

Water enhances photoluminescence intensity of europium (III), terbium (III) and samarium (III) tris- β -diketonates in toluene solutions and chemiluminescence intensity of europium (III) and samarium (III) tris- β -diketonates in the reaction with dioxetane

A.I. Voloshin*, N.M. Shavaleev, V.P. Kazakov

*Institute of Organic Chemistry, Ufa Scientific Center of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russia*

Received 10 April 2000; accepted 17 July 2000

Abstract

Water enhances photoluminescence quantum yield of concentrated $>10^{-4}$ M toluene solutions of samarium, terbium and europium tris- β -diketonates ($\text{Ln}(\text{L})_3 \cdot n\text{H}_2\text{O}$) by shifting the dimer–monomer equilibrium of the chelate and by decreasing the nonradiative losses through the ligand-to-metal charge-transfer state. Water also alters the chemiluminescence intensity of $\text{Ln}(\text{L})_3 \cdot n\text{H}_2\text{O}$ excited from decomposition of a dioxetane by changing both the chemiexcitation mechanism and the photoluminescence quantum yield of Ln^{3+} . Water quenches chemiluminescence of Tb^{3+} , Dy^{3+} , Yb^{3+} , Nd^{3+} and of coordination-unsaturated Eu^{3+} β -diketonates, and enhances chemiluminescence of coordination-saturated Eu^{3+} and Sm^{3+} chelates. © 2000 Elsevier Science S.A. All rights reserved.

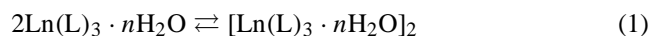
Keywords: Luminescence; Chemiluminescence; β -Diketonate complexes; Lanthanide; Terbium; Samarium; Europium; Dioxetane

1. Introduction

Photo- [1–14], electro- [15–17], thermo- [18], radio- [19], tribo- [20–22], electrochemi- [23] and chemiluminescence [24–28] of lanthanide β -diketonates is being extensively studied in order to improve the Ln^{3+} luminescence efficiency. The quenching of Ln^{3+} luminescence occurs by the exchange of the Ln^{3+} electronic energy to the vibrations of proximate bonds [1–14,29–31] and water molecules possessing high-energy OH-vibrations ($\nu = 3700 \text{ cm}^{-1}$) are the most efficient quenchers.

However, recently we have observed that photoluminescence of concentrated ($>10^{-4}$ M) toluene solutions of Eu^{3+} , Sm^{3+} and Tb^{3+} tris- β -diketonates ($\text{Ln}(\text{L})_3 \cdot n\text{H}_2\text{O}$) is enhanced by water [32–34]. In concentrated solutions the chelate is partially dimerized (Eq. (1)), and the luminescence quantum yield (ϕ) of dimer is significantly lower than for monomer due to a quenching in the ligand and cross-relaxation of Ln^{3+} . Addition of water shifts equilibrium (1) to the

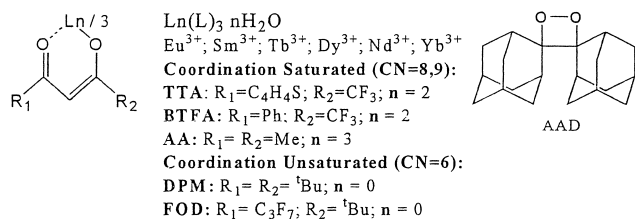
monomer and enhances Ln^{3+} luminescence quantum yield and lifetime [34]. However, in diluted $<10^{-4}$ M anhydrous toluene solutions the chelate already exists as monomer and addition of water quenches its luminescence.



Addition of water quenches luminescence of Dy^{3+} , Nd^{3+} and Yb^{3+} chelates due to a high $> 2 \times 10^4 \text{ s}^{-1}$ rate constant of deactivation of these ions by OH-group (k_{OH}), while water enhances luminescence of Eu^{3+} , Sm^{3+} and Tb^{3+} since k_{OH} for these ions is $< 2 \times 10^4 \text{ s}^{-1}$ [30].

