Water enhances quantum yield and lifetime of luminescence of europium(III) tris-β-diketonates in concentrated toluene and acetonitrile solutions

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Abstract

Europium tris-β-diketonates ($Eu(L)_3 \cdot nH_2O$) show concentration quenching of luminescence in toluene solutions due to the formation of weakly luminescent dimers. Addition of water to the concentrated toluene solutions of $Eu(L)_3 \cdot nH_2O$ unexpectedly enhances quantum yield (ϕ) and lifetime of Eu^{3+} luminescence by causing dissociation of dimers and by reducing quenching of excited Eu^{3+} through the ligand-to-metal charge transfer (LMCT). Water also enhances ϕ of $Eu(L)_3 \cdot nH_2O$ in acetonitrile (although to a lower extent than in toluene) only by reducing LMCT quenching of Eu^{3+}. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Concentration quenching of luminescence; Lanthanide; Europium; β-Diketonate complexes

1. Introduction

Luminescent lanthanide β-diketonates [1–25] have found wide application as light-converting optical devices [5,7,19,21,23]; as emitters in liquid lasers [16] and in electroluminescence devices [8]; as chemiluminescence activators [4,10]; as thermo-luminescence dosimeters [9]; for luminescent determination of Ln^{3+} [11,17,18], etc. and a lot of efforts are being made to improve their emission properties.

The luminescence of Ln^{3+} is efficiently quenched by nonradiative exchange of electronic energy of Ln^{3+} to the high vibrational modes of O–H, N–H and C–H bonds [26–31]. Among

these, water molecules, possessing O–H groups are considered to be the most efficient quenchers of Ln^{3+} luminescence. Removal of O–H groups from the inner coordination sphere of Ln^{3+} generally enhances its luminescence efficiency.

However, recently we have observed that luminescence quantum yield (ϕ) of Sm^{3+} and Tb^{3+} tris-β-diketonates ($Ln(L)_3 \cdot nH_2O$) in concentrated ($> 10^{-4}$ M) toluene solutions is *enhanced* by water [1–3]. In such solutions the $Ln(L)_3 \cdot nH_2O$ is partially dimerized (Eq. 1) [32–34], and ϕ of dimer is significantly lower than for monomer [1]. Probably, the dimer is obtained by replacing the H_2O from the inner coordination sphere of Ln^{3+} by second molecule of chelate (Eq. (1)) with simultaneous formation of $Ln \cdots O \cdots Ln$ bridge where oxygen belongs to the β-diketonate ligand [32,34]. Addition of water shifts equillibrium (1) to

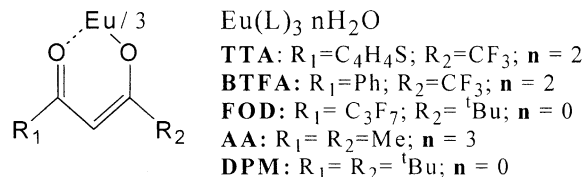*Corresponding author. Fax: +7-347-2-35-6066.

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the left and thus enhances the ϕ of Ln^{3+}. In diluted $< 10^{-4}$ M anhydrous solutions the chelate is monomeric and water quenches its luminescence.

$$2Ln(L)_3 \cdot nH_2O \leftrightarrows [Ln(L)_3 \cdot (n-x)H_2O]_2 + 2xH_2O. \quad (1)$$
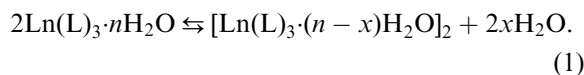
As early as in 1967, Springer et al. mentioned that water enhances luminescence of solid complexes $Ln(FOD)_3$ ($Ln = Eu^{3+}$, Tb^{3+}) [35] while in 1995, Piguet et al. noted that water enhances luminescence of Eu^{3+} chelates with 2,6-bis(benzimidazol)-pyridines in acetonitrile solutions, by reducing energy losses in the ligand [36]. These seem to be the only previous reports describing unusual enhancement by water of luminescence of Ln^{3+} compounds.

We have noted [2,3] that luminescence of europium β-diketonates may also be enhanced by water and herein we will discuss the influence of water on the luminescence of $Eu(L)_3 \cdot nH_2O$ in toluene and acetonitrile (MeCN) solutions.

