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Water enhances the luminescence intensity of β-diketonates of trivalent samarium and terbium in toluene solutions

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Abstract

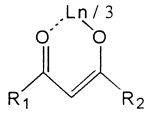
The influence of water on the luminescence of toluene solutions of lanthanide β-diketonates ($Ln(L)_3{\cdot}nH_2O$, where L is benzoyltrifluoroacetone, thenoyltrifluoroacetone, acetylacetone, dipivaloylmethane) was studied. It was shown that in toluene the luminescence of dysprosium, neodymium and ytterbium β-diketonates is quenched by water while the luminescence of samarium and terbium β-diketonates is enhanced by water at $[Ln(L)_3{\cdot}nH_2O]>10^{-4}$ M. The concentration quenching of the luminescence of $Ln(L)_3{\cdot}nH_2O$ in toluene was observed due to the formation of dimers $[Ln(L)_3{\cdot}nH_2O]_2$. The quenching in dimers is caused by deactivation in both the ligand (before the energy transfer to Ln^{3+} ion takes place) and by cross-relaxation in the Ln^{3+} ion. It is suggested that introduction of water in toluene causes dissociation of dimers to monomers which results in the enhancement of the luminescence intensity of Sm^{3+} and Tb^{3+}, while the quenching of Nd^{3+}, Dy^{3+} and Yb^{3+} luminescence is due to the efficient deactivation of these ions by OH-groups. Probably addition of water enhances ligand-to-Ln^{3+} energy-transfer efficiency and lowers cross-relaxation efficiency of Ln^{3+}.

Keywords: Luminescence; Concentration quenching; β-Diketonate complexes; Terbium; Samarium; Lanthanide ions

1. Introduction

Water molecules efficiently quench the luminescence of lanthanide ions through non-radiative exchange of electronic energy of Ln^{3+} to the high vibrational modes of OH-groups (ν=3700 cm^{-1}) [1–12]. Each OH-group quenches the excited Ln^{3+} independently, and the quenching efficiency decreases as the distance $Ln^{3+}\cdots OH$ increases, so that the quenching by outer-sphere coordinated water is usually negligible. Deuterated OD-group possess lower quenching efficiency than OH, since it has lower vibrational energy (ν=2600 cm^{-1}) and deuteartion of solvent enhances the quantum yield and lifetime of Ln^{3+} luminescence [1]. One may determine the number of water molecules coordinated with Ln^{3+} [8–12] by measuring luminescence lifetime of Ln^{3+} in H_2O and D_2O. This technique was applied in many systems giving excellent results.

However, recently [13–14] we have reported that the addition of water to toluene solutions of fluorinated europium β-diketonates $Eu(FOD)_3$ and $Eu(BTFA)_3{\cdot}2H_2O$ enhances luminescence intensity and lifetime of Eu^{3+}. We ascribed this unexpected effect to the association between water and chelate by hydrogen bonding of fluorine atom of ligand with OH-group of water. As early as in the 1960s it was observed that water enhances the luminescence intensity of $Ln(FOD)_3$ (Ln=Eu^{3+}, Tb^{3+}) [15], but it seems that no further studies of the effect appeared until recently [13–14]. In the present work we have studied the influence of water on the luminescence of β-diketonates of trivalent samarium, terbium, dysprosium, neodymium and ytterbium ($Ln(L)_3{\cdot}nH_2O$) solutions in anhydrous toluene, acetonitrile (MeCN) and DMSO.



$Ln(L)_3\ nH_2O$
Ln: Sm^{3+}; Tb^{3+}; Dy^{3+}; Nd^{3+}; Yb^{3+}
L:
TTA: $R_1=C_4H_4S$; $R_2=CF_3$; **n** = 2
BTFA: $R_1=C_6H_5$; $R_2=CF_3$; **n** = 2
AA: $R_1=R_2=CH_3$; **n** = 3
DPM: $R_1=R_2=tC_4H_9$; **n** = 0
FOD: $R_1=C_3F_7$; $R_2=tC_4H_9$; **n** = 0

The investigation of luminescent properties of Ln^{3+} β-diketonates is of great importance [16–37], since they are used as light-converting optical materials [23–24]; as luminescent dopants in different materials (e.g. Langmuir–

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Blodgett films [25], polymers [26–27], sol–gel derived glasses [28] and thin films [29]); as an active media for liquid lasers [6]; in electroluminescent devices [30–33]; for analytical determination of Ln^{3+} [34–35] and as luminescent stains in clinical immunoassays [36–37].