Lanthanide chelates (β -diketonates [24–28], polyamino-carboxylates [24,35], etc.) are used to enhance emission intensity of various chemiluminescent reactions and it was of interest to study the influence of water on the chemiluminescence of Ln^{3+} . Herein, we have compared the influence of water on the photoluminescence intensity of Sm^{3+} , Eu^{3+} , Dy^{3+} , Tb^{3+} , Nd^{3+} and Yb^{3+} tris- β -diketonates in toluene and on their chemiluminescence excited from decomposition of adamantylideneadamantane-1,2-dioxetane (AAD) [25–28].

* Corresponding author. Fax: +7-347-2-356066.
E-mail address: chemlum@ufanet.ru (A.I. Voloshin).



2. Experimental

Synthesis of the chelates [25–26] and AAD [36] was described elsewhere. Toluene was dried and distilled over Na; H₂O was bidistilled.

Photoluminescence of Ln³⁺ was collected at 180° relative to excitation beam, in optically dense solutions. Water was added by 1 μl microsyringe to 2 ml of Ln(L)₃·nH₂O toluene solution at 85°C in quartz cell and dissolved until transparent homogeneous solutions were obtained. Concentration of [H₂O] = 0.056 M corresponds to the 2 μl of H₂O in 2 ml of toluene.

Chemiluminescence was studied on home-built equipment [25–26]. Water was added by microsyringe to 2 ml of Ln(L)₃·nH₂O and AAD toluene solution at 85°C and

dissolved. The conversion of AAD during experiment was <0.5%. Uncorrected CL spectra (Figs. 3 and 4) were recorded in toluene at 95°C with [Ln(L)₃·nH₂O] = 2 × 10⁻² M and [AAD] = 5 × 10⁻³ M.

For more experimental details see notes to the Table 1.

3. Results and discussion

3.1. Photoluminescence of Ln³⁺ β-diketonates

Absorption spectra of lanthanide β-diketonates consist of intense broad ligand bands in UV and weak ff-absorption lines of Ln³⁺ ion (Fig. 1). Excitation of chelate to the ligand or ion results in the ff-luminescence of Ln³⁺. In the former case the Ln³⁺ levels are populated by intramolecular energy transfer: L_S* → L_T* → Ln³⁺*, where L_S* and L_T* are the first excited singlet and the triplet ligand states, respectively [1–14].

Photoluminescence of Sm³⁺, Tb³⁺, Dy³⁺, Nd³⁺ and Yb³⁺ β-diketonates is observed from resonant level only. Only for Eu³⁺ the luminescence arises from two excited levels, resonant ⁵D₀ and upper-lying ⁵D₁ level (Fig. 2).

Table 1

Photoluminescence quantum yields (φ) at 25 and 85°C, relative chemiluminescence intensities (φ_{CL}) and influence of water on the photoluminescence and chemiluminescence of Ln³⁺ β-diketonates in toluene solutions

