shows the absorption spectrum of PDMS before and after irradiation by a DRSh-500 lamp at 313 nm (exposure time 60 min).



**Figure 3.** PL intensity decay for  $\text{Eu}^{3+}$  ions ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  transition) during UV irradiation by a DRSh-500 lamp at 313 nm in various samples (Table 1).

in the intensity of both components of the ligand absorption band, as well as of the narrow 464.8-nm absorption band ( ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  transitions of  $\text{Eu}^{3+}$  ions). The obtained result

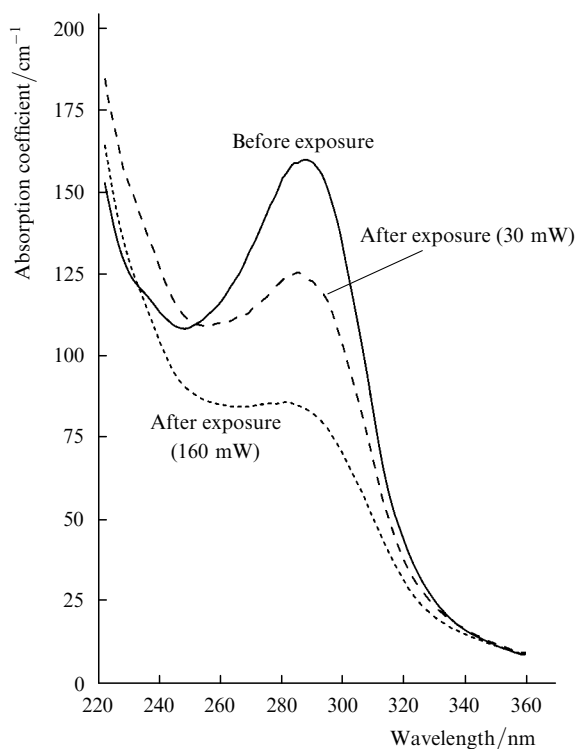
can be attributed to the mechanism of decay of the initial  $\text{Eu}(\text{fod})_3$  complex and a simultaneous change in the charge state of the europium ions ( $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ ). Similar results were presented in [17], where the UV absorption spectra were studied for the solution of  $\text{Eu}(\text{fod})_3$  in  $\text{CH}_2\text{Cl}_2$  before and after UV irradiation at 300 nm. In this case, a decrease in the absorption band intensity of the ligand and an increase in the  ${}^4\text{f} \rightarrow {}^5\text{d}$  absorption band intensity of  $\text{Eu}^{3+}$  ions were also observed.

Such an effect under identical excitation conditions into the singlet absorption band was described in [18] for manganese acetyl acetate complexes  $[\text{Mn}(\text{AA})_3]$  in ethyl alcohol, which have a similar structure and in which the effect of the  $\text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$  transition was observed by the EPR technique. By analysing the absorption spectroscopy and EPR data, the authors of [18] came to the conclusion that the process of charge transfer in Mn ions is accompanied by a transformation of the ligand component with the formation of a radical at one of the ligands. Unfortunately, we were unable to detect the emergence of paramagnetic  $\text{Eu}^{2+}$  ions in PDMS samples exposed to UV radiation under our experimental conditions. Measurements were made at room temperature on a 3-cm RE-1306 spectrometer. The difficulties in the detection of such centres are associated with a large width of the paramagnetic absorption lines themselves due to the presence of two isotopes  ${}^{151}\text{Eu}$  and  ${}^{153}\text{Eu}$  with nuclear spins 5/2 in the composition of europium. In addition, if a radical on a ligand is located in the vicinity of a paramagnetic  $\text{Eu}^{2+}$  ion, the EPR signal may not be detected at all due to strong spin-spin interactions. By the way, such a situation was also considered in [18] for  $[\text{Mn}(\text{AA})_3]$  molecules in frozen ethyl alcohol solutions.