$Eu(L)_3\ nH_2O$
TTA: $R_1 = C_4H_4S$; $R_2 = CF_3$; **n** = 2
BTFA: $R_1 = Ph$; $R_2 = CF_3$; **n** = 2
FOD: $R_1 = C_3F_7$; $R_2 = {}^tBu$; **n** = 0
AA: $R_1 = R_2 = Me$; **n** = 3
DPM: $R_1 = R_2 = {}^tBu$; **n** = 0

2. Experimental

Toluene was dried and distilled over Na. MeCN was distilled over P_2O_5. H_2O/D_2O used was bidistilled. FOD and DPM chelates were sublimed. Synthesis of TTA, BTFA and AA chelates is given in [4].

Water was added by microsyringe to 2 ml of chelate solution in a 1 cm quartz cell and dissolved by heating ($\sim 90°C$ for toluene) and shaking. (1). Luminescence of Eu^{3+} excited into the ion ff-absorption bands (465 or 535 nm) was registered at $90°$ on spectrofluorimeter MPF-4 "Hitachi". Optical density of solutions at λ_{exc} was < 0.07. The correction was made for the change of ff-absorption at addition of water when calculating the change of luminescence intensity of Eu^{3+}. (2). Luminescence of Eu^{3+} excited into ligand absorp-

tion band (λ_{exc} was 365 or 313 nm) was registered at $180°$, in optically dense solutions. All light was absorbed by the solution.

Absorption spectra were recorded on spectrophotometer "Specord M-40". The ϕ of Eu^{3+} was measured relative to aqueous solution of $[Ru(bipy)_3] \cdot Cl_2$ [28]. The lifetime of $^5D_0$-luminescence (τ) of Eu^{3+} excited by N_2-laser (337.1 nm), was measured on home-built equipment with detection limit $\sim 40\,\mu s$. Errors of determination of ϕ—30%, τ—20%.

3. Results

Absorption spectra of Eu^{3+} β-diketonates consist of intense broad ligand-centered (LC) absorption in UV with $\varepsilon_{max} \approx 10^4 - 10^5$ $(M\,cm)^{-1}$ and weak ff-absorption lines of Eu^{3+} ion in visible with $\varepsilon_{max} < 10$ $(M\,cm)^{-1}$ (Figs. 1 and 2). The ligand-to-metal charge-transfer band (LMCT) appears in the absorption spectra of Eu^{3+} β-diketonates since the Eu^{3+} is easily reducible to divalent state [22,25]. The LMCT is clearly observed in the spectrum of $Eu(DPM)_3$, where it appears as an absorption shoulder on LC-band tailing into visible with $\varepsilon_{max} < 10^3$ $(M\,cm)^{-1}$ and it is not observed in the spectrum of DPM chelate of poorly reducible Pr^{3+}

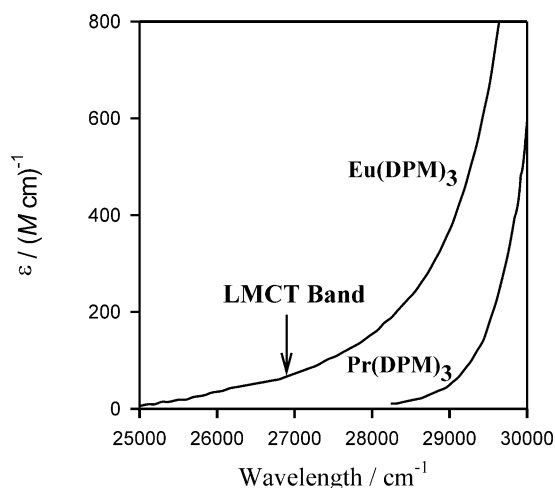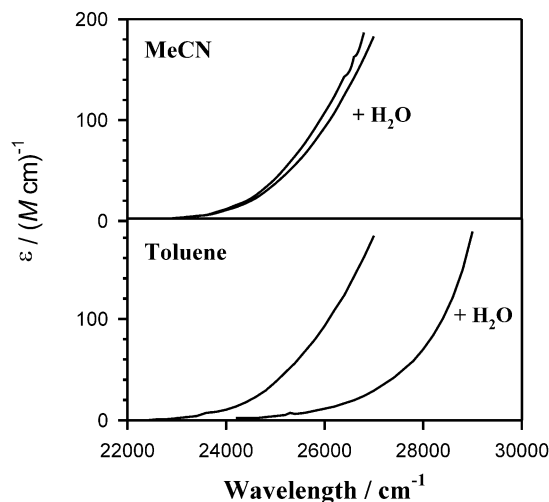Fig. 1. Absorption spectra of 10^{-3} M solutions of $Eu(DPM)_3$ and $Pr(DPM)_3$ in anhydrous toluene at 25°C.