2. Experimental

2.1. Materials

Toluene was distilled over Na. DMSO was vacuum-distilled over NaOH. MeCN was distilled over P_2O_5. H_2O and D_2O were bidistilled. Ethanol (95%) was distilled.

Fourteen chelates were studied: BTFA and TTA chelates for all the ions shown; acetylacetonates (AA) of Sm^{3+}, Tb^{3+}, Dy^{3+} and $Dy(DPM)_3$. Synthesis of $Ln(L)_3{\cdot}nH_2O$ was given in [38]. $Dy(DPM)_3$ was sublimed.

2.2. Methods and equipment

Water was successively added from a 1 μl microsyringe to 2 ml solution of $Ln(L)_3{\cdot}nH_2O$ in 1 cm quartz cell. Water in toluene dissolved at heating and vigorous shaking until the transparent homogeneous solutions were obtained. Due to the poor solubility of water in toluene, the experiments could only be performed at elevated temperatures (>50°C). Maximum concentration of added H_2O in toluene reached 0.083 M (3 μl of water in 2 ml of toluene).

The influence of water on the luminescence of $Ln(L)_3{\cdot}nH_2O$ was studied by two methods. (1) The visible luminescence of Ln^{3+} (450–700 nm) was registered at 90° to the excitation beam, on spectrofluorimeter MPF-4 'Hitachi'. Optical density of solution at excitation wavelength (λ_{exc}) was <0.07. Absorption and luminescence spectrum of $Ln(L)_3{\cdot}nH_2O$ were measured together at each addition of water, since water changes the absorption spectrum of chelate. The luminescence intensities were always corrected for the change of absorption. (2) The visible and IR luminescence of Ln^{3+} was registered at 180° relative to excitation beam on home-built equipment [38]. Solutions were optically thick at λ_{exc} (365 or 313 nm lines of Hg-lamp) and the excitation light was completely absorbed by solution.

The luminescence spectra of Ln^{3+} do not change on the addition of water and the luminescence intensity was measured as the height of the most intense peak (Fig. 1): Sm^{3+} — 645 nm; Tb^{3+} — 545 nm; Dy^{3+} — 575 nm; Nd^{3+} — 880 and 1060 nm and Yb^{3+} — 980 nm. The chelates $Dy(TTA)_3{\cdot}2H_2O$, $Dy(BTFA)_3{\cdot}2H_2O$, $Tb(TTA)_3{\cdot}2H_2O$, $Sm(AA)_3{\cdot}3H_2O$ could not be studied since they show very weak luminescence.

Luminescence quantum yields for Sm^{3+} chelates at excitation into ligand absorption (ϕ) were measured relative to $[Ru(bipy)_3]{\cdot}Cl_2$ (λ_{exc}=400 nm, ϕ=2.8% in water [39], perpendicular geometry); for Tb^{3+} and Dy^{3+} chelates are relative to $Tb(AA)_3{\cdot}3H_2O$ (λ_{exc}=313 nm, ϕ=19% in ethanol [16], in-line geometry).

Absorption spectra were registered on spectrophotometer Specord M-40. The lifetime of Ln^{3+} luminescence, excited by N_2 laser pulse at λ_{exc}=337 nm, was measured on home-built equipment.

The $Ln(L)_3{\cdot}nH_2O$ luminescence enhancement ratio is $\eta = I/I_0$, where I and I_0 are emission intensities in the presence and absence of added water. Abbreviation $[H_2O]/[Ln]$ is used instead of $[H_2O]/[Ln(L)_3{\cdot}nH_2O]$, where $[H_2O]$ is a concentration of added water.

3. Results

Absorption spectra of Ln^{3+} β-diketonates consist of intense broad ligand-centered absorption (LC-absorption) in UV with $\varepsilon \approx 10^4$–10^5 $(M\,cm)^{-1}$ and weak sharp ff-absorption bands of Ln^{3+} ion with $\varepsilon < 10^2$ $(M\,cm)^{-1}$. Excitation of Ln^{3+} β-diketonates in ff- or LC-absorption bands results in the ff-luminescence of Ln^{3+}. In the latter case the ff-levels of Ln^{3+} are populated by energy transfer route: excited ligand singlet→ligand triplet→Ln^{3+} levels [16,18]. Luminescence of Ln^{3+} ions is due to intra-ion ff-transitions from Ln^{3+} emitting level to lower lying states (Fig. 1). The luminescence of Ln^{3+} β-diketonates was registered by LC-excitation, and for Sm^{3+} chelates also by excitation into the weak ff-absorption at 490 nm. The measured luminescence quantum yields of $Ln(L)_3{\cdot}nH_2O$ at LC-excitation were always lower in toluene compared to polar solvents, such as MeCN (Table 1), DMSO and C_2H_5OH.

