Radiation effects on Eu-complex-doped PMMA and nanosilver compounds after exposure to γ-irradiation

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ABSTRACT

The evaluation of the stability of PMMA/europium (III) complexes with various ligands: 3-thenoyltrifluoroacetonate (TTA), triphenyl phosphine oxide (TTPO) and water assisted by γ-irradiation is the goal of this study. The nonisothermal chemiluminescence (CL) measurements reveal the dependence of this stability on the filler concentration. The values of onset oxidation temperature (OOT) obtained from CL spectra are the basic characterization criteria, which are correlated with the sample composition, the irradiation dose and the environment containing the radiolysis fragments. The systems investigated were the luminescent systems PMMA:Ag:$Eu(tta)_3$ and PMMA:Ag:$Eu(tta)_3(tppo)_2$ obtained from the PMMA doped with europium (III) complexes. The inclusion of silver nanoparticles into the molecular structures of complexes diminishes the rate of oxidation through the mechanism of $RO^{\cdot}$ scavenging by action of the nanosilver. The Europium ion emitter, surrounded by the ligand had Eu(III) luminescence enhancement, rationalized by the local field enhancement produced by the surface plasmons in silver NPs. The results indicate that these materials have optical marker properties for integrating special devices subjected to high energy transfers.

Keywords: Europium complexes, radiochemical degradation, chemiluminescence, irradiation

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1. Introduction

The optical properties of lanthanide complexes attract the extensive attention of several investigators due to their intensities and selectivities (Nehra et al., 2022; Hooda et al., 2023; Dalal et al., 2023). These studies emphasize the importance of molecular architecture containing the fluorinated groups (CF_3) on the optical transitions (Saloutin et al., 2022), which is the basic start point for the involvement in several areas as biomedical applications (Xian et al., 2023), the security anti-counterfeiting and information encryption (Wu et al., 2023 a), the fabrication of security inks or chiral sensing displays (Bispo-Jr et al., 2025), the preparation of supramolecular hydrogels (Ahmed et al., 2024), the manufacture of special nanomagnets (Jankowski et al., 2023), where the emission of photons indicates structural or abnormal states.

The emerging implementations of lanthanide (III) complexes-containing polymers are illustrated by their compatibility allowing the production of high performance materials used in the light-conversion films, organic light-emitting diodes, temperature sensitive bio-imaging applications (Yang et al., 2024), pollution sensors (Du et al., 2024), and many others .

The luminescence of lanthanide ions, whose 4f-4f transitions are implicated, is placed on the near-infrared (NIR) spectral range being influenced by the surrounding ligands (Jin et al., 2020). The Jablonski diagram explains the “antenna effect” of ligand, whose transition from the $^1S_1$ excited state onto triplet $^3T_1$ background state allows the characterization of the material environment interference (Bünzli, 2015). According to the involvement of donor activities of

ligands, the molecular responses illustrate the local interactions showing the sensitive behavior of polymer molecules (Hasegawa and Ishii, 2020). Logically, all the applications involving an energetic transfer, where polymer-based flexible materials are included, have to be sustained by a detailed study on the material resistance under the action of sudden exposure to high energy radiation.

The incorporation of Eu complexes in the bulk of polymers allows us to indicate the structural changes due to the possibility of co-ordination by more than six oxygen atoms (Pan et al., 2006). Eu complexes hosted in the polymer matrix of poly(methylmethacrylate) (PMMA), a transparent material, can afford several optical implementations. Their red emission placed at 615 cm^{-1} is an interesting way for the interpretation of component interaction with the environment, being a reliable tool of structural investigation. Though the stability study accomplished on the polymer composites has been reported (Foster et al., 2009; Rao et al., 2010; Kalyani et al., 2013; Łyszczek, et al., 2019, Yu et al., 2019; Essahili et al., 2024; Parra et al., 2024), the radiation effects describing on the stability evaluation was not performed yet. Due to the medical applications of Eu(III) complexes (Hooda et al., 2022), the development of bioimaging for cytoplasmatic assays (Wu et al., 2023 b), specific biological investigations into metabolic cycles (Syamchand and Sony, 2015), the advanced proved stability is demanded, as it was earlier demonstrated by copper complexes (Zaharescu et al., 2016). The probing of polymer stability is based on the electronic interaction between the inorganic structure, where the central atom Eu (III) has a free inner orbital and the radiolysis fragments, which possess a free unpaired electron (Shurygin et al., 2021). This interaction investigated by an appropriate method like chemiluminescence (Rychlý et al., 2011) reveals the modifications that occur in polymer matrices, when the exposure to the scission action of ionizing radiation produces serious structural changes.

The present paper offers the behavior details on the structural alterations occurred in poly(methyl methacrylate) due to the interactions with various Eu(III) complexes providing different electronic densities around the central atoms. This assay accomplished by the radiation processing completes the previous studies on the radiation effects on PMMA (Güven and Uzun, 1993; Lin et al., 2003; Barton et al., 2013; Tiwari et al., 2014; Bo et al., 2016; Bel et al., 2019; Pickler et al., 2021; Michelas et al., 2024).

2. Experimental

The complex [Eu(tta)3(tppo)2] was obtained by dissolving the complex [$Eu(tta)_3(H_2O)_2$] in acetone, followed by the addition of the secondary ligand already dissolved in a stoichiometric ratio of complex:secondary ligand equal to 1:2.