### 3.2 Argon laser irradiation

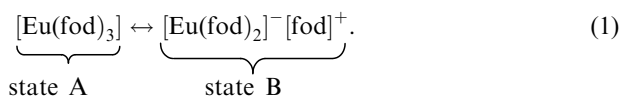
Argon laser radiation used in our experiments also leads to photobleaching of the singlet absorption band of  $\text{Eu}(\text{fod})_3$  molecules. Figure 4 shows the absorption spectra of PP samples doped with this MOC, recorded before and after irradiation. The bleaching effect is quite considerable, especially for a radiation power density of  $8 \text{ W cm}^{-2}$  when the band peak intensity decreases by several times compared to its initial value. In this case, the radiation wavelength is located far from the maximum of the  $\text{S}_0 \rightarrow \text{S}_1$  singlet-singlet absorption band and apparently does not fall into the  $\text{S}_0 \rightarrow \text{T}_1$  singlet-triplet absorption band of the ligand component at 440 nm [19]. We assume that in this situation, the molecule is excited into the ligand-metal charge transfer (LMCT) band at 360 nm. Indeed, measurements of absorption spectra of PP samples with a high concentration of  $\text{Eu}(\text{fod})_3$  molecules (higher than  $10^{19} \text{ cm}^{-3}$ ) revealed absorption in this region that can be attributed to the LMCT band [20]. The intensity of this band is found to be at least two orders of magnitude lower than the intensity of the singlet transition band. Nevertheless, it can be assumed that excitation into this band by high-power laser radiation (more intense than the mercury lamp radiation) leads to the efficient decay of the singlet absorption band and hence to a decrease in the intensity of red PL.

The experimental results presented below and obtained by excitation of samples into this absorption band also reveal certain features of the decay of  $\text{Eu}(\text{fod})_3$  molecules. Figure 5 shows the dependence of the red PL intensity on

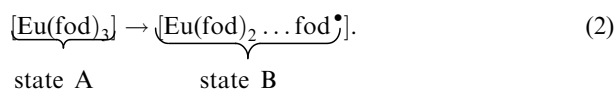


**Figure 4.** Absorption spectrum of PP before and after irradiation by an argon laser at 351 and 364 nm (exposure time 30 min).

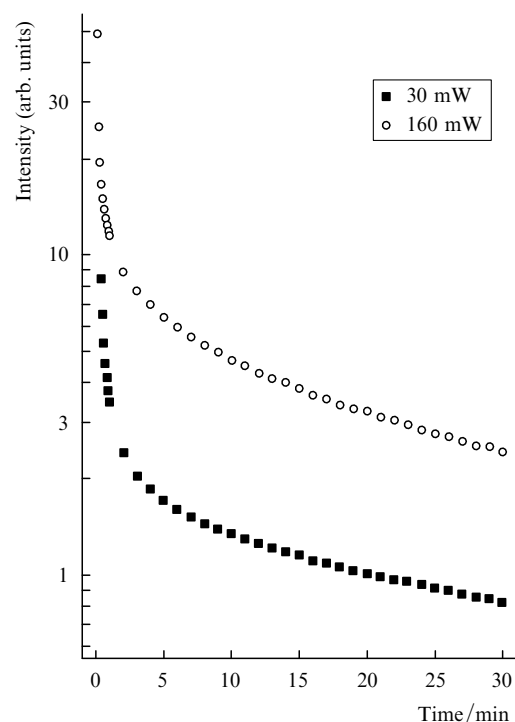
the exposure time of the doped PP sample. As the incident radiation power is increased, the decay efficiency increases but the form of the kinetic curve remains unchanged. In contrast to the above case of mercury lamp irradiation, the curves in this case display a two-stage kinetic decay. The first stage corresponds to a rapid decay and corresponds to a time of the order of 0.1–0.3 min, while the second stage corresponds to a decay over a longer time period, the duration of this stage being an order of magnitude longer (see Table 2). It can be assumed that excitation of molecules by light quanta of different energies leads to two possible types of transformation. One possibility is connected with excitation to the LMCT band as a result of charge redistribution in the molecule itself:



This process corresponds to the stage of the rapid decay. The state B may be reversible under certain conditions (as shown by our subsequent experiments), for example, at room temperature. The second possibility is connected with a higher-energy excitation of MOC to the singlet absorption band of the ligand. In this case, we are dealing with the slow stage of decay of molecules and, apparently, the matrix participates in the stabilisation of the final decay products:



Here, the process of the charge variation  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  is observed simultaneously. Such a reaction was presented in [18] as a possible version of photodissociation of ethyl-alcohol solutions of manganese acetyl acetate molecules upon UV excitation. It is quite possible that prolonged or high-intensity laser irradiation may transform centres from the state B to the final state C and the state B can then be considered as an intermediate state in this case. The above prepositions are confirmed by subsequent experiments involving excitation of doped PP samples with the help of a UV LED.

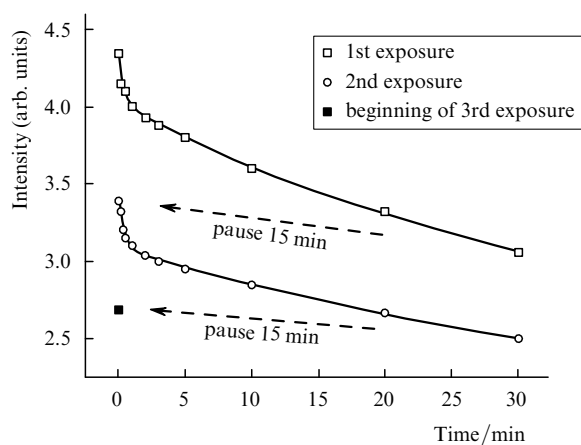


**Figure 5.** PL intensity decay for  $\text{Eu}^{3+}$  ions ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  transition) in PP during UV irradiation by an argon laser at 351 and 364 nm for two radiation powers.