Addition of H_2O to toluene quenched the ff-emission of AA and DPM chelates of Dy^{3+} and BTFA and TTA chelates of Nd^{3+} and Yb^{3+}. Contrary to that, addition of H_2O to toluene enhanced the luminescence intensity of BTFA and TTA chelates of Sm^{3+}, and BTFA and AA chelates of Tb^{3+}

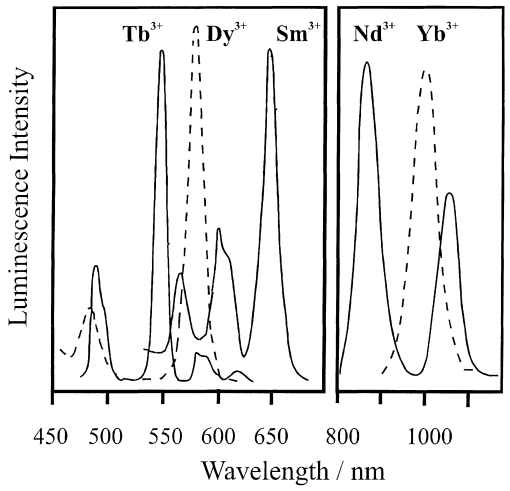

Fig. 1. Luminescence spectra of $Ln(L)_3{\cdot}nH_2O$ in toluene solution on ligand excitation (λ_{exc}=365 or 313 nm). Emission slits: Sm^{3+}, Tb^{3+}, Dy^{3+} — 10 nm; Nd^{3+}, Yb^{3+} — 20 nm.

Table 1
Luminescence quantum yields and relative luminescence intensities of the 10^{-3} M solutions of $Ln(L)_3 \cdot nH_2O$ in toluene (or MeCN as shown in parenthesis) at room temperature[a]

	k_{OH} (s^{-1})[b]	Quantum yields (%)[c]			
		BTFA	TTA	AA	DPM
Tb^{3+}	100–200	0.07 (0.09)	$<10^{-3}$	15 (19)	–
Sm^{3+}	18000	0.05 (1.2)	0.06 (0.95)	$<10^{-3}$	–
Dy^{3+}	20000	$<10^{-3}$	$<10^{-3}$	0.005	0.27
Yb^{3+}	3.5×10^5	80[d]	100[d]	–	–
Nd^{3+}	$>3.5\times10^5$	31[d]	35[d]	–	–

[a] Notes: The rate constants of quenching of resonant levels of Ln^{3+} by one OH group (k_{OH}). Errors of determination of quantum yields and relative intensities for Sm^{3+} — 30%, for other ions — 20%.

[b] The values are taken from [3].

[c] λ_{exc}=313 nm.

[d] Relative intensities (a.u.); λ_{exc}= 365 nm. Luminescence quantum yields for Yb^{3+} and Nd^{3+} are less than 10^{-3}% [6,19]. Relative intensities of Yb^{3+} and Nd^{3+} can be compared.

(Figs. 2–4). Temperature change in the range from 50 to 90°C lowers the η value by 5–10%. Further experiments in toluene were carried out at 70°C. Enhancement of luminescence intensity of $Tb(AA)_3 \cdot 3H_2O$ (Fig. 4) on addition of water is not accompanied by the change of its luminescence lifetime: τ=730 μs at 60°C. For other chelates the τ was<50 μs in toluene, thus, they could not be studied.

At equal ratio of $[H_2O]/[Ln]$, the η value increases with the increase of $Ln(L)_3 \cdot nH_2O$ concentration. At $[Ln(L)_3 \cdot nH_2O] < 10^{-4}$ M water quenches the luminescence of all Ln^{3+} β-diketonates (Figs. 2 and 3).

