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IR Luminescence of Nd^{3+}, Sm^{3+}, and Yb^{3+} β-Diketonates in Different Aggregate States

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Abstract—The influence of the aggregate state on the IR luminescence is studied for the Nd(III), Sm(III), and Yb(III) complexes with the thienyl, phenyl, and alkyl derivatives of acetylacetone in solutions and as sorbates on the polymer matrix. It is found that the luminescence intensity of the sorbates of the complexes is 2–3 orders of magnitude higher than that in solutions due to the elimination of diffusion and respective intermolecular nonradiative losses of the excitation energy.

Keywords: lanthanide β-diketonates, IR luminescence, aggregate state

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INTRODUCTION

Lanthanide ions (Ln^{3+}) chelated by β-diketones represent a unique class of compounds exhibiting luminescence in the visible and near-IR spectral ranges. The luminescence properties are most widely studied for the Eu(III) and Tb(III) complexes (red and green luminescence) [1–4], whereas they are studied to a lower extent for the Nd(III) and Yb(III) β-diketonates emitting in the IR spectral range [5–10]. Studies on the IR luminescence of Sm(III) β-diketonates are nearly lacking, although its intensity is comparable with that observed in the visible spectral range.

The deuteration of ligands at the central carbon atom and the introduction of long fluoroalkyl substituents (R_F) result in the enhancement of the luminescence of Ln(III) β-diketonates [11] and hydrophobicity of the ligands, which causes the displacement of the water molecules ("OH-oscillators") from the internal coordination sphere of the complex and a decrease in intramolecular nonradiative losses of the excitation energy [12–15]. An increase in both the luminescence intensity and lifetime (τ) was shown for the Nd(III) complexes with various fluorine-substituted derivatives of acetylacetone (AA) in a series of R_F: CF_3–C_3F_7–C_6F_{13}–C_8F_{17}. In the case of the heteroligand complexes containing 1,10-phenanthroline, the increase is 1.6–11.5 times higher than that for $Nd(\beta d)_3$ [7]. A consecutive increase in the quantum yield (φ) and τ of luminescence of the Yb(III) complexes is observed in the same series of β-diketones [16].

The bis(β-diketones) forming binuclear complexes with Ln^{3+} ions were synthesized [10] in order to observe the high-intensity luminescence of Nd^{3+} and Sm^{3+}. The found luminescence quantum yield of Nd^{3+} was 0.3%.

The decrease in the luminescence of the Ln(III) complexes in solutions is due not only to intramolecular nonradiative losses of the excitation energy. It was mentioned [17, 18] that diffusion processes predominated in liquid media resulting in collisions of molecules and nonradiative transfer of the excitation energy via cross relaxation. It was shown [19] using the Tb(III) complexes with pyrazolones-5 and pyrazolecarboxylic acids that the elimination of intramolecular losses of the energy led to a threefold increase in the luminescence intensity, whereas the increase is 50 times if intermolecular losses are excluded. That is why, Ln(III) β-diketonates are used in the solid state (sorbates, films) [6, 20].

The purpose of the present study is to reveal the influence of the aggregate state of the Nb, Sm, and Yb β-diketonates in the series solution–sorbate on polymethyl methacrylate (PMMA) on the IR luminescence of Nd^{3+}, Sm^{3+}, and Yb^{3+}.

EXPERIMENTAL

α-Thienyl, phenyl, and alkyl derivatives of AA with different chain lengths and structures of R_F, including that with the included oxygen heteroatom, were used. The AA derivatives containing three and more carbon atoms in R_F were synthesized using a described procedure [21]. The content of the major substance was not lower than 99%. They were identified by IR spectroscopy, ^1H NMR spectroscopy, gas liquid chromatography, and elemental analysis. The rest β-diketones used and other reagents were reagent grade or analytical grade.

The starting 1×10^{-2} M acetone solutions of β-diketones and PMMA were prepared using exact weighed samples of the preparations. The starting 1×10^{-2} M solutions of Nd^{3+}, Sm^{3+}, and Yb^{3+} were prepared by the treatment of weighed samples of their oxides with HCl followed by the evaporation of its excess and dissolution of the dry residue in water. Solutions with a lower concentration were prepared by the dilution of the initial solutions with the corresponding solvent.