5.1 mg of [$Eu(tta)_3(H_2O)_2$] dissolved in 5 mL of acetone were added, followed by 10.0 mg of the secondary ligand tppo dissolved in 5 mL of acetone. The two solutions were mixed and stirred for an hour and a half under heating to evaporate the solvent. After drying, the complex [$Eu(tta)_3(tppo)_2$] was stored in a vacuum desiccator. After the development of films doped with the precursor complexes $Eu(tta)_3(H_2O)_2$ and secondary complexes $Eu(tta)_3(tppo)_2$, films were developed for encapsulating the silver nanoparticles, with the need to modify the dissolution of the complex. In this step, the silver nanoparticle solution was mixed with the solvent N,N-dimethylformamide. Then, a PMMA solution containing 0.500 mg of PMMA in 10 mL of acetone was developed. The solution was heated to 80 °C under constant stirring. The films of the luminescent systems PMMA:Ag:$Eu(tta)_3$ and PMMA:Ag:$Eu(tta)_3(tppo)_2$ was prepared using the casting method, followed by evaporation of the solvent with the aid of a hot plate at a temperature of 60 °C. The ligands of 3-thenoyltrifluoroacetonate (TTA), triphenyl phosphine oxide (TTPO) structures are presented in Fig.1.

The radiation exposure was accomplished by γ-processing in the irradiation unit provided with ^{60}Co source (Ob Servo Sanguis, Budapest, Hungary). The dose rate was 0.5 kGy h^{-1}, which is suitable for the degradation experiments. Three doses (0, 25 and 50 kGy) were taken into consideration for the characterization of thermal and radiation resistances of composite specimens.

The chemiluminescence (CL) measurements were carried out with LUMIPOL produced by Institute of Polymers, Academy of Sciences, Bratislava (Slovakia). The nonisothermal method was preferred, because it allows the accurate evaluation of thermal stability by sweeping the assay range from room temperature up to 250 ^{o}C (Matisova – Rycha and Rychly, 1996). The selected heating rates were 5, 10, 15 and 20 ^{o}C. These determinations provide the values of onset oxidation temperature (OOT) and afford the comparison of thermal strength shown by various analogous compositions on medium and high temperature ranges. The CL measurements were performed immediately after the end of the exposure irradiation, because the accurate evaluation of stability must be addresses to all types of radical including the short life intermediates.

3. Results and discussion

The involvement of Eu(III) complexes in the finding optimal solutions for the identification of radiation effects on polymers is a promising way by which inorganic phase allows to identify the occurred structural modifications (Mensati at al., 2022; Erkarslan et al., 2024). In this regard, the flexible composites seem to be appropriate (Foster et al., 2009). The lack of this approach is now filled by the present assay, which extends the vision on the resulting interaction between various structures of Eu(III) complexes with radiolysis intermediates of poly(methylmethacrylate).

The initiation and propagation of oxidative degradation are important steps in the applications of the studied composites as optical substrates (Zhang et al., 2021), functionalization of fiberglass paper (Li et al., 2024), preservation of cultural relics (Lv et al., 2023) or sensors for

the production of optical thermometry (Zou et al., 2021). Fig. 1S affords to be emphasized the small dissimilarities between the progresses in the thermal degradation testing on our unirradiated composites. The smooth increase in the CL emission intensities individualizes the behavior of the studied composites by similar augmentation of signal by which the oxidation process is accelerated as the sample temperature is growing. The dissimilar degradation comportments of analogous samples with different filler concentrations illustrated by the atypical behavior of some isolated examples (Fig. 1S) allows to assume that the competition between complex particles for the interaction with radiolysis intermediates influences the mitigation in the accumulation of the inactivated oxidation precursors. The increase in the loadings of europium complex produces the promotion of polymer ageing due to the local hindering of scavenged radicals.

The radiolysis mechanism of PMMA was previously depicted (Zaharescu and Jipa, 2013) as an acrylic representative polymer. The appeared free radicals are formed with a scission yield value of 1.5 (Yoshida and Ichikawa, 1995). Under this circumstance, the Eu(III) complexes surrounded by the radiolysis intermediates are subjected to the modification of their electron density arounding central atom. Accordingly, the development of degradation is described by the variation of emission CL intensity that follows the structural changes. The estimation of oxidation degree reached in the polymer phase during the stability assays becomes possible by the determination of the onset oxidation temperature, the value that indicates the temperature of starting oxidation due to the surpassing the minimal intensity threshold of measurement sensitivity (Rychlý et al., 2001, Zaharescu et al., 2024).

The influence of ligand distributions around Eu central atoms on the radiation stability of PMMA-based composites may be learned from Fig. 2. The common feature that characterizes the CL emission from the radio-oxidizing polymer is the generation of molecular fragments possessing

the unpaired electrons. In the nonisothermal CL spectra of PMMA/Eu complex samples an emission peak is placed at 119 °C. It indicates the formation of some carbon centered radicals as it is suggested in Fig. 3 (Tabata and Sohma, 1980; Chang and La Verne, 2001; Tiwari et al., 2016). The differences between the stabilities of PMMA composites may be caused by various structural factors; the polarity of surrounding ligands, the radical concentrations placed around complex particles, the unlike values of the diffusion coefficients describing the feeding degradation by oxygen, the assumed radiation effects on the decomposition induced in the added Eu(III) compounds. When the unirradiated samples do not show this peak, its heights increase with dose in the exposed samples. This essential statement demonstrates that the presence of radiolysis fragments influences in a large extent the evolution of degradation by their interaction with inorganic particles.

As it is presented in Table 1, the action of γ-radiation on PMMA/Eu(III) complex specimens is recognized by the stability differences between the inorganic structures in the presence or lack of silver nanoparticles significantly revealed at 50 kGy. The stabilization efficiency of Ag loadings is demonstrated everywhere (Alcântara et al., 2020; Nikolić et al., 2023). The integration of this component into the present composites brings an essential assistance in the mitigation of radiation oxidative degradation. While the accumulation of radical occurs at a certain threshold, the increasing amounts of complexes in the composite formulations diminished the oxidation consequences. Fig. 4 exemplifies this ascertainment by which the silver stabilization activity is demonstrated.