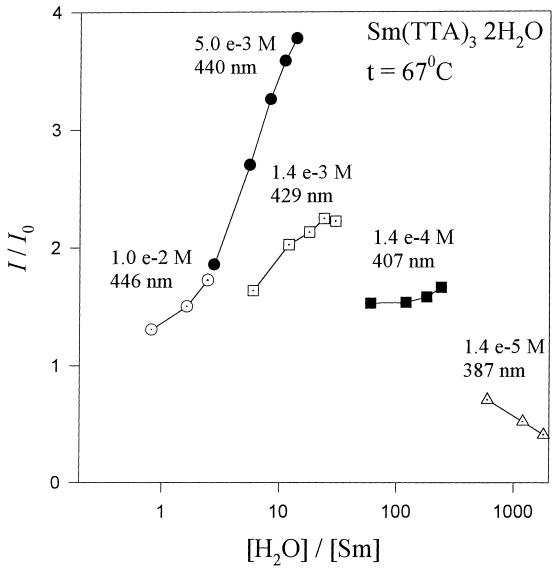

Fig. 2. Enhancement of luminescence intensity of $Sm(TTA)_3 \cdot 2H_2O$ in toluene on the addition of water. Shown in the figure are excitation wavelengths (nm) and concentrations of $Sm(TTA)_3 \cdot 2H_2O$ in (M). Luminescence registered at 90° to excitation beam.

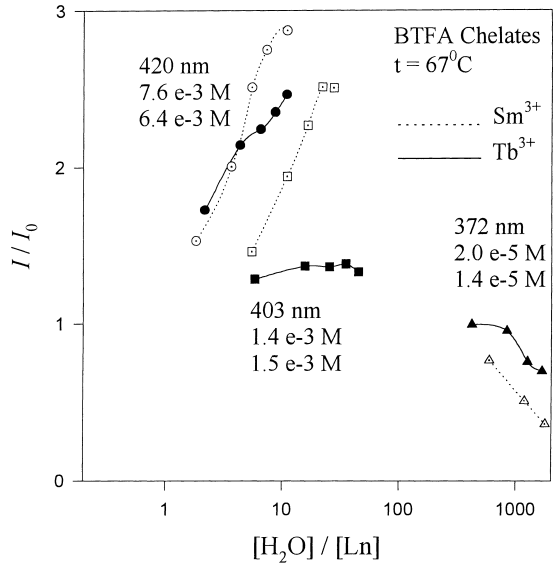

Fig. 3. Enhancement of luminescence intensity of BTFA chelates of Sm^{3+} and Tb^{3+} in toluene on the addition of water. Shown in the figure are excitation wavelengths (nm) and concentrations Sm^{3+} and Tb^{3+} chelates (M). Luminescence registered at 90° to excitation beam.

At the same time concentration quenching (CQ) of $Ln(L)_3 \cdot nH_2O$ luminescence is observed in toluene at LC-excitation (Fig. 5). The CQ in most cases obeys the Stern–Volmer equation (Eq. (1)), where a is a constant and K_{CQ} is a Stern–Volmer constant of quenching. However, for $Sm(L)_3 \cdot nH_2O$ and $Dy(AA)_3 \cdot 3H_2O$ the deviation from Eq. (1) is observed at $[Ln] > 5\times10^{-3}$ M, thus the K_{CQ} were estimated in the range $[Ln] < 5\times10^{-3}$ M. For a given ligand, the K_{CQ} values decrease in the order $Sm^{3+} > Tb^{3+} > Dy^{3+} > Yb^{3+} \gg Nd^{3+}$ (Fig. 5, Table 2). No CQ

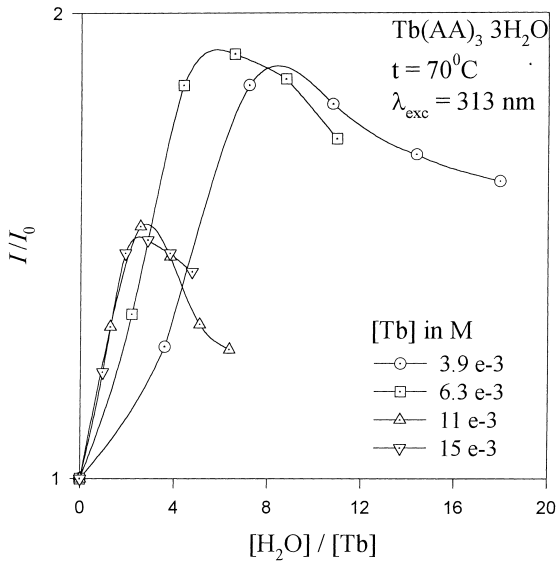

Fig. 4. Enhancement of luminescence intensity of $Tb(AA)_3 \cdot 3H_2O$ in toluene on the addition of water. Luminescence registered at 180° to excitation beam.