Fig. 2. LC-absorption spectra of 5×10^{-3} M solutions of Eu(DPM)$_3$ in anhydrous toluene and MeCN and in toluene or MeCN with [H$_2$O] = 0.069 M at 60°C. Similar change of LC-absorption in the presence of water was observed for BTFA, TTA and FOD chelates of Eu^{3+}.

Fig. 3. Luminescence spectrum of Eu(BTFA)$_3 \cdot 2$H$_2$O (emission slit = 5 nm) in toluene at 25°C. Luminescence of Eu^{3+} originates from resonant ^{5}D$_0$ and upper-lying ^{5}D$_1$ levels. The band at 540 nm is due to transition ^{5}D$_1 \rightarrow$ ^{7}F$_0$, at 610 nm—^{5}D$_0 \rightarrow$ ^{7}F$_2$.

(Fig. 1) [22]. Probably, the LMCT-absorption for fluorinated chelates is also situated on the red edge of LC-band.

Excitation of Eu^{3+} β-diketonates either to the ff- or LC-absorption bands results in the line-like ff-luminescence of Eu^{3+} that originates from the resonant ^{5}D$_0$ and upper lying ^{5}D$_1$ levels (Fig. 3), with >99% of room-temperature emission arising from ^{5}D$_0$ level. The contribution of ^{5}D$_1$-emission to the total intensity increases somewhat at higher temperatures to become <3%, probably due to thermal population of ^{5}D$_1$ level from ^{5}D$_0$ one ($\Delta E \sim 1750$ cm^{-1}) [14]. However, only dominating D$_0$-luminescence will be considered further in this work.

The quantum yields and lifetimes of ^{5}D$_0$-luminescence of 10^{-3} M solutions of Eu(L)$_3 \cdot n$H$_2$O in toluene and MeCN are given in Table 1. Both ϕ and τ of fluorinated chelates increase on passing from toluene to MeCN while the contrary trend is observed for nonfluorinated ones. Temperature rise in the 25–60°C range lowers both ϕ and τ of Eu^{3+}, with ϕ quenched to a larger extent than τ (Table 1). The luminescence decay of some Eu^{3+} chelates is nonexponential [3,14] indicating that several Eu^{3+} species are present in solution.
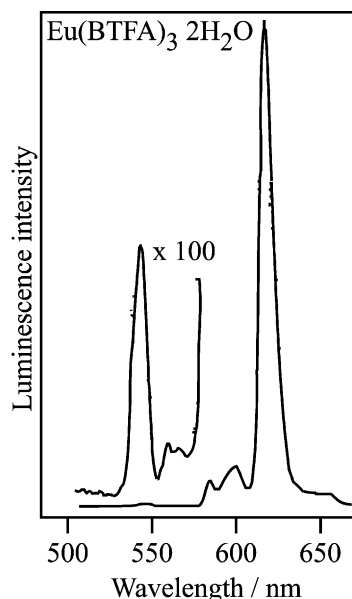
Table 1
Luminescence quantum yields and lifetimes of 10^{-3} M solutions of Eu^{3+} β-diketonates in toluene and MeCN at 25 and 60°C[a]

	t (°C)	$\phi/(\%)$		τ/μs	
		Toluene	MeCN	Toluene	MeCN
BTFA	25	0.7	1.9	130	500
	60	0.08	0.4	70	510
TTA	25	0.9	0.9	90	450
	60	0.06	0.1	<70	340
FOD	25	1.2	1.8	190	510
	60	0.2	0.5	100	230
DPM	25	0.1	0.02	320	160
	60	0.05	0.002	330	[b]
AA	25	0.1	0.05	310	180
	60	0.05	0.01	230	110

[a] Excitation was performed into LC-absorption band: $\lambda_{exc} = 313$ or 365 nm.
[b] The low ϕ prevented measuring τ.

Further we will consider only the most intense component of τ giving >90% of the total emission of Eu^{3+} (Tables 1 and 2).