The susceptivity of polymer to the sustainment of oxidative degradation may be appreciated by the comparison between the influence of filler concentration on the attained degradation degrees or the rate of oxidation at the inspecting doses for increasing temperatures. While the amounts of

Eu (III) complexes determine the decrease of the starting oxidation temperatures, the discrepancies between the progresses of oxidation for various compositions at 50 kGy become larger. This assessment is valid either for the structures consisted of TTA and TPPO, or for the compositions including water molecules. The enlarging of the temperature basic line for hydrated Eu(III)complex, where the water molecules are constitutive parts of complexes, is explained by the sustained polarization effects. This activity associated with the acceleration of oxidation during the propagation stage is promoted by the charge carrier fragments, which surround the central atoms and modify the electronic density on it. The direct consequences of these interferences are the basic argument for the unlike thermal behavior of PMMA/Eu(III) complex composites. These presented results are the consequences of redox interactions between radiolysis fragments and nanosilver as a RO· scavenger. The central metal, because the rigidity of the system Eu(III) and ligands TTA and TPPO, is not altered by RO·. Nanosilver enhances the Eu(III) luminescence via the balance between high local field gradients and ion-to-NPs energy transfer effects, and consequently luminescence enhancement is observed in the presence of Ag-NPs. (Couto dos Santos et al. (2016), Malta et al. (1985), Carneiro Neto et al. (2019).

Figure 2S

4. Conclusion

The stability investigation of γ-irradiated PMMA/Eu(III) complexes that include various ligands (TTA, TTPO and water) states the electronic interaction between central atoms of Eu and the radical intermediates formed during the radiolysis of polymer substrate. The concentration of complexes in the studied composites played an essential role in the control of degradation rate. The dissimilarities in the development of oxidation for various compositions are ascribed to the

polarization of electrons in the coordination sphere. PMMA doped with nanosilver, under irradiation, showed more stability than PMMA doped without nanosilver, confirming the scavenger activity of nanosilver.

Both properties are observed with the insertion of nanosilver in luminescent polymer system Eu: 1) Before irradiation - Enhancement of luminescence by the presence of nanosilver, and 2) During irradiation - RO$^{\bullet}$ scavenger of the nanosilver in the system PMMA doped with europium (III)complexes. Unlike europium-doped glass materials, in which the viscosity is much higher compared to PMMA polymer, the mobility of silver nanoparticles in the polymer should, as we assume, guide them to operate by both mechanisms.

The increase in CL emission intensities as the dose is increased demonstrates the essential effects of composition and abundance of degradation intermediates on material stability. These arguments should be considered when these flexible composites are subjected to sustained energy transfer. The results demonstrate that the durability of these composite products is directly influenced by the material history, as well as by the oxidation resistance of the polymer. In this sense, the results indicate that these materials have optical marker properties for integrating special devices subjected to high energy transfers.

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CRediT authorship contribution statement

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T. Zaharescu: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis. **D. F. Parra**: Investigation, Conceptualization,

Formal analysis, Methodology, Data curation, Writing – original draft, Validation, Supervision. **A. B. Lugão**: Writing – review & editing, Visualization, Validation, Resources and **V. S. Lima**: Investigation, Methodology, Formal analysis.

DATA AVAILABILITY – The data will be made available upon request.

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Figures

Fig. 1. Molecular structures of organic ligands.

Fig. 2. The nonisothermal CL spectra recorded on the PMMA modified with Eu (III) complexes and, partially, Ag nanoparticles at various irradiation γ-doses.

Heating rate:10 ^{o}C min^{-1}

(1) 0 kGy; (2) 25 kGy; (3) 50 kGy.

(2) (a) P 1; (b) P 2; (c) P 3; (d) P 4; (e) P 5; (f) P 6; (g) P 7; (h) P 8; (i) P 9; (j) P 10; (k) P 11; (l) P 12.

Fig. 3. Scheme illustrating the radiolysis of PMMA

Fig. 4. The nonisothermal CL spectra recorded on some PMMA/Eu(III) complexes composites.

Heating rate: 5 ^{o}C min^{-1}

(a) PMMA[Eu(TTA)$_3$(TTPO)$_2$], (b) PMMA[Ag/Eu(TTA)$_3$(TTPO)$_2$],

(c) PMMA[$Eu(TTA)_3(H_2O)_2$], (d) PMMA[$Ag/Eu(TTA)_3(H_2O)_2$]

Complex concentrations: (1) 5 wt%, (2) 7 wt%, (3) 10 wt%, (4) 0.5 wt%, (5) 1 wt%.