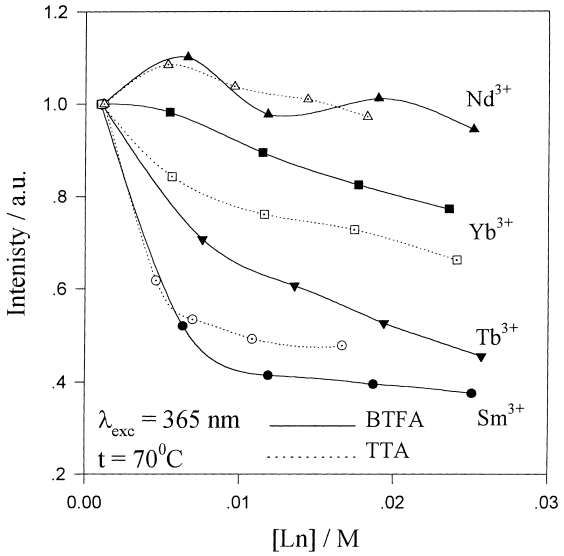

Fig. 5. Concentration quenching of luminescence of BTFA and TTA chelates of Ln^{3+} in toluene at LC-excitation. Concentration range studied is 0.001–0.03 M. Luminescence registered at 180° to excitation beam.

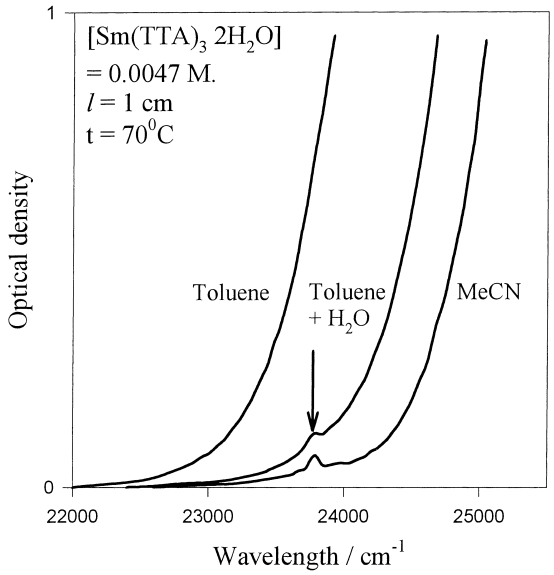

Fig. 6. Ligand-centered absorption of $Sm(TTA)_3{\cdot}2H_2O$ in MeCN, anhydrous toluene and in toluene with $[H_2O]$=0.056 M. The arrow points out ff-absorption of Sm^{3+}.

was observed for $Tb(AA)_3{\cdot}3H_2O$ and $Dy(DPM)_3$. In polar solvents, the quenching obeys Eq. (1) and the K_{CQ} values are lower than in toluene (Table 2).

$$I^{-1} = a + aK_{CQ}[Ln] \quad (1)$$

Addition of water to toluene, blue-shifts the LC-absorption of fluorinated Ln^{3+} β-diketonates (Fig. 6) and red-shifts the LC-absorption of non-fluorinated ones (Fig. 7). In anhydrous toluene, the LC-absorption of $Ln(L)_3{\cdot}nH_2O$, especially of fluorinated ones, is red-shifted in relation to the spectra in polar solvents (Figs. 6 and 7). For all chelates water does not change the LC-absorption in MeCN.

Water added to toluene, blue-shifts the hypersensitive ff-absorption band ($^4G_{5/2} \rightarrow {}^4I_{9/2}$) of fluorinated Nd^{3+} β-diketonates situated at 568–610 nm and lowers its intensity. Similar changes of ff-absorption of $Nd(FOD)_3$ in non-polar solvents in the presence of water were noted in [40].

In polar solvent such as DMSO, water up to 0.07 M did not change the luminescence intensity of Ln^{3+}, while in CH_3CN, the added H_2O quenched emission of Sm^{3+} did not change the emission of $Tb(BTFA)_3{\cdot}2H_2O$, and enhanced the luminescence intensity of $Tb(AA)_3{\cdot}3H_2O$, although to a lower extent than in toluene (these experiments were conducted at t=30°C).