Increase of [Eu(L)$_3 \cdot n$H$_2$O] in toluene in the range 0.001–0.02 M results in the concentration

Table 2
Influence of water (X_2O, X = H or D) on the luminescence quantum yield and lifetime of 5×10^{-3} M solutions of Eu^{3+} β-diketonates in toluene or MeCN at 60°C

		η^a			$\tau/\mu s^b$	
		Ligand	465 nm	535 nm	τ_0	$\tau(X_2O)$
BTFA	Toluene	11 (20)[c]	13	13	70	130 (140)[c]
	MeCN	1.8	1.4	1.4	540	520
TTA	Toluene	9.7 (14)	9.9	7	60	130 (170)
	MeCN	1.6	1.4	1.3	350	340
FOD	Toluene	9.1 (17)	5.3	3.7	40	200 (310)
	MeCN	1.9	1.2	1.2	250	260
DPM	Toluene	4.6 (16)	<3.8	<3.2	360	350 (800)
	MeCN	2.0	1.7	1.4	d	d
AA	Toluene	1.0 (1.6)	0.4	0.4	250	130 (150)

[a] $\eta = \phi(X_2O)/\phi_0$ is a ratio of luminescence quantum yield of Eu^{3+} solution in the presence of water ([H_2O] = 0.069 M or [D_2O] = 0.063 M) to that of anhydrous solution at LC- (313 or 365 nm) or ff-excitation (465 or 535 nm).
[b] Luminescence lifetime of 5×10^{-3} M solutions β-diketonates of Eu^{3+} in anhydrous solution—τ_0 or in solution with [H_2O] = 0.069 M or [D_2O] = 0.063 M—$\tau(X_2O)$.
[c] Shown in the brackets are the values for the D_2O added to toluene solutions.
[d] The low ϕ prevented measuring τ.

quenching (CQ) of their luminescence quantum yields (Fig. 4). The CQ for europium(III) chelates in toluene decreased in the order DPM ≈ FOD > TTA > BTFA (Fig. 4). For $Eu(AA)_3 \cdot 3H_2O$ in toluene and for all chelates in MeCN the concentration quenching in the range studied is absent.

Increase of [$Eu(FOD)_3$] from 10^{-3} to 5×10^{-3} M results in the quenching of its luminescence lifetime from 100 to 40 µs (Tables 1 and 2). For DPM and AA chelates of Eu^{3+} the CQ of τ is absent, while short values of τ prevented measuring the CQ for BTFA and TTA chelates.

Addition of H_2O to toluene or MeCN solutions of chelates enhances the quantum yield of $^5D_0$-luminescence of Eu^{3+} at LC- or ff-excitation without alteration of their emission spectra. At the same time the H_2O added either enhances the luminescence lifetime of Eu^{3+} to a lower extent than ϕ or leaves τ unaltered (Table 2). Further in the text, the ratio $\phi(X_2O)/\phi_0$ is abbreviated as η, where $\phi(X_2O)$ and ϕ_0 stand for quantum yields of Eu^{3+} luminescence in the presence and in the absence of water (X = H or D), respectively.

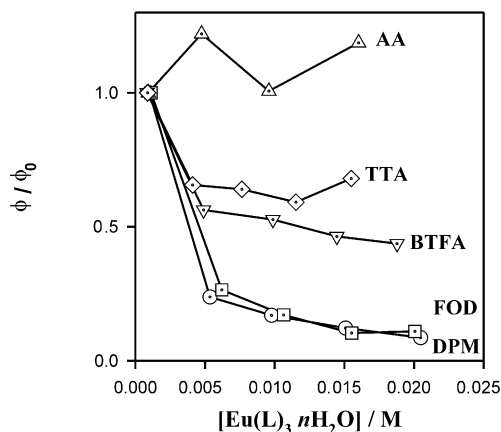At equal ratio of [H_2O]/[Eu] in toluene, the η is higher at higher chelate concentrations, while in

Fig. 4. Concentration quenching of luminescence of Eu^{3+} β-diketonates in toluene at LC-excitation. Luminescence was registered at 180° in optically dense soltions.

diluted solutions at [Eu] < 10^{-4} M the addition of water quenches Eu^{3+} luminescence. For AA chelate the quenching is already observed at [Eu] = 5×10^{-3} M (Table 2). Temperature rise in the 60–85°C range at equal [H_2O]/[Eu] ratio results in an ~15% increase of η for DPM and in an ~10% decrease of η for other chelates.

Thus, the majority of experiments were carried out at 60°C, adding 2.5 μl of water to the 2 ml of 5×10^{-3} M chelate solution that gave $[H_2O] = 0.069$ M or $[D_2O] = 0.063$ M. That is the highest concentration of water that could be dissolved at 60°C in toluene. The changes of the ϕ and τ of 5×10^{-3} M chelate solutions in toluene and MeCN by water are given in Table 2.