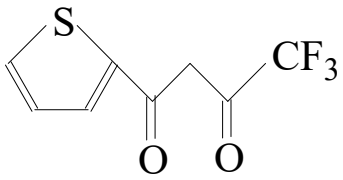
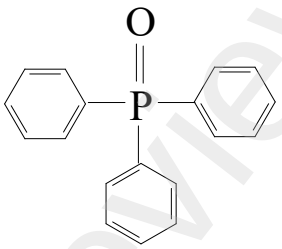
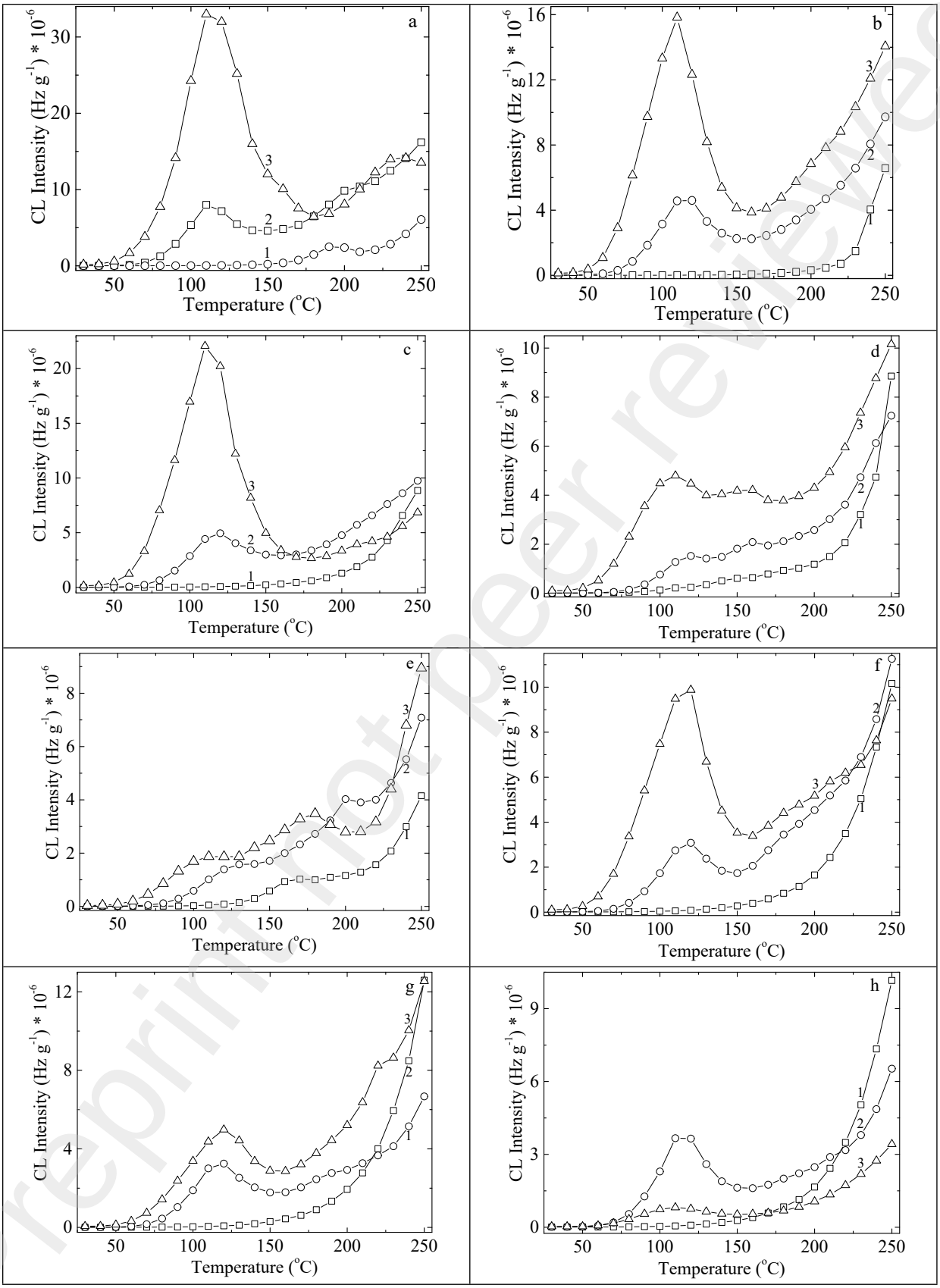
	
3-Thenoyltrifluoroacetonate (TTA)	Triphenyl phosphine oxide (TTPO)

Fig.1.