| | Quantum yields (%) ^a | | φ(H ₂ O)/φ ^c at 85°C | φ _{CL} ^d at 85°C | φ _{CL} (H ₂ O)/φ _{CL} ^e at 85°C |
|--|---------------------------------|----------|--|--------------------------------------|---|
| | φ (25°C) | φ (85°C) | | | |
| AAD | – | – | – | – | 1.0 |
| Sm(BTFA) ₃ ·2H ₂ O | 0.05 | 0.03 | 2.4 | 100 | 1.1 |
| Sm(TTA) ₃ ·2H ₂ O | 0.06 | 0.03 | 2.3 | 89 | 1.2 |
| Eu(BTFA) ₃ ·2H ₂ O | 0.7 | 0.02 | 4.3 | 1 | 1.8 |
| Eu(TTA) ₃ ·2H ₂ O | 0.9 | 0.008 | 4.3 | 1 | 1.6 |
| Eu(FOD) ₃ | 1.2 | 0.06 | 11 | 100 | 0.3 |
| Eu(DPM) ₃ | 0.1 | 0.03 | 21 | 1 | 0.5 |
| Tb(AA) ₃ ·3H ₂ O | 15 | 8.8 | 1.5 | 100 | 0.7 |
| Tb(BTFA) ₃ ·2H ₂ O | 0.07 | 0.008 | 1.6 | 4 | 0.5 |
| Tb(TTA) ₃ ·2H ₂ O | <0.001 | – | – | 2 | 0.5 |
| Dy(DPM) ₃ | 0.27 | 0.06 | 0.3 | 100 | 0.2 |
| Dy(AA) ₃ ·3H ₂ O | 0.005 | – | – | 1 | <0.8 |
| Dy(BTFA) ₃ ·2H ₂ O | <0.001 | – | – | <1 | <0.7 |
| Dy(TTA) ₃ ·2H ₂ O | <0.001 | – | – | <1 | <1 |
| Yb(TTA) ₃ ·2H ₂ O | 100 ^b | – | 0.8 | 72 | 0.8 |
| Yb(BTFA) ₃ ·2H ₂ O | 80 ^b | – | 0.8 | 100 | 0.7 |
| Nd(BTFA) ₃ ·2H ₂ O | 31 ^b | 43 | 0.7 | – | 0.5 |

^a Photoluminescence quantum yields of 10⁻³ M chelate solutions, determined as described in [34].

^b Only relative photoluminescence intensities are given for Yb³⁺ and Nd³⁺ that can be compared between each other [25].

^c Influence of water on the photoluminescence quantum yield of Ln³⁺. [Ln(L)₃·nH₂O] = 0.02 M, [H₂O] = 0.056 M. Given is the ratio of photoluminescence quantum yield in the presence of water — φ(H₂O) to that in anhydrous solution — φ. Photoluminescence spectra of Ln³⁺ (except Eu³⁺) are not altered by water and emission intensity was measured by the height of the most intense peak. For Eu³⁺ the change of photoluminescence intensity of ⁵D₀ → ⁷F₂ transition at 610 nm was measured.

^d Relative chemiluminescence intensities of Ln³⁺. [AAD] = 10⁻³ M, [Ln(L)₃·nH₂O] = 0.02 M. CL emission intensity was measured by selecting the required spectral range by cut-off filters. Relative CL intensities can be compared only between different chelates of the same Ln³⁺ ion.

^e Influence of water on the chemiluminescence intensity of Ln³⁺. [AAD] = 5 × 10⁻⁴ M, [Ln(L)₃·nH₂O] = 0.02 M, [H₂O] = 0.056 M. Given is the ratio of chemiluminescence intensity in the presence of water — φ_{CL}(H₂O) to that in anhydrous solution — φ_{CL}.

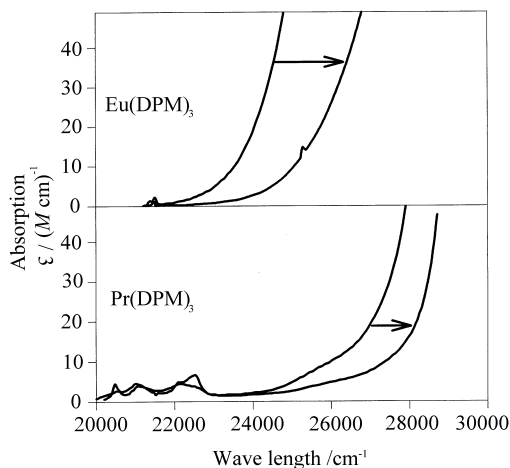


Fig. 1. Absorption spectra of 0.02 M solutions of $\text{Eu}(\text{DPM})_3$ and $\text{Pr}(\text{DPM})_3$ in anhydrous toluene and in toluene with $[\text{H}_2\text{O}] = 0.056 \text{ M}$. Weak line-like bands are ff-absorptions of Ln^{3+} ion. LMCT state appears in the absorption of $\text{Eu}(\text{DPM})_3$ as a long wavelength shoulder that is absent in the $\text{Pr}(\text{DPM})_3$ spectrum. Addition of water blue-shifts LMCT absorption of $\text{Eu}(\text{DPM})_3$ to a larger extent than the ligand absorption of $\text{Pr}(\text{DPM})_3$.