The absorption spectra of Eu^{3+} β-diketonates in toluene and MeCN almost coincide (Fig. 2). Water added to the chelate solution blue-shifts the LC-band (Fig. 2), and the shift is more pronounced in toluene than in MeCN. Only for
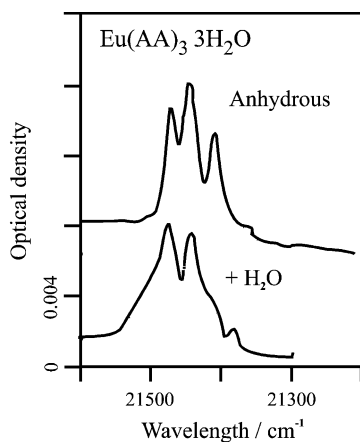

Fig. 5. Absorption spectra of the $^7F_0 \rightarrow {}^5D_2$ transition of Eu^{3+} in $[Eu(AA)_3 \cdot 3H_2O] = 0.0048$ M in anhydrous toluene and in toluene with $[H_2O] = 0.069$ M at 60°C. The spectra are vertically shifted.

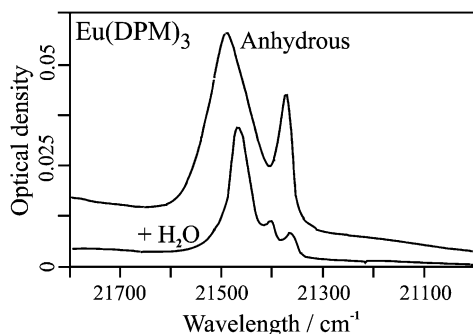Fig. 6. Absorption spectra of the $^7F_0 \rightarrow {}^5D_2$ transition of Eu^{3+} in $[Eu(DPM)_3] = 0.021$ M in anhydrous toluene and in toluene with $[H_2O] = 0.056$ M at 85°C.

$Eu(AA)_3 \cdot 3H_2O$ the LC-band is not altered by water. Addition of water completely changes ff-absorption of Eu^{3+} at 465 nm ($^7F_0 \rightarrow {}^5D_2$ transition) for nonfluorinated AA and DPM chelates in toluene (Figs. 5 and 6). With other chelates in toluene and for all chelates in MeCN solutions the water only slightly reduced intensity of this ff-absorption band.

4. Discussion

The excited $Eu(L)_3 \cdot nH_2O$ in toluene deactivates not only by energy transfer to the CH-groups of ligands and toluene molecules and to the OH-groups of coordinated water, but also by concentration quenching mechanism. The observed CQ of luminescence of Eu^{3+} β-diketonates in toluene (Fig. 4) is probably due to the formation of weakly luminescent dimers (Eq. 1) as discussed in [1]. In accordance with this suggestion, the largest quenching was observed for coordination-unsaturated anhydrous FOD and DPM chelates, since they tend to saturate the free coordination sites of Eu^{3+} by sharing oxygens of β-diketonate ligand in dimer structure [32–34]. Moreover, the CQ of Eu^{3+} luminescence was not observed in MeCN since the ability of lanthanide β-diketonates to form dimers is lower in polar and coordinating solvents [32].

Probably the water added to concentrated chelate solutions induces the dissociation of dimers to form strongly luminescent monomers (Eq. (1)) thus enhancing luminescence efficiency of Eu^{3+}. In diluted solutions the chelates are monomeric and addition of water quenches monomer luminescence both by the nonradiative exchange of electronic excitation energy of Eu^{3+} on the vibrations of OH-groups of water and by hydrolysis of chelate.

Dissociation of dimers probably occurs at coordination of H_2O both to the Eu^{3+} ion and/or to the ligand by forming HOH $\cdots$ F or HOH $\cdots$ O hydrogen bonds [34], that is reflected in the changes of the ff- and LC-absorptions, respectively. However, complete change of ff-absorption of AA and DPM chelates in toluene by water (Figs. 5 and 6) is probably caused by the

partial hydrolysis of chelate with formation of $EuOH(L)_2 \cdot nH_2O$ [37]. The hydrolysis products precipitate at dissolution of water in toluene solutions of the AA and DPM chelates. Probably hydrolysis of $Eu(AA)_3 \cdot 3H_2O$ results in the quenching of its luminescence in 5×10^{-3} M solution (Table 2).