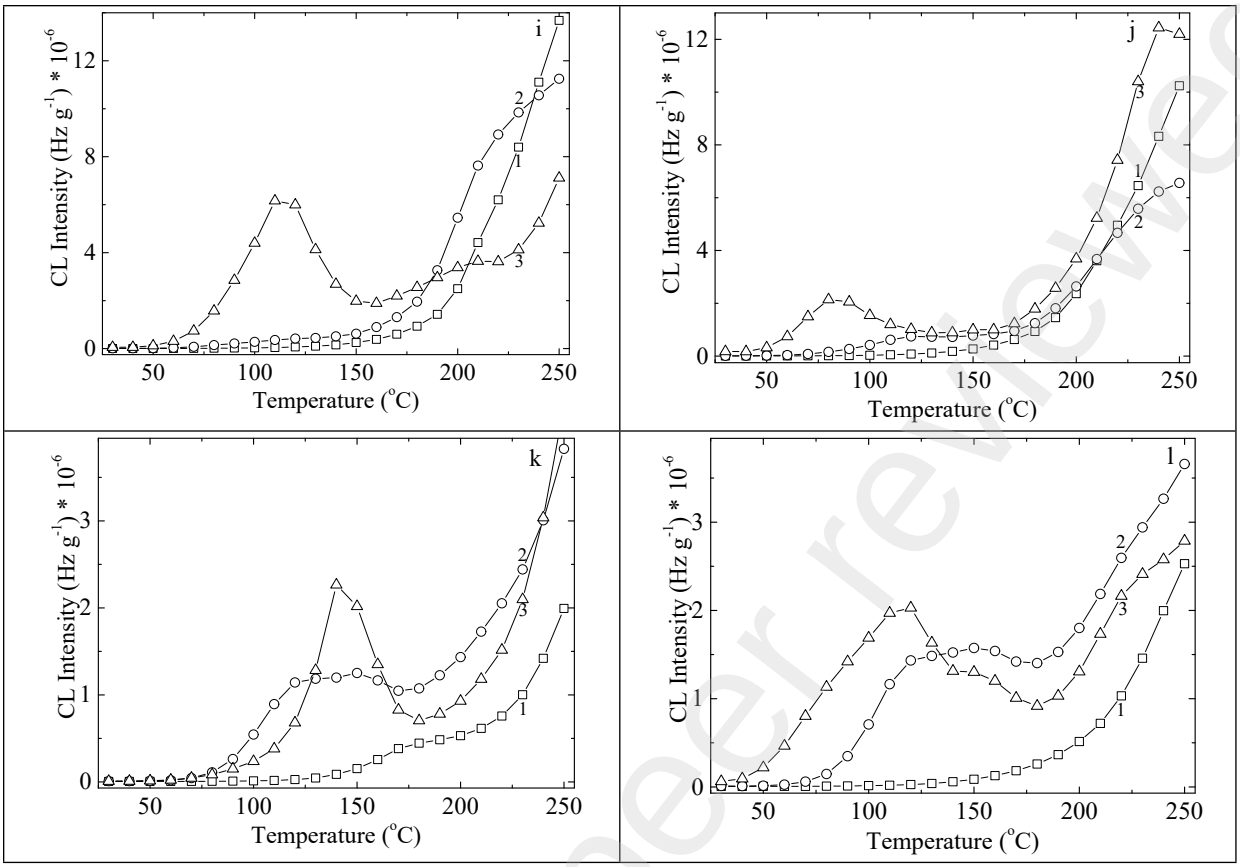


Fig. 2.

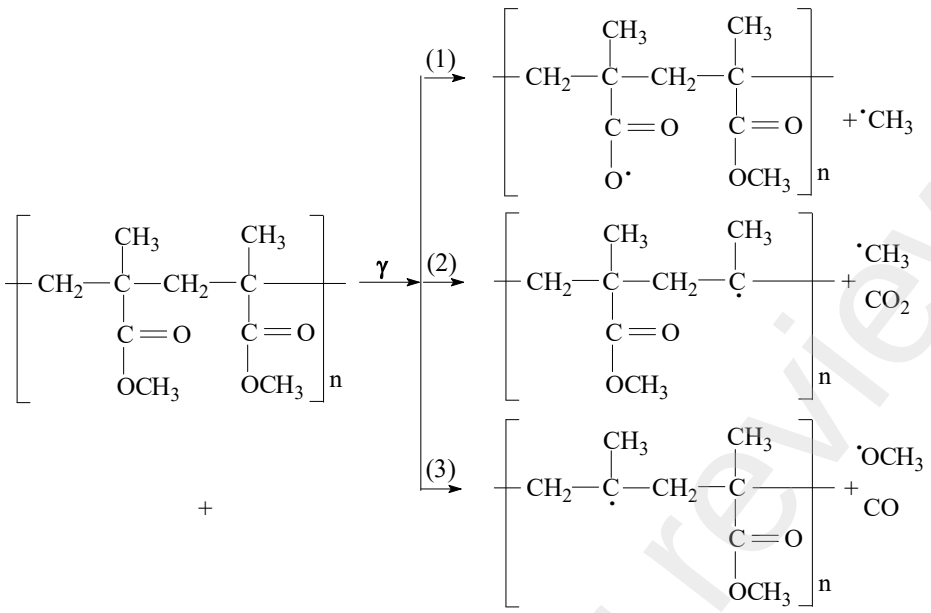


Fig. 3.