Sorbates of the complexes on PMMA were prepared by the addition of an acetone solution (0.5 mL) of PMMA (5 mg/mL) to an aqueous solution of the complex (5–10 mL) and stirring for 10–15 s. After this, PMMA was isolated as thin filaments forming a ball, which was separated and placed in a cell for solid samples with a diameter of the hole of 8 mm, and luminescence was detected.

Acetate–ammonia buffer solutions were used to achieve a necessary pH. The acidity of the medium was monitored using a pH-150MA pH-meter–millivoltmeter.

The excitation and luminescence spectra of the complexes were recorded on an SDL-1 spectrometer (LOMO, Russia) with a DRSh-250 mercury–quartz lamp and on a Fluorolog FL3-22 Horiba Jobin Yvon spectrofluorimeter (France) with a 450 W xenon lamp. All measurements were carried out at room temperature (21–23°C). The luminescence spectra of Sm^{3+} ions were recorded in the range 850–1000 nm with $\lambda_{max} = 950$ nm (transition ${}^4G_{5/2} \rightarrow {}^6F_{5/2}$), those of Nd^{3+} ions were recorded in a range of 850–1100 nm with λ_{max} = 898, 903 nm (${}^4F_{3/2} \rightarrow {}^4I_{9/2}$) and also 1060 nm (${}^4F_{3/2} \rightarrow {}^4I_{11/2}$), and the spectra of Yb^{3+} ions were recorded in a range of 950–1100 nm with λ_{max} = 980 nm (${}^2F_{5/2} \rightarrow {}^2F_{7/2}$).

The luminescence of solutions of the complexes was detected in a quartz cell (l = 10 mm), and that of the sorbates of the complexes on PMMA was detected in a cell for solid samples. The energies of triplet levels of organic reagents were calculated from the phosphorescence spectra of the gadolinium complexes with the corresponding organic ligand at 77 K [2].

RESULTS AND DISCUSSION

The list and characterization of β-diketones used in the work are presented in Table 1. Since the luminescence of the Ln(III) complexes is due to the energy transfer from the ligand in the excited state to the metal, it is important that the energy of the triplet level of the ligand would be higher than the emitting level of lanthanide. In this case, E_{T1} of the used β-diketones is higher than the energy of the emitting levels of Sm^{3+} (17900), Nd^{3+} (11500), and Yb^{3+} (10200 cm^{-1}).

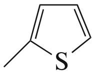
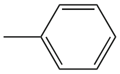
The excitation and luminescence spectra of solutions of the Sm^{3+} complexes with the thienyl and phenyl derivatives of AA are presented in Fig. 1. The luminescence spectrum of Sm^{3+} contains two bands with maxima at 885 and 950 nm corresponding to the transition ${}^4G_{5/2} \rightarrow {}^6F_{5/2}$. A more intense band with λ = 950 nm is used for the analytical determination of Sm^{3+} in the IR spectral range [22]. A comparison of the spectra shows that the intensities of both excitation (Fig. 1a) and luminescence (Fig. 1b) increase with the elongation of R_F from $-CF_3$ to $-C_6F_{13}$ and $-C_8F_{17}$ (cf. spectra *1* and *2*, *4* and *6*).

It is seen for the Nd(III) complexes as an example (Fig. 2) that not only the elongation of R_F but also the character of the cyclic substituent ("photoantenna") affect on the luminescence of the complexes (cf. spectra *1* and *2*). The introduction of the oxygen heteroatom into R_F and shortening of the substituent length (cf. plots *1*, *2*, and *3*) result in a substantial decrease in the luminescence at 898 and 903 nm (transition ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$) and 1060 nm (${}^4F_{3/2} \rightarrow {}^4I_{11/2}$).

Unlike all Ln^{3+} exhibiting luminescence in the IR spectral range, the Yb^{3+} ion is characterized by the lowest nonradiative losses of the excitation energy due to one emitting level and one ground level [23]. Its luminescence maximum at 980 nm is caused by the transition ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$. The excitation and luminescence spectra of solutions of the Yb(III) complexes with some thienyl and phenyl derivatives of AA are presented in Fig. 3. As in the case of the Nd(III) and Sm(III) complexes, the elongation of R_F results in an increase in the radiation intensity (cf. spectra *1* and *2*, *3* and *4*, *5* and *6*). The influence of the aggregate state on I_{lum} is seen for the Yb(III) complexes with the phenyl derivatives of AA (Fig. 4). The spectra of these complexes in solutions (Fig. 4, insets) are presented for comparison with the excitation and luminescence spectra of the complexes in the form of sorbates on PMMA. The spectra are similar in shape, while their intensities differ by an order of magnitude and more.