Luminescence quantum yields of 10^{-3} M toluene solutions of $\text{Ln}(\text{L})_3 \cdot n\text{H}_2\text{O}$ are listed in Table 1. At higher $[\text{Ln}^{3+}]$ the concentration quenching of Ln^{3+} luminescence is observed caused by dimerization (Eq. (1)) [34].

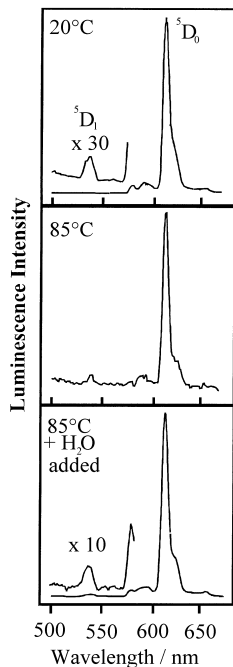
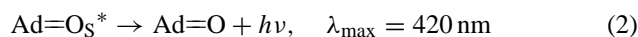
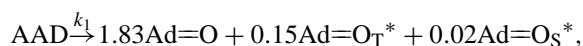


Fig. 2. Photoluminescence spectrum of $\text{Eu}(\text{FOD})_3$ (emission slit: 5 nm). Luminescence of Eu^{3+} is due to transitions from resonant $^5\text{D}_0$ and upper-lying $^5\text{D}_1$ level to $^7\text{F}_j$ levels. The band at 540 nm is due to $^5\text{D}_1 \rightarrow ^7\text{F}_0$ transition, the band at 610 nm is $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. Influence of temperature (upper and middle spectra) and addition of water (middle and lower spectra) on the $^5\text{D}_1$ -luminescence of Eu^{3+} . The concentration of H_2O after addition was 0.056 M. Intensities cannot be compared. Spectra were recorded on Hitachi MPF-4 spectrofluorimeter.

Temperature rise in the 25–85°C range lowers the ϕ of all Ln^{3+} chelates, except Nd^{3+} for which 30% enhancement of ϕ is observed. For Eu^{3+} the contribution of $^5\text{D}_1$ -emission to the total intensity increases at higher temperatures (Fig. 2) [5]. This indicates that $^5\text{D}_1$ level is thermally populated from $^5\text{D}_0$ level [37] ($\Delta E \sim 1750 \text{ cm}^{-1}$).

3.2. Chemiluminescence of Ln^{3+} β -diketonates

The reaction of AAD decomposition giving adamantanone in lowest excited singlet ($\text{Ad}=\text{O}_\text{S}^*$) and triplet ($\text{Ad}=\text{O}_\text{T}^*$) states (Eq. (2)) is practically a stationary source of excited species, since the rate constant k_1 in Eq. (2) is $< 10^{-6} \text{ s}^{-1}$ up to 100°C [36]. Chemiluminescence of AAD is due to the fluorescence of $\text{Ad}=\text{O}$ ($\lambda_{\text{max}} = 420 \text{ nm}$).