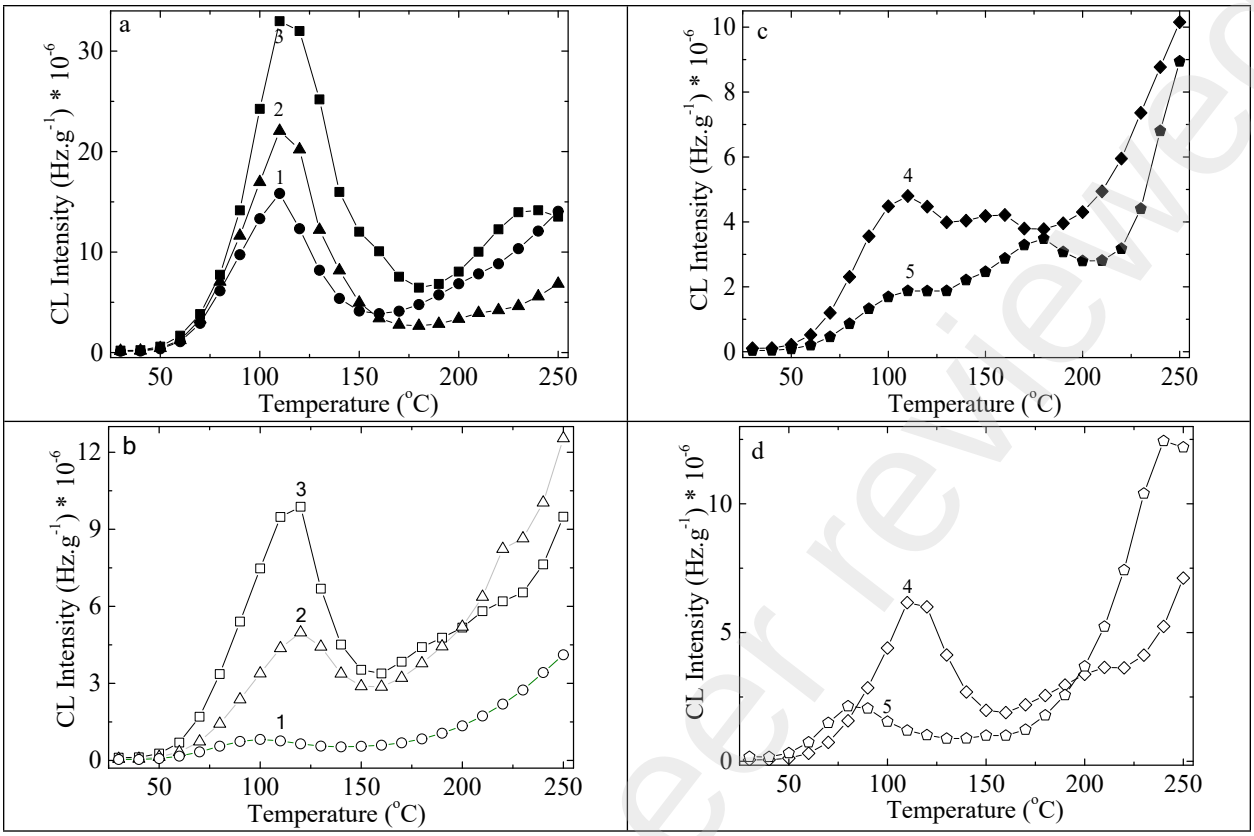


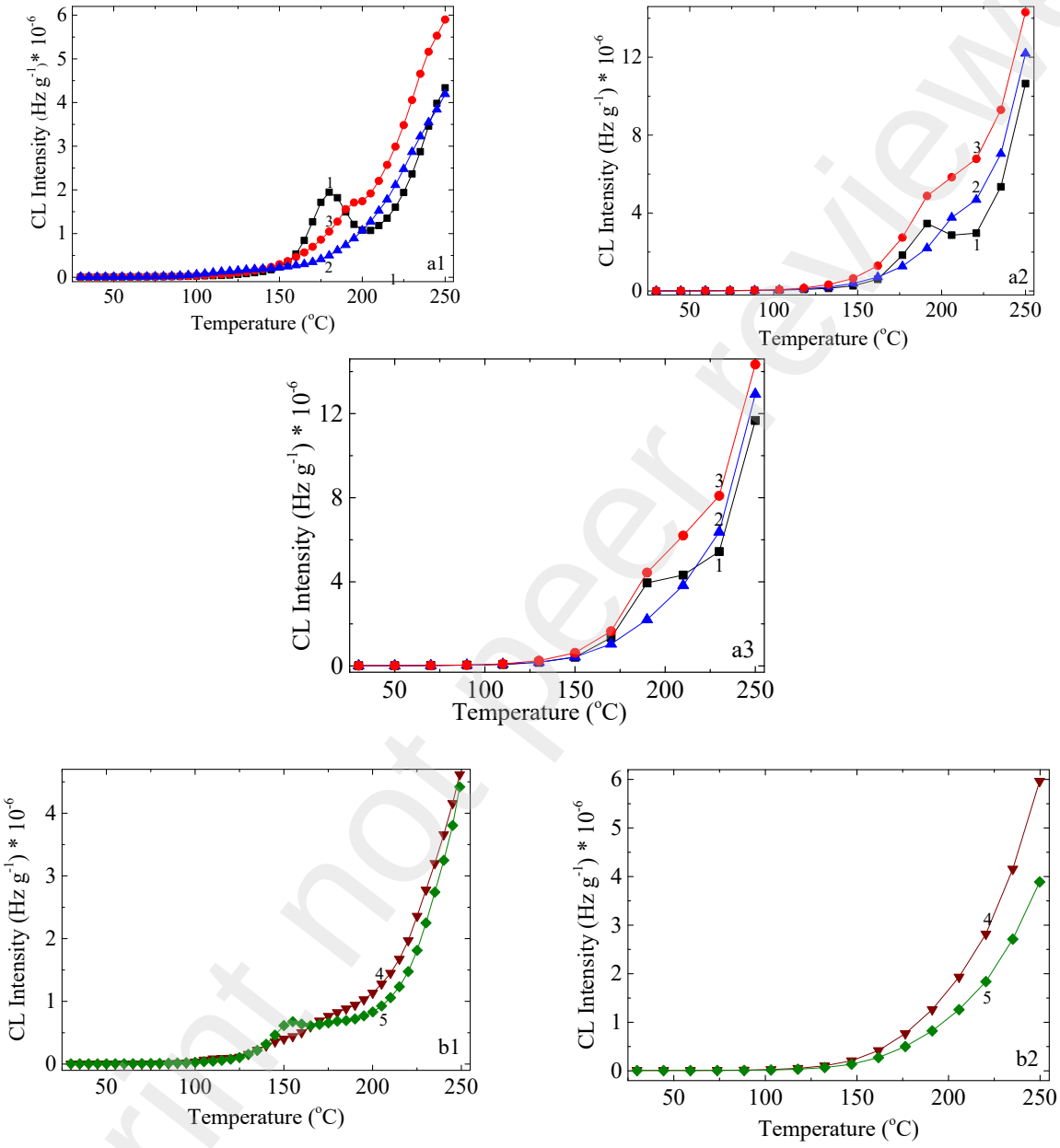
Fig. 4.

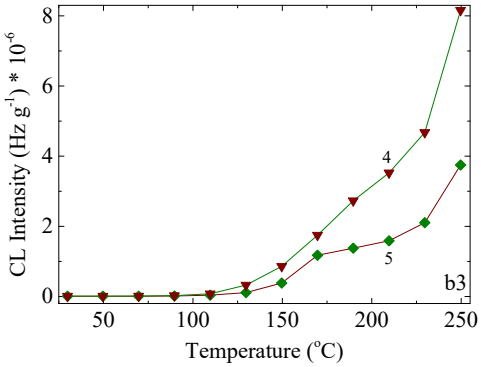
Table 1. The compositions and two parameters for the oxidative degradation of PMMA modified with Eu(III) complexes