These changes in the luminescence of the Nd(III), Sm(III), and Yb(III) complexes with the studied thienyl, phenyl, and alkyl derivatives of AA in solutions and in the form of sorbates on PMMA are presented in Table 2. In the case of solutions of the complexes, the luminescence intensity of Nd^{3+}, Sm^{3+}, and Yb^{3+} increases with the elongation of R_F. This is observed for the compounds with both the thienyl and phenyl and alkyl derivatives of AA. The pattern remains unchanged if R_F contains the oxygen heteroatom (Table 2). The inverse dependence of I_{lum} on the length of R_F of β-diketone is observed in the case of the sorbates of the complexes on PMMA. Both free Ln^{3+} ions and those bound into tris(chelate) are coordinated to the oxygen atoms of the carbonyl groups of PMMA. Therefore, steric hindrances for the coordi-

Table 1. Used β-diketones $R_1–CO–CH_2–CO–R_2$ and their characterization ($c_{Gd} = 1 \times 10^{-4}$ M, $c_{\beta d} = 5 \times 10^{-4}$ M, $T = 77$ K)

β-Diketones			λ_{exc}, nm	λ_{phosph}, nm	E_{T1}, cm^{-1}
$–R_1$	$–R_2$	Compound (abbreviation)			
$–CF_3$	 $(–C_4H_3S)$	TTA	364	491	20365
$–C_3F_7$		THFA	364	493	20285
$–C_6F_{13}$		TTDFA	365	492	20285
$–CF_2–O–CF_3$		TOPFA	365	492	20325
$–CF_3$	 $(–C_6H_5)$	BTFA	350	462	20645
$–C_3F_7$		BHFHA	336	462	20645
$–C_6F_{13}$		BTDND	336	462	20645
$–C_8F_{17}$		BHDFD	327	466	21460
$–CF_2–O–CF_3$		BOPFA	352	461	21690
$–CF_2–CF_2–O–CF_3$		BOHFA	352	461	21690
$–CF_3$	$–CH_3$	TFAA	321	463	21600
$–CF_3$	$–C(CH_3)_3$	PTFA	320	470	21275
$–CF_2–O–CF_3$		POPFA	320	472	21185
$–CF_2–CF_2–O–CF_3$		POHFA	318	469	21320