Emission bands of Ln^{3+} appear in the CL spectrum of AAD in the presence of the lanthanide β -diketonates studied. Chemiluminescence spectra of Ln^{3+} are given in Figs. 3 and 4, and relative chemiluminescence intensities (ϕ_{CL}) in Table 1. For all Ln^{3+} chelates, except Eu^{3+} , the photoluminescence and chemiluminescence spectra coincide. For Eu^{3+} , e.g. for $\text{Eu}(\text{FOD})_3$ the chemiluminescence is observed from $^5\text{D}_0$ and $^5\text{D}_1$ levels and $^5\text{D}_1$ -chemiluminescence at 540 nm is much more efficient than photoluminescence

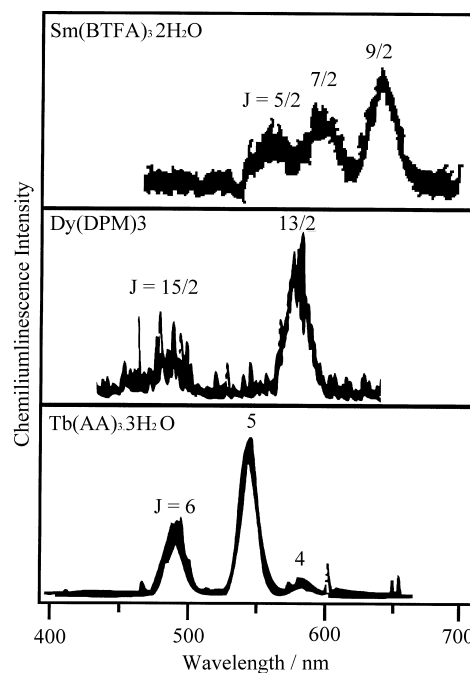


Fig. 3. Chemiluminescence spectra of $\text{Sm}(\text{BTFA})_3 \cdot 2\text{H}_2\text{O}$, $\text{Dy}(\text{DPM})_3$ and $\text{Tb}(\text{AA})_3 \cdot 3\text{H}_2\text{O}$. Emission of Sm^{3+} is due to transitions from resonant $^4\text{G}_{5/2}$ to $^6\text{H}_j$ levels; Dy^{3+} — due to transitions $^4\text{F}_{9/2} \rightarrow ^6\text{H}_j$; Tb^{3+} — due to transitions $^5\text{D}_4 \rightarrow ^7\text{F}_j$. In all cases photoluminescence and chemiluminescence spectra coincide.

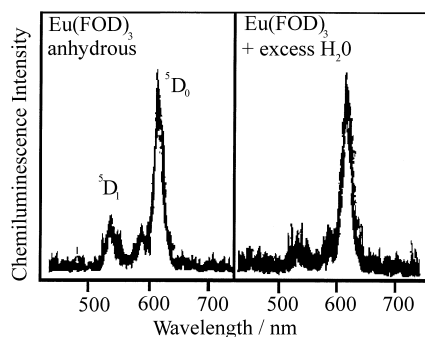


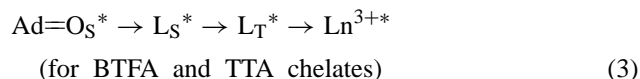
Fig. 4. Chemiluminescence spectra of $\text{Eu}(\text{FOD})_3$ in anhydrous toluene and in toluene with $[\text{H}_2\text{O}] = 0.056 \text{ M}$. Chemiluminescence and photoluminescence (Fig. 2) spectra of Eu^{3+} do not coincide, since in the former the $^5\text{D}_1$ -emission at 540 nm is more efficient.

(compare Figs. 2 and 4) [28]. The CL of Nd^{3+} and Yb^{3+} was studied in [25,26].

3.3. Chemiluminescence intensity and chemiexcitation mechanisms of Ln^{3+} β -diketonates

Chemiexcitation of Ln^{3+} in the system studied might occur by intermolecular and intracomplex energy transfer from $\text{Ad}=\text{O}^*$ [25,26].