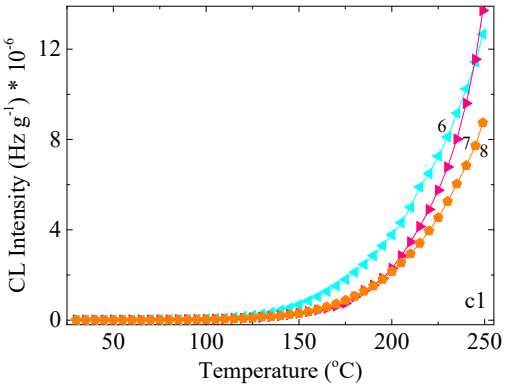
Identification number	Formula	Complex concentration (wt%)	OOT (°C)	I_{CLmax} at 118°C (Hz g^{-1}).10^6	
				25 kGy	50 kGy
P 1	PMMA[$Eu(TTA)_3(TTPO)_2$]	5	165/218	8.5	33.2
P 2		7	180	4.2	15.8
P 3		10	183	4.5	24.1
P 4	PMMA[$Ag/Eu(TTA)_3(TTPO)_2$]	0.5	210	1.5	4.8
P 5		1.0	142/215	1.7 [a]	1.9 [b]
P 6		5	185	2.9	9.8
P 7		7	172	3.5 [c]	4.8 [c]
P 8		10	160	0.8	2.6
P 9	PMMA[$Eu(TTA)_3(H_2O)_2$]	7	184	0.4	6.1
P 10		10	180	0.5	2.3
P 11	PMMA[$Ag/Eu(TTA)_3(H_2O)_2$]	0.5	146/204	1.3 [d]	2.6 [d]
P 12		1.0	190	2.1 [d]	1.6 [c]

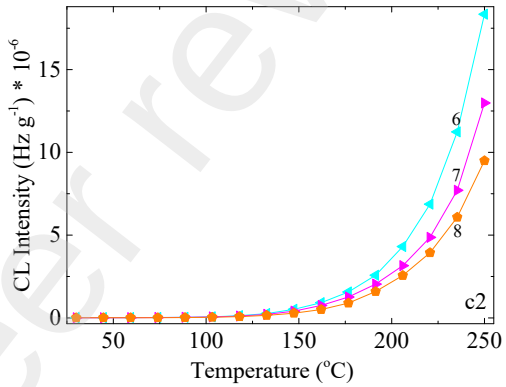
[a] peak @ 128 °C; [b] peak @ 175 °C; [c] peak @ 125 °C; [d] peak @ 145 °C

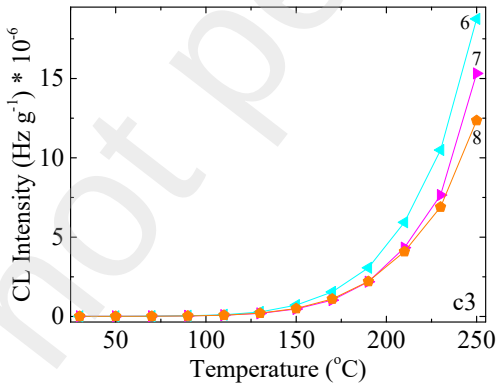
Figure 1 S.