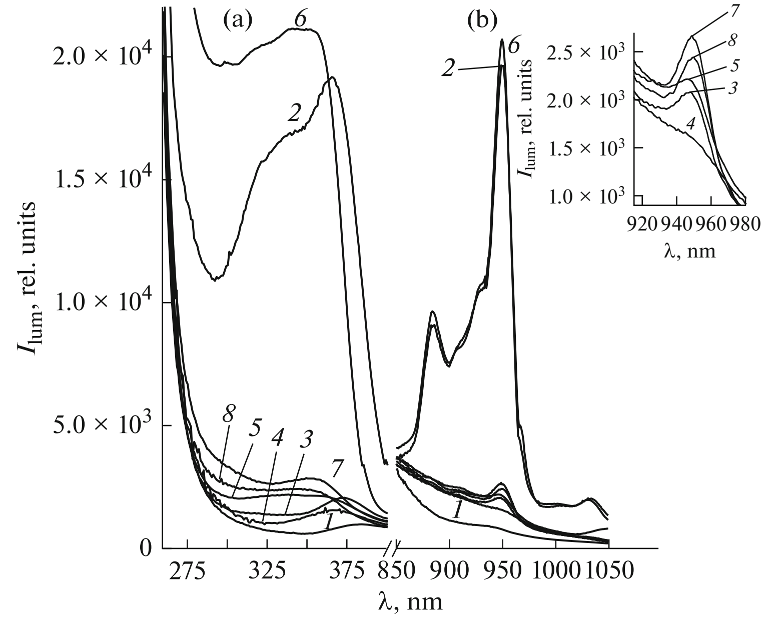


Fig. 1. (a) Excitation ($\lambda_{lum} = 950$ nm) and (b) luminescence spectra of solutions of the Sm^{3+} complexes: (*1*) TTA, $R_F = –CF_3$; (*2*) TTDFA, $R_F = –C_6F_{13}$; (*3*) TOPFA, $R_F = –CF_2–O–CF_3$; (*4*) BTFA, $R_F = –CF_3$; (*5*) BTDND, $R_F = –C_6F_{13}$; (*6*) BHDFD, $R_F = –C_8F_{17}$; (*7*) BOPFA, $R_F = –CF_2–O–CF_3$, and (*8*) BOHFA, $R_F = –(CF_2)–O–CF_3$. $c_{Sm} = 1 \times 10^{-5}$ M, $c_{\beta d} = 1 \times 10^{-4}$ M; 10% EtOH; $\lambda_{exc} = 365$ (*1*–*4*) and 350 nm (*5*–*8*).

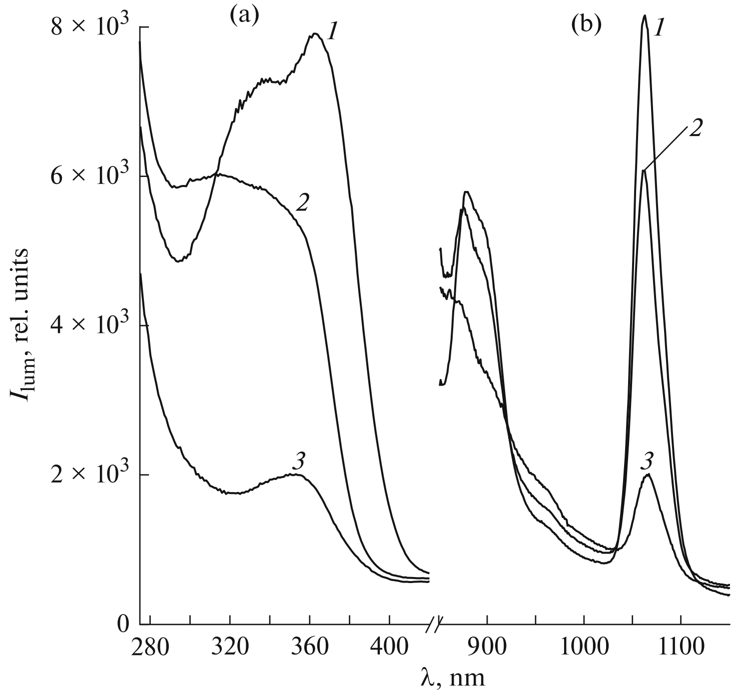


Fig. 2. (a) Excitation (λ_{lum} = 1060 nm) and (b) luminescence spectra of solutions of the Nd^{3+} complexes: (*1*) TTDFA, $R_F = -C_6F_{13}$; (*2*) BHDFD, $R_F = -C_8F_{17}$; and (*3*) BOPFA, $R_F = -CF_2-O-CF_3$. $c_{Nd} = 1 \times 10^{-5}$ M, $c_{\beta d} = 1 \times 10^{-4}$ M; 10% EtOH; cf. λ_{exc} = 360 nm.