Table 2
Stern–Volmer concentration quenching constants of $Ln(L)_3{\cdot}nH_2O$ in toluene and (MeCN as shown in parenthesis)[a]

	K_{CQ} (l mol^{-1})	
	BTFA	TTA
Nd^{3+}	<7	<9
Tb^{3+}	47 (≈0)	–
Sm^{3+}	>150[b] (15)	>150[b] (12)[c]
Yb^{3+}	15	20

[a] Notes: For $Dy(AA)_3{\cdot}3H_2O$ K_{CQ}=36 l mol^{-1}; for $Tb(AA)_3{\cdot}3H_2O$ and $Dy(DPM)_3$ $K_{CQ}\approx$0. The K_{CQ} were measured in the range of 0.001–0.03 M at λ_{exc}=313 or 365 nm in in-line geometry in toluene at 70°C and in MeCN at 30°C.

[b] Concentration quenching does not obey Eq. (1) and K_{CQ} were determined at $[Ln]<5\times10^{-3}$ M.

[c] No concentration quenching was observed for $Sm(TTA)_3{\cdot}2H_2O$ in DMSO at 30°C.

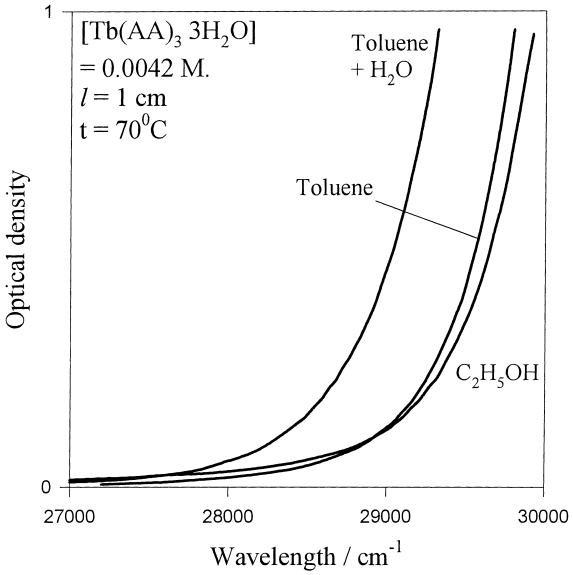

Fig. 7. Ligand-centered absorption of $Tb(AA)_3{\cdot}3H_2O$ in EtOH, anhydrous toluene and in toluene with $[H_2O]$=0.056 M.

4. Discussion

Determination of luminescence quantum yields showed that in toluene the ϕ of $Ln(L)_3{\cdot}nH_2O$ is lower than in polar solvents (Table 1). Even in 95% ethanol which has OH-groups, the ϕ of $Ln(L)_3{\cdot}nH_2O$ is higher than in toluene. Unexpectedly low luminescence lifetime of $Eu(FOD)_3$ in toluene as compared to polar solvents (alcohols, ethers, ketones) was noted in [20].

The excited $Ln(L)_3{\cdot}nH_2O$ in toluene deactivates not just by energy transfer to CH-groups of toluene and to OH-groups of coordinated water, but also by concentration quenching mechanism. The CQ might be due to: (a) intermolecular energy transfer: $Ln(L)_3{\cdot}nH_2O^* + Ln(L)_3{\cdot}nH_2O \rightarrow 2\ Ln(L)_3{\cdot}nH_2O$; (b) formation of dimers $[Ln(L)_3{\cdot}nH_2O]_2$ in which excited Ln^{3+} undergoes efficient quenching, since Ln^{3+} β-diketonates easily dimerize in non-polar solvents [41–44]. In benzene the $Tb(AA)_3{\cdot}3H_2O$ exists as dimer at concentrations of 0.005 M [42] and $Ln(BTFA)_3{\cdot}2H_2O$ are partially dimerized [44].

We suggest that the observed CQ of Ln^{3+} β-diketonates luminescence in toluene is due to the formation of dimers that have lower luminescence quantum yield compared to monomers. Dimerization might take place by the bridging of two Ln^{3+} β-diketonates either by oxygen of water, or by oxygen of the ligand [41,45–46]. Probably, the dimers in toluene are formed on substituting H_2O in chelate with another $Ln(L)_3{\cdot}nH_2O$ molecule Eq. (2). In polar solvents, however, only substitution of the H_2O for solvent takes place without dimerization of chelate.

$$2Ln(L)_3 \cdot nH_2O \rightleftarrows [Ln(L)_3 \cdot (n-x)H_2O]_2 + 2xH_2O \quad (2)$$