Intermolecular energy transfer. Includes singlet–singlet energy transfer from $\text{Ad}=\text{O}_\text{S}^*$ to the ligand singlet state (Eq. (3)). This process was shown [25,26] to be possible only for TTA and BTFA chelates of Ln^{3+} since their L_S^* states are lower in energy than $\text{Ad}=\text{O}_\text{S}^*$ (Fig. 5)



Also, all the chelates can be excited by exothermic triplet–triplet energy transfer from $\text{Ad}=\text{O}_\text{T}^*$ to the ligand triplet (Fig. 5) and further to the Ln^{3+} levels (Eq. (4)) [38]

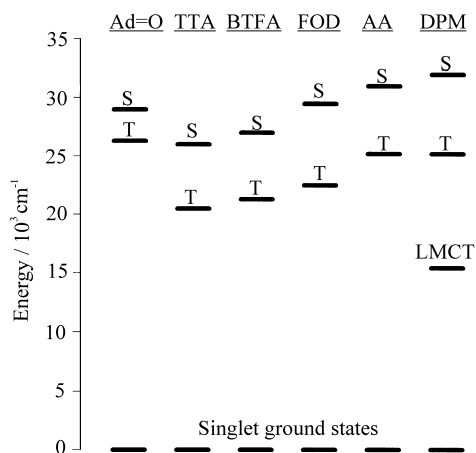
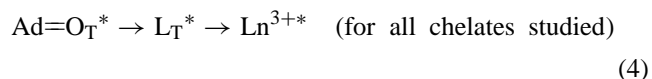
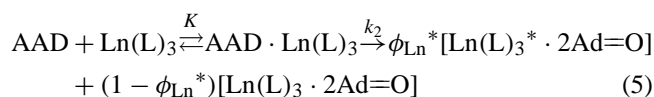


Fig. 5. Energy levels of $\text{Ad}=\text{O}$ and β -diketonate ligands of $\text{Ln}(\text{L})_3 \cdot n\text{H}_2\text{O}$ [25]. Energy of DPM_T^* is assumed to be equal to AA_T^* . Energy of LMCT state $\text{Eu}(\text{DPM})_3$ is taken from [12].



It should be noted that both chelate monomers and dimers may act as energy acceptors in Eqs. (3) and (4).

Intracomplex energy transfer to the excited levels of Ln^{3+} . The title mechanism is realized by decomposition of $\text{AAD} \cdot \text{Ln}(\text{L})_3$ complex (Eq. (5))



The Ln^{3+} in the complex is coordinated by AAD oxygens, and catalyzes its decomposition. The rate constant of $\text{AAD} \cdot \text{Ln}(\text{L})_3$ decay — k_2 in Eq. (5) is usually 10^2 – 10^3 times higher than k_1 in Eq. (2) [27]. Since the CL intensity is proportional to the rate of chemiluminescent reaction, one may expect that Ln^{3+} emission would be higher for chelate that catalyzes AAD decomposition according to Eq. (5), than for chelate that acts only as an energy acceptor of $\text{Ad}=\text{O}^*$ in Eqs. (3) and (4).

Formation of $\text{AAD} \cdot \text{Ln}(\text{L})_3$ and intracomplex chemiexcitation is probable for coordination-unsaturated DPM and FOD chelates [25,27], where only six out of eight to nine coordination sites of Ln^{3+} are occupied. Intracomplex excitation is less probable for coordination-saturated hydrated TTA, BTFA and AA chelates, however, even their chemiluminescence can be largely determined by the reaction (5) [25], due to formation of trace amounts of $\text{AAD} \cdot \text{Ln}(\text{L})_3$ and high rate constant k_2 .

In fact, the highest chemiluminescence emission is observed for the chelates that catalyze AAD decomposition, e.g. $\text{Eu}(\text{FOD})_3$ and $\text{Dy}(\text{DPM})_3$. CL emission of $\text{Eu}(\text{FOD})_3$ is 100 times higher than for TTA and BTFA chelates of Eu^{3+} (Table 1). Actually, intracomplex excitation (Eq. (5)) is the reason for the unusually efficient CL emission of Eu^{3+} from $^5\text{D}_1$ level (Figs. 2 and 4) [28]. ϕ_{CL} for $\text{Eu}(\text{DPM})_3$ is lower than for $\text{Eu}(\text{FOD})_3$ since the former inefficiently catalyzes AAD decomposition [27].