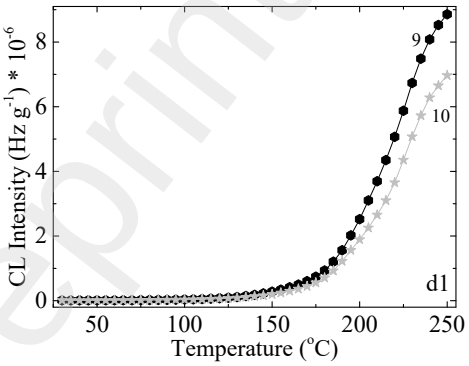


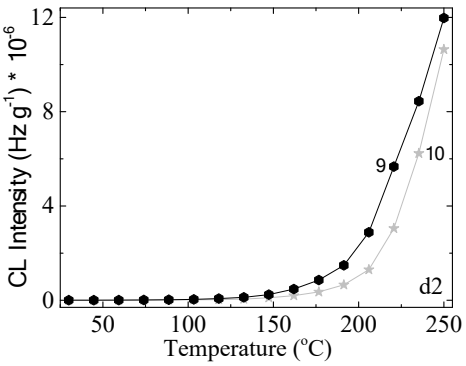












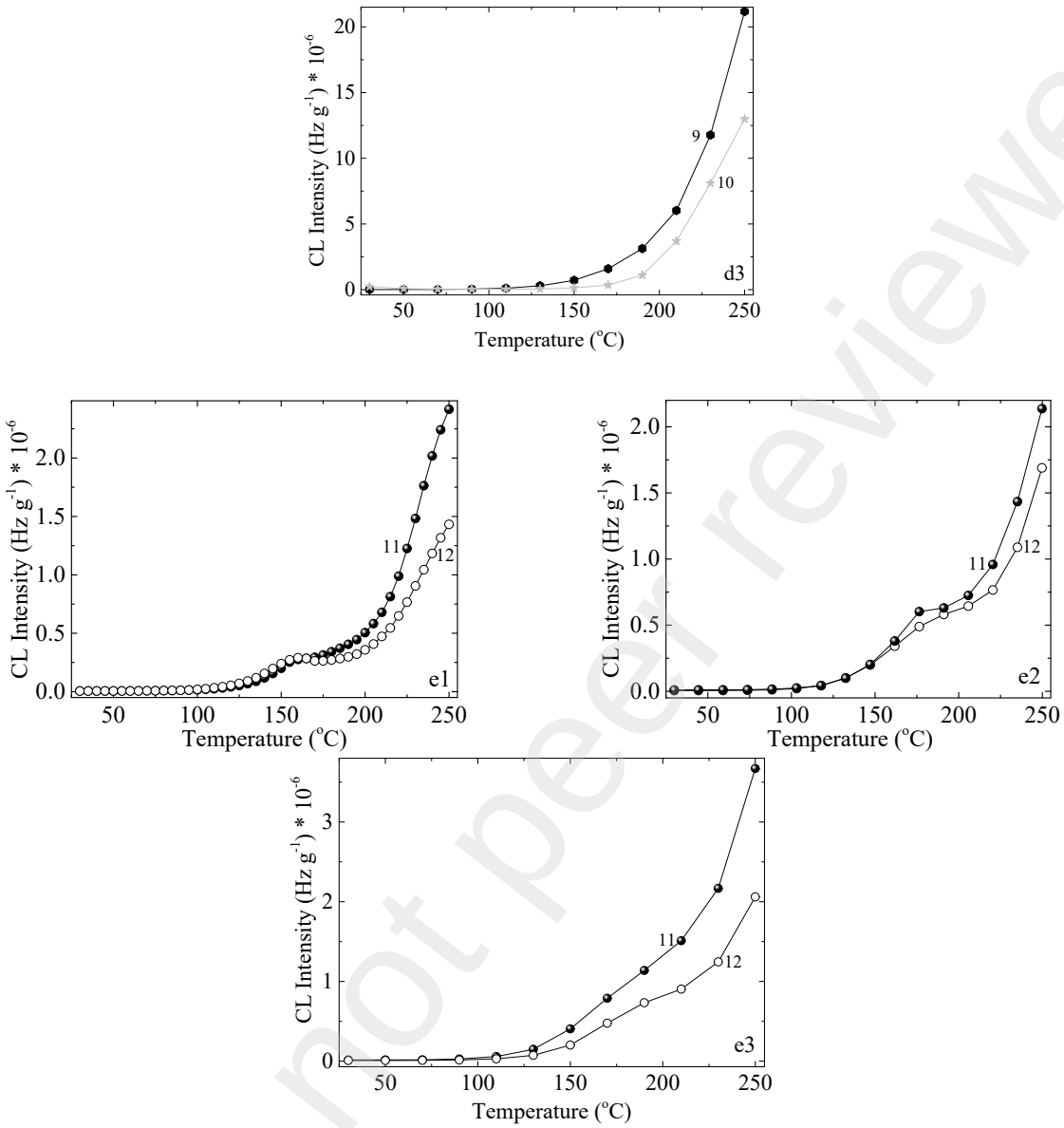


Figure 1 S. The nonisothermal CL spectra recorded on the unirradiated europium complexes.

The numbers of the curves represent the number of samples.

Heating rates: 5 ^{o}C min^{-1} (a1, b1, c1, d1, e1), 15 ^{o}C min^{-1} (a2, b2, c2, d2, e2), 20 ^{o}C min^{-1} (a3, b3, c3, d3, e3).

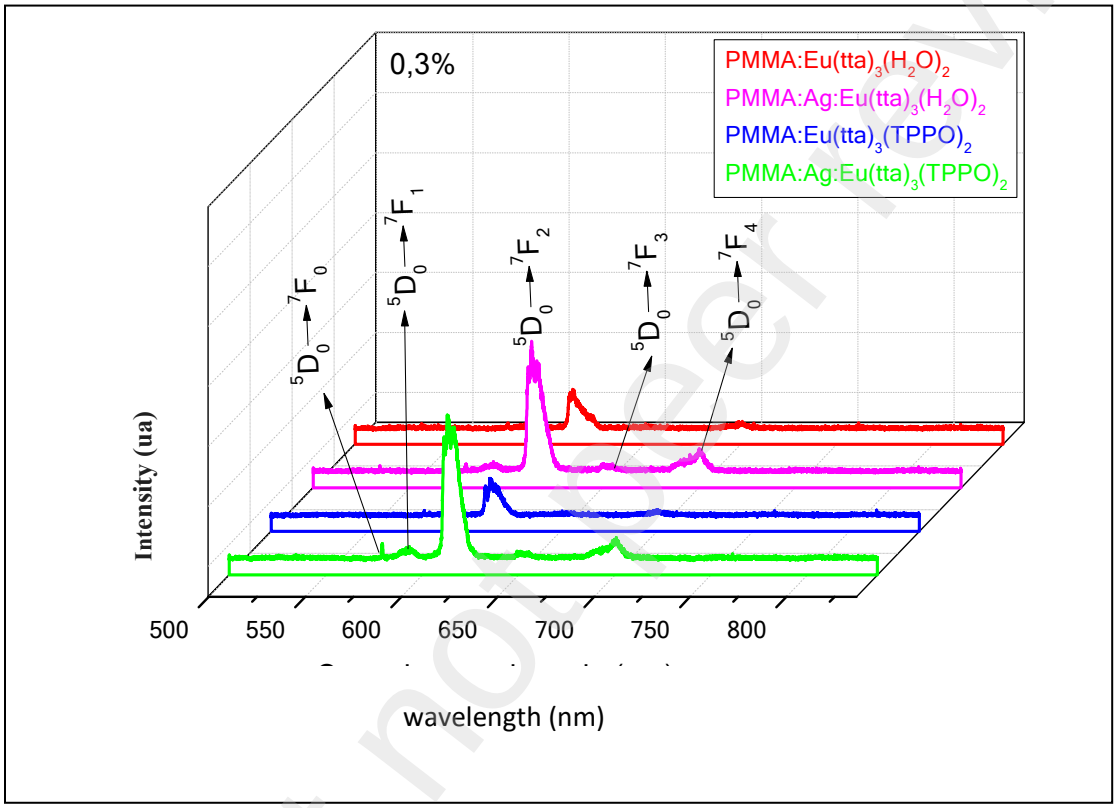


Figure 2 S. Emission spectra of PMMA:$Eu(tta)_3(TPPO)_2$ and $Eu(tta)_3(H_2O)_2$ in concentration of 0,3%, with and without silver nanoparticules Ag°. Spectra recorded in the interval 550 to 750 nm under excitation of 350 nm, and 25°C. For both PMMA(tta)3$(H_2O)_2$, and PMMA:$Eu(tta)_3(TPPO)_2$ the presence of Ag° intensify the luminescence.