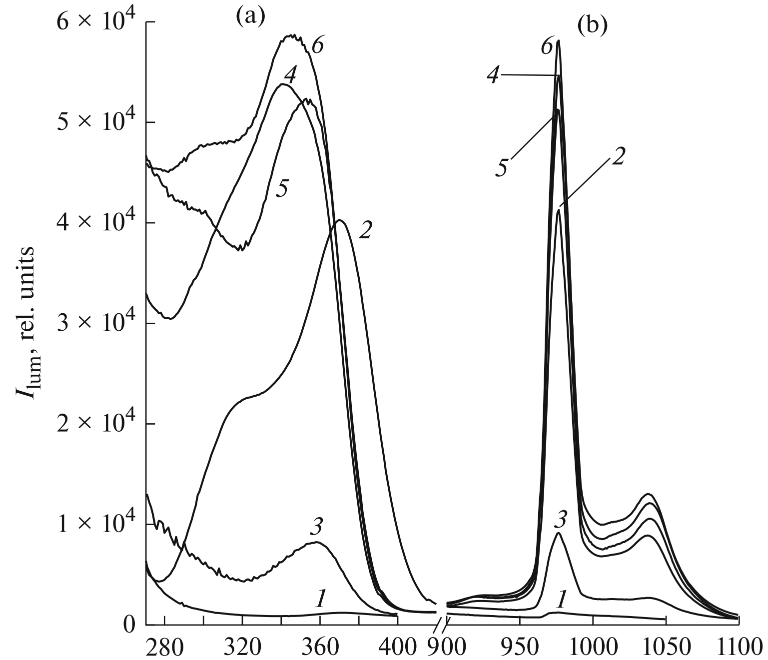


Fig. 3. (a) Excitation (λ_{lum} = 980 nm) and (b) luminescence spectra of solutions of the Yb^{3+} complexes: (*1*) TTA, $R_F = -CF_3$; (*2*) TOPFA, $R_F = -CF_2-O-CF_3$; (*3*) BTFA, $R_F = -CF_3$; (*4*) BTDHD, $R_F = -C_6F_{13}$; (*5*) BOPFA, $R_F = -CF_2-O-CF_3$; and (*6*) BOHFA, $R_F = -(CF_2)-O-CF_3$. $c_{Yb} = 1 \times 10^{-5}$ M, $c_{\beta d} = 1 \times 10^{-4}$ M; 10% EtOH; λ_{exc} = 370 (*1–3*) and 355 nm (*4–8*). Thienyl (*1*, *2*) and phenyl derivatives of AA (*3–6*).

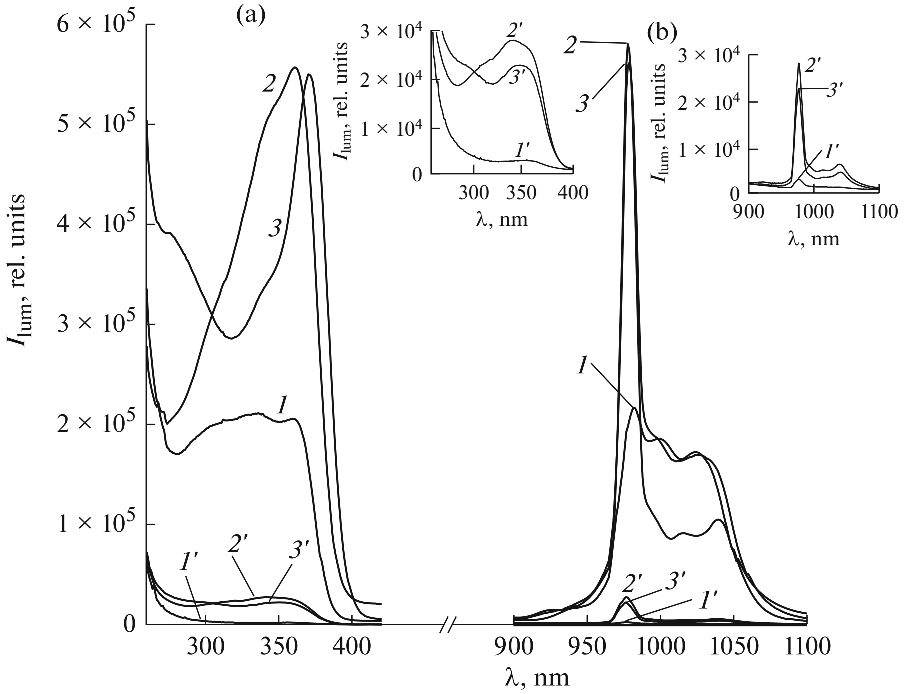
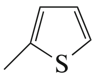
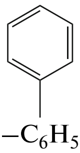


Fig. 4. Excitation (a) and luminescence (b) spectra of the sorbates on PMMA of the Yb^{3+} complexes with the phenyl derivatives of AA: (*1*) BTFA, $R_F = -CF_3$, $\lambda_{exc} = 340$ nm; (*2*) BTDHD, $R_F = -C_6F_{13}$, $\lambda_{exc} = 361$ nm; and (*3*) BOPFA, $R_F = -CF_2-O-CF_3$, $\lambda_{exc} = 371$ nm. Insets: spectra of these complexes in solution (*1'*, *2'*, and *3'*, respectively).