High ϕ_{CL} may also be observed for coordination-saturated chelates provided that they possess high ϕ , e.g. $\text{Tb}(\text{AA})_3 \cdot 3\text{H}_2\text{O}$ (Table 1).

3.4. Enhancement of photoluminescence intensity of Eu^{3+} , Tb^{3+} and Sm^{3+} β -diketonates by water

Addition of water ($[\text{H}_2\text{O}] = 0.056 \text{ M}$) to the 0.02 M toluene solutions of chelates enhances ϕ of Eu^{3+} , Sm^{3+} and Tb^{3+} and quenches ϕ of Dy^{3+} , Nd^{3+} , Yb^{3+} (Table 1). The $\phi(\text{H}_2\text{O})/\phi$ ratio for a given ligand decreases in the order $\text{Eu}^{3+} > \text{Sm}^{3+} > \text{Tb}^{3+}$.

Nonradiative deactivation for Eu^{3+} β -diketonates may occur by ligand-to-metal charge transfer (LMCT), especially at elevated temperatures [5,11,12,14]. LMCT-absorption is observed as a long wavelength shoulder in the $\text{Eu}(\text{DPM})_3$

absorption spectrum [12]. This shoulder is absent in the $\text{Ln}(\text{DPM})_3$ spectra, where $\text{Ln} = \text{Pr}^{3+}, \text{Dy}^{3+}$, (Fig. 1). Introduction of electron-accepting groups to the ligand (e.g. fluorine atoms) increases the energy of LMCT state and enhances Eu^{3+} luminescence efficiency [14].

Probably, water enhances the ϕ of Eu^{3+} chelates not only by shifting the equilibrium (1), but also by increasing the energy of LMCT state. Actually, addition of water blue-shifts LMCT-absorption of $\text{Eu}(\text{DPM})_3$, and this shift is larger than the one observed for ligand-centered absorption of $\text{Pr}(\text{DPM})_3$ (Fig. 1).

The photoluminescence spectrum of Eu^{3+} is changed by water, the ${}^5\text{D}_0$ -emission intensity is significantly enhanced relative to ${}^5\text{D}_1$ -emission (Fig. 2). This is probably caused by quenching of ${}^5\text{D}_1$ -level through energy exchange of ${}^5\text{D}_1 \rightarrow {}^5\text{D}_0$ transition to the O–H vibrations.

3.5. Enhancement of chemiluminescence intensity of BTFA and TTA chelates of Eu^{3+} and Sm^{3+} by water

Since the water changes the ϕ of lanthanide β -diketonates it should also influence their chemiluminescence emission. Water does not change the CL intensity of AAD, while it significantly alters emission of Ln^{3+} in $\text{AAD}\cdot\text{Ln}(\text{L})_3\cdot n\text{H}_2\text{O}$ system (Table 1, Fig. 6).

The influence of water on photoluminescence and chemiluminescence of Ln^{3+} were studied in identical conditions, i.e. at 85°C at $[\text{Ln}^{3+}] = 0.02 \text{ M}$ and with added $[\text{H}_2\text{O}] = 0.056 \text{ M}$ and the results for $\phi(\text{H}_2\text{O})/\phi$ and $\phi_{\text{CL}}(\text{H}_2\text{O})/\phi_{\text{CL}}$ entries in Table 1 can be compared.