Contrary to Sm^{3+} and Tb^{3+} the nonradiative deactivation for Eu^{3+} chelates may occur by ligand-to-metal charge transfer [14,22,25,38,39]. It is known that the *higher* the energy of LMCT state the *less* is the quenching of excited Eu^{3+} ion by CT mechanism. Actually, introduction of electron-withdrawing groups to the β-diketonate ligand (e.g. fluorine atoms) in $Eu(L)_3 \cdot nH_2O$ increases the energy of LMCT state and thus enhances Eu^{3+} luminescence efficiency [25]. Probably, water enhances the luminescence of Eu^{3+} chelates in toluene not only by shifting the equilibrium (1), but also by increasing the energy of LMCT which is evidenced by the blue-shift of LMCT-band of $Eu(DPM)_3$ induced by water (Fig. 2).

The water also enhances luminescence quantum yield of Eu^{3+} in MeCN although to a lower extent than in toluene. In anhydrous MeCN the Eu^{3+} chelates are monomeric, however, they are still quenched by LMCT. Probably the H_2O added to MeCN reduces LMCT quenching of Eu^{3+} by lifting up the energy of CT state as indicated by the blue-shift of CT-band of $Eu(DPM)_3$ (Fig. 2). It should be noted, that the emission of Sm^{3+} and Tb^{3+} chelates is quenched by water in MeCN [1] since these chelates are monomeric in MeCN and LMCT-quenching is not operative with them.

The H_2O added to chelate solution still contributes to nonradiative deactivation of excited Eu^{3+} due to the energy transfer to OH-groups. This quenching can be removed by using D_2O instead of H_2O since O–D bond is a poor quencher of excited Eu^{3+} compared to O–H bond [26–31]. In fact D_2O enhances both τ and ϕ of Eu^{3+} luminescence to a much higher degree than H_2O (Table 2).

Quantum yield of $Eu(L)_3 \cdot nH_2O$ luminescence on LC excitation (ϕ) is a product of ligand-to-metal energy transfer efficiency (Φ_{ET}) and luminescence quantum yield of Eu^{3+} on ff-excitation (ϕ_{Eu})

(Eq. (2)). The quenching of Eu^{3+} in dimer might be caused by decrease of ϕ_{Eu} due to efficient cross-relaxation of excited Eu^{3+} on the ff-levels of neighboring ion, since the $Eu^{3+} \cdots Eu^{3+}$ distance in dimer is estimated to be only ≈ 4 Å [34]. However one cannot exclude that the energy in dimer is lost on ligand levels before energy transfer to Eu^{3+} occurs and this will lead to reduced Φ_{ET}.

$$\phi = \Phi_{ET} \cdot \phi_{Eu}. \tag{2}$$

The Eu^{3+} luminescence enhancement ratio—η depends on the λ_{exc} and is higher on LC- than on ff-excitation, as is illustrated by DPM and FOD chelates (Table 2). For $Eu(AA)_3 \cdot 3H_2O$ the water does not change the ϕ (LC-excitation) while it quenches ϕ_{Eu} by a factor of two ($\lambda_{exc} = 465$ or 535 nm) (Table 2). The higher enhancement of ϕ compared to ϕ_{Eu} by H_2O reflected in the dependence of η on the λ_{exc} and the much lower enhancement of τ by H_2O compared to ϕ (Table 2) indicates that added water reduces energy losses in the ligand thus increasing the ligand-to-metal energy transfer efficiency—Φ_{ET} (Eq. (2)). It should be noted that for BTFA and TTA chelates selective excitation of Eu^{3+} with 465 nm light cannot be achieved since LC and ff-bands partially overlap. Moreover for all chelates the values of η (535 nm) are obtained with a large error due to a low absorption intensity of $^7F_0 \rightarrow {}^5D_1$ transition.

The luminescence quantum yield at ff-excitation—ϕ_{Eu} and lifetime of Eu^{3+} are defined through corresponding radiative (k_r) and nonradiative (k_{nr}) decay rate constants of the ion as: $\phi_{Eu} = k_r/(k_r + k_{nr})$ and $\tau = (k_r + k_{nr})^{-1}$. The lower enhancement of luminescence lifetime of TTA, BTFA and DPM chelates of Eu^{3+} compared to the enhancement of their quantum yields ϕ_{Eu} at ff-excitation at 465 or 535 nm (Table 2) indicates that water both decreases the nonradiative decay rate constant and increases the radiative rate constant of Eu^{3+}.

5. Conclusions

In toluene the Eu^{3+} β-diketonates show significant concentration quenching due to formation of weakly-luminescent dimers. The presence of

water in toluene and MeCN causes dissociation of dimers to give monomers and enhances the energy of LMCT state and both changes result in the unexpected significant enhancement of the luminescence intensity and lifetime of Eu^{3+} β-diketonates by water.

Acknowledgements

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