Table 2. Luminescence intensity of Nd^{3+}, Sm^{3+}, and Yb^{3+} β-diketonates in solutions and sorbates on PMMA*

β-Diketone		pH_f	I_{lum}, rel. units/I_1/I_0 **					
$-R_1$	$-R_2$		Nd^{3+}		Sm^{3+}		Yb^{3+}	
			solution (I_0)	sorbate on PMMA (I_1)	solution (I_0)	sorbate on PMMA (I_1)	solution (I_0)	sorbate on PMMA (I_1)
$-CF_3$	 ($-C_4H_3S$)	7.0	0.1	13.0/**130.0**	0.5	2142.0/**4284.0**	1.3	1908.0/**1467.7**
$-C_3F_7$		7.5	0.4	45.8/**114.5**	2.0	2034.0/**1017.0**	26.7	2538.0/**95.1**
$-C_6F_{13}$		7.5	0.5	31.0/**62.0**	6.3	2790.0/**442.9**	57.5	3168.0/**55.1**
$-CF_2-O-CF_3$		6.5	4.3	26.5/**6.2**	15.8	1944.0/**123.0**	373.8	2952.0/**7.9**
$-CF_3$	 ($-C_6H_5$)	7.0	0.5	60.8/**121.6**	1.0	2448.0/**2448.0**	13.0	1269.0/**97.6**
$-C_3F_7$		7.5	0.9	56.0/**62.2**	9.0	2403.0/**267.0**	29.0	1782.0/**61.4**
$-C_6F_{13}$		7.5	3.0	74.7/**24.9**	15.0	2250.0/**150.0**	54.0	1670.0/**30.9**
$-C_8F_{17}$		9.5	2.7	44.7/**16.6**	20.0	2088.0/**104.4**	82.8	1566.0/**18.9**
$-CF_2-O-CF_3$		6.5	0.3	60.3/**201.0**	4.6	498.0/**108.3**	276.0	2898.0/**10.5**
$-(CF_2)_2-O-CF_3$		6.0	0.4	65.3/**163.3**	8.6	135.0/**15.7**	409.0	2970.0/**7.3**
$-CF_3$	$-CH_3$	6.5	0.2	8.8/**44.0**	1.0	73.8/**73.8**	0.4	610.5/**1526.3**
$-CF_3$	$-C(CH_3)_3$	9.0	0.4	20.8/**52.0**	7.2	580.3/**80.6**	2.7	657.0/**243.3**
$-CF_2-O-CF_3$		6.5	0.6	24.3/**40.5**	13.7	580.3/**42.4**	11.6	657.0/**56.6**
$-(CF_2)_2-O-CF_3$		8.0	0.7	21.3/**30.4**	14.9	786.5/**52.8**	17.5	765.0/**43.7**

* For the thienyl and phenyl derivatives of AA: $c_{Ln} = 1 \times 10^{-5}$ M, $c_{\beta d} = 1 \times 10^{-4}$ M; for the alkyl derivatives of AA: $c_{Ln} = 1 \times 10^{-4}$ M; $c_{\beta d} = 1 \times 10^{-3}$ M; λ_{exc}, nm (λ_{lum}, nm): 365 (950) for Sm, 1060 for Nd, and 980 for Yb.

** I_0 is the luminescence intensity of the complex in solution; I_1 is the luminescence intensity of the sorbate on PMMA.

nation of the complex with PMMA increase with an elongation of R_F. At the same time, the luminescence intensity of the sorbates multiply (by 2–3 orders of magnitude) exceeds its values for the complexes in solutions due to a decrease in diffusion and nonradiative intermolecular losses of the excitation energy related to diffusion.

To conclude, the present studies showed the possibility of a significant increase in the luminescence intensity of the Nd(III), Sm(III), and Yb(III) complexes with the thienyl, phenyl, and alkyl derivatives of AA in the near-IR spectral range by the isolation of the complexes as sorbates on the polymer matrix of PMMA. The intermolecular nonradiative transfer of the excitation energy decreases due to the coordination of the Ln^{3+} ions with the oxygen atoms of the carbonyl groups of PMMA and to the elimination of diffusion.

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