If the Ln^{3+} chemiexcitation occurred *only* by $\text{AAD}\cdot\text{Ln}(\text{L})_3$ decomposition, then the addition of water that expels AAD by reaction (6) would decrease $\text{AAD}\cdot\text{Ln}(\text{L})_3$ concentration and quench Ln^{3+} chemiluminescence, independent of the change of ϕ

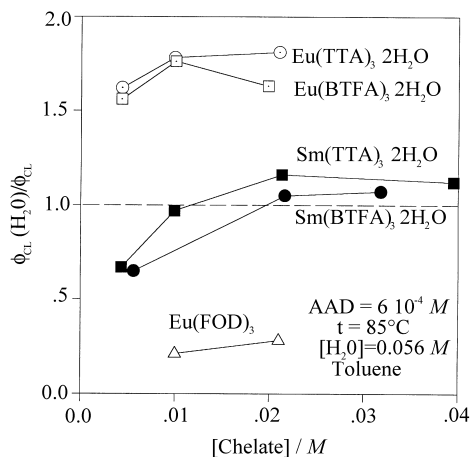
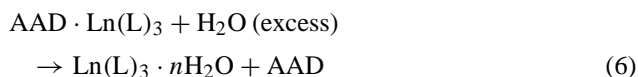


Fig. 6. Influence of water on the chemiluminescence intensity of Ln^{3+} β -diketonates in toluene.

However, if the Ln^{3+} chemiexcitation occurred *only* by intermolecular energy transfer (Eqs. (3) and (4)), then the change of ϕ_{CL} and ϕ by water would be identical.

Coordination-unsaturated FOD and DPM chelates:

Intracomplex chemiexcitation largely determines the CL intensity of the title chelates. Water quenches chemiluminescence of FOD and DPM chelates of Eu^{3+} , by reaction (6), and the loss of intracomplex chemiexcitation is not compensated by a >10 -fold increase of ϕ of Eu^{3+} by water (Table 1). Water changes the chemiluminescence spectrum of $\text{Eu}(\text{FOD})_3$, by decreasing contribution of ${}^5\text{D}_1$ -emission (Fig. 4). Actually, in the presence of water, the triplet–triplet excitation of $\text{Eu}(\text{FOD})_3$ (Eq. (4)) becomes important, and it does not lead to efficient ${}^5\text{D}_1$ -chemiluminescence of Eu^{3+} [28]. Similar changes of $\text{Eu}(\text{FOD})_3$ CL spectrum are observed by addition of other competing complex forming agents that expel AAD from inner coordination sphere of Ln^{3+} [28]. Water also quenches emission of $\text{Dy}(\text{DPM})_3$ both by reaction (6) and by additionally decreasing its ϕ (Table 1).

Coordination-saturated BTFA, TTA and AA chelates:

For coordination-saturated chelates of Ln^{3+} the intermolecular and intracomplex chemiexcitations may give comparable contribution to ϕ_{CL} [25,26]. Water quenches chemiluminescence of Nd^{3+} , Yb^{3+} and Dy^{3+} since it decreases their ϕ . Water also quenches emission of Tb^{3+} , since the loss of intracomplex chemiexcitation is not compensated by ~ 1.5 -fold enhancement of ϕ of Tb^{3+} by water.

However, water enhances chemiluminescence intensity of BTFA and TTA chelates of Eu^{3+} and Sm^{3+} (Fig. 6). The $\phi_{\text{CL}}(\text{H}_2\text{O})/\phi_{\text{CL}}$ ratio is higher when concentrated chelate solutions are used while in diluted solutions water quenches chelate emission (Fig. 6). Both the ϕ_{CL} and ϕ for Eu^{3+} chelates are enhanced by water to a larger extent than for Sm^{3+} .

Probably at high chelate concentrations in anhydrous solutions energy transfer from $\text{Ad}=\text{O}^*$ occurs both to the dimers and monomers of $\text{Ln}(\text{L})_3\cdot n\text{H}_2\text{O}$. In the presence of water only monomers act as energy acceptors, and since they have higher ϕ than dimers, it results in the net enhancement of Eu^{3+} and Sm^{3+} CL intensity. However intracomplex chemiexcitation of Eu^{3+} and Sm^{3+} in anhydrous solutions