If the concentration quenching of Ln^{3+} luminescence is due to dimerization then the K_{CQ} values (Table 2) will be equal to the stability constant of the dimer. The equilibrium (2) is shifted to the left in polar solvents [41–43] and indeed the K_{CQ} decrease in polar MeCN and DMSO as compared to toluene (Table 1). The ability of $Ln(L)_3{\cdot}nH_2O$ to dimerize decreases with the decrease of ionic radii of Ln^{3+} [41,45–46], in the order $Nd^{3+}>Sm^{3+}>Tb^{3+}>Dy^{3+}>Yb^{3+}$. This order is reflected in the values of K_{CQ} (Fig. 5, Table 2), with the only exception of Nd^{3+}. Small K_{CQ} for $Nd(L)_3{\cdot}nH_2O$ and lack of CQ for $Tb(AA)_3{\cdot}3H_2O$ might indicate that these chelates are completely dimerized at concentration 0.001 M. It is known that $Ln(DPM)_3$ are monomeric in solutions [47–48] and no quecnhing is observed for $Dy(DPM)_3$ in toluene.

The water enhances the Ln^{3+} luminescence intensity only at $[Ln(L)_3{\cdot}nH_2O]>10^{-4}$ M (Figs. 2 and 3) and this might indicate that added water enhances emission of Ln^{3+} by inducing dissociation of poorly luminescent dimers to give monomers, e.g. shifts the equilibrium (2) to the left. On the contrary, at $[Ln(L)_3{\cdot}nH_2O]<10^{-4}$ M, the monomer form dominates in solution and its luminescence is quenched by water. However, at low $[Ln(L)_3{\cdot}nH_2O]$ and/or at large ratio $[H_2O]/[Ln]$ the chelate hydrolysis might take place with the loss of ligand resulting in the diminished luminescence efficiency of Ln^{3+}.

Concentration quenching in toluene is observed for chelates of all Ln^{3+} ions (Fig. 5). Why then, luminescence of only the selected Ln^{3+} chelates is enhanced by water? It should be noted that H_2O added to toluene enhances the luminescence of Ln^{3+} through dissociation of dimers and quenches Ln^{3+} emission by energy transfer to OH-groups. The rate constants for quenching of emitting level of Ln^{3+} ion by OH-group (k_{OH}) [3] are given in Table 1. The high values of k_{OH} for Nd^{3+}, Yb^{3+} and Dy^{3+} result in the quenching of emission of their β-diketonates by water in toluene. The Sm^{3+} and Tb^{3+} chelates show effective concentration quenching of luminescence in toluene coupled with a rather small k_{OH} and it results in the net enhancement of their emission by water.

Previously [13–14] we suggested that hydrogen bonding of water with the fluorine atoms of the ligand ($HOH\cdots F$) redistributes electronic density in the fluorinated Eu^{3+} β-diketonates and thus enhances their ϕ and τ. The $HOH\cdots F$ bond was observed in crystallographic study of $Pr_2(FOD)_6{\cdot}2H_2O$ [45], and H_2O also forms hydrogen bonds with the oxygen of β-diketonate ligand $HOH\cdots O$ [45–46]. Dissociation of dimers Eq. (2) probably occurs on coordination of water to the Ln^{3+} ion and/or to the ligand through formation of $HOH\cdots F$ or $HOH\cdots O$ bonds [45–46]. Both types of coordination are reflected in the changes of the ff- and LC-absorptions of $Ln(L)_3{\cdot}nH_2O$ in the presence of water. Considerable red-shift of LC-absorption of fluorinated Ln^{3+} β-diketonates in toluene as compared to polar solvents might be due to the presence of dimers (Fig. 6). Addition of water results in the dissociation of dimers and blue shifts the LC-absorption. However red-shift of the LC-absorption of $Tb(AA)_3{\cdot}3H_2O$ at addition of water in toluene probably indicates formation of hydrolysis products (Fig. 7), since $Ln(AA)_3{\cdot}3H_2O$ are easily hydrolysed [49]. These products precipitate at large ratio $[H_2O]/[Tb(AA)_3{\cdot}3H_2O]$, and this is also accompanied by the decrease of η (Fig. 4).

The luminescence enhancement of Tb^{3+} and Sm^{3+} in toluene is higher when D_2O is added instead of H_2O. D_2O also enhances emission of Dy^{3+}, Nd^{3+} and Yb^{3+} chelates although these are quenched by H_2O. It might be due to the exchange reaction $Ln(L)_3{\cdot}nH_2O + nD_2O \rightarrow Ln(L)_3{\cdot}nD_2O + nH_2O$ coupled with the lower quenching efficiency of O-D group as compared to O-H [1].