Note in conclusion of this section that the absorption curves recorded in the range 200–400 nm after the end of the rapid stage of the PL intensity decay, coincide in shape with the curves obtained at the slow decay stage. The obtained results indicate that these stages correspond to both forms (basic and hydrolysed [14, 16]) of molecules responsible for the total singlet–singlet absorption band.

### 3.3 UV LED irradiation

Experiments on the observation of the red PL decay kinetics in doped PP samples excited by an UV LED whose wavelength also falls into the LMCT band confirm the reversibility effect for transformed molecules (state B). As in the case of argon laser irradiation, a two-stage decay of PL intensity was observed (Fig. 6). It should be emphasised that the rapid decay stage (state B) was observed upon repetition of switching on/off of the LED with a gradually diminishing reversibility effect. The time between individual exposures, i.e., between the instant of completion of the last act of irradiation and the beginning of the next act, was of the order of 15 minutes. Note that the reversibility effect



**Figure 6.** PL intensity decay for  $\text{Eu}^{3+}$  ions ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  transition) in PP during UV irradiation by a LED at 380 nm for various exposures.

was not observed in samples that were preliminarily exposed to argon laser or mercury lamp radiation.

Thus, the results presented by us indicate that upon a prolonged or high-intensity irradiation (by a UV LED or an argon laser, respectively) into the LMCT band, the process  $\text{A} \rightarrow \text{B} \rightarrow \text{C}$  can occur, i.e., the state B can be treated as an intermediate state for the transformed molecule. In this case, we assume that the final state of a transformed molecule in a two-stage process coincides with the state C, which is analogous to the state B [see reaction (2)], although this statement requires further argumentation. It should be noted that such photoinduced processes for colour centres involving the participation of an intermediate thermally reversible state are well known for certain radiative centres in vitreous  $\text{SiO}_2$  and have been studied experimentally in  $\gamma$ -irradiated silica glass fibres [21].

#### 4. Conclusions

Thus, we have studied variations in the absorption spectra and the PL intensity decay kinetics for  $\text{Eu}^{3+}$  ions ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  transitions) excited by UV laser or incoherent radiation in nanoporous Vycor glass and some transparent polymers doped with  $\text{Eu}(\text{fod})_3$  molecules through supercritical  $\text{CO}_2$  solution. The molecules were excited either into the singlet–singlet absorption band of the ligand (the 312.6-nm and 313.2-nm lines from the mercury lamp) or to the LMCT band of the  $\text{Eu}(\text{fod})_3$  complex (argon laser or UV LED radiation). It was found that in both cases, the decrease in the PL intensity is caused by the decomposition of the ligand component of MOC which, in turn, is manifested in a decrease in the intensity of the singlet–singlet absorption band at 290 nm. The rate of decay upon excitation to the singlet band depends strongly on the type of matrix and is found to be maximum and minimum in Vycor glass and PP, respectively. It was assumed that this effect is associated with an increase in the free volume occupied by  $\text{Eu}(\text{fod})_3$  molecules.

Peculiarities of the mechanism of photodissociation of  $\text{Eu}(\text{fod})_3$  molecules excited to the LMCT band at 360 nm were studied in doped PP samples. It was found that the kinetics of the PL intensity decay has two stages, with the rapid component with the decay time 0.1–0.3 min. The appearance of such a component upon excitation into the

LMCT band points towards certain differences in the mechanism of photodissociation of these molecules for different types of irradiation.

A model has been proposed according to which excitation to the LMCT band is accompanied by a molecular transformation associated with charge redistribution between the ligand part and the rare-earth ion (state B). This process corresponds to the rapid stage of PL intensity decay. Excitation to the singlet absorption band of the ligand leads to stronger variations associated with the formation of a complex of divalent europium and a radical at the ligand (the state C). In this case, the relaxation of the final states of molecules depends on the properties of the matrix.

The obtained experimental results lead to the conclusion that the state B of the molecule is an intermediate state between the initial state A and the final state C. For large UV radiation doses, excitation to the LMCT band may involve a two-stage decay mechanism for  $\text{Eu}(\text{fod})_3$  molecules, i.e.,  $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ . For small radiation doses, a reverse molecular transformation  $\text{B} \rightarrow \text{A}$  may take place.

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