It is known that H_2O cannot substitute DMSO coordinated with Ln^{3+} [10] thus the luminescence of $Ln(L)_3{\cdot}nH_2O$ is not quenched by water in DMSO. However, H_2O substitutes MeCN [10] and quenches Sm^{3+} emission in MeCN. Luminescence enhancement of $Tb(AA)_3{\cdot}3H_2O$ by H_2O in MeCN might be due to its partial dimerization in MeCN [42].

Luminescence quantum yield of $Ln(L)_3{\cdot}nH_2O$ on excitation into LC-absortption ϕ is a product of ligand-to-ion energy transfer efficiency (Φ_{ET}) and luminescence quantum yield of Ln^{3+} ion (ϕ_{Ln}) Eq. (3). ϕ_{Ln} is measured when

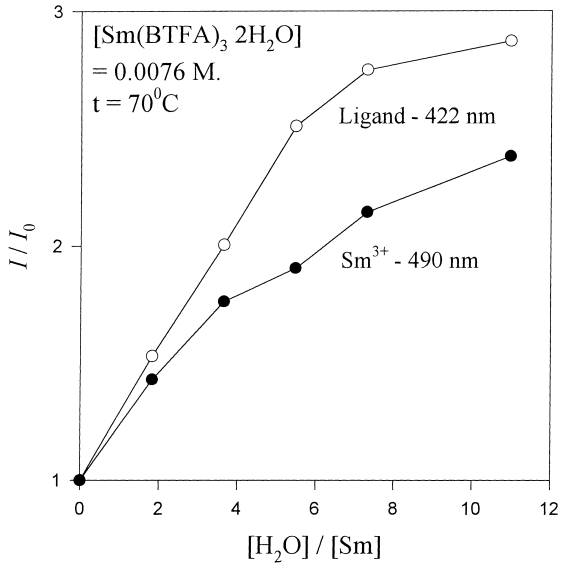

Fig. 8. Dependence of luminescence intensity enhancement of $Sm(BTFA)_3{\cdot}2H_2O$ at addition of water on the excitation wavelength. LC-excitation — 422 nm, ff-excitation — 490 nm. Luminescence registered at 90° to excitation beam.

one excites Ln^{3+} luminescence directly into its ff-levels. The decrease of ϕ in dimer compared to monomer might be caused by ϕ_{Ln} decrease due to cross-relaxation of excited Ln^{3+} on the ff-levels of neighboring Ln^{3+}. The efficiency of cross-relaxation will be determined by a small $Ln^{3+}\cdots Ln^{3+}$ distance in dimer estimated to be $\approx$4 Å [42,45,46]. However, one cannot exclude that the energy in dimer is lost on ligand levels before energy transfer to Ln^{3+} occurs which leads to Φ_{ET} decrease.

$$\phi = \Phi_{ET}\phi_{Ln} \quad (3)$$

The luminescence enhancement of BTFA and TTA chelates of Sm^{3+} by water depends on the excitation wavelength which is higher when one excites into LC than in the ff-absorption band (Fig. 8). The higher enhancement of ϕ compared to ϕ_{Ln} indicates that water increases the ligand-to-ion energy transfer efficiency — Φ_{ET} Eq. (3). Moreover, the invariability of the luminescence lifetime of $Tb(AA)_3{\cdot}3H_2O$ in toluene on the addition of H_2O indicates that water increases only Φ_{ET} (as evidenced by intensity enhancement) without changing the ϕ_{Ln}. These evidences indicate that energy loss in dimers of Ln^{3+} β-diketonates occurs both in ligand and Ln^{3+} excited levels.

5. Conclusions

In toluene, the Ln^{3+} β-diketonates show significant concentration quenching due to the formation of dimers at high concentrations of chelate. The dimers have lower luminescence quantum yields compared to monomers due to energy losses both in the ligand and in the Ln^{3+} ion. The presence of water in toluene causes dissociation of poorly luminescent dimers to give monomers which results in an quite unexpected significant enhancement of the luminescence intensity of Sm^{3+} and Tb^{3+} β-diketonates by water. Nevertheless, water quenches the luminescence of Dy^{3+}, Nd^{3+} and Yb^{3+} β-diketonates due to an efficient deactivation of excited states of these ions by the OH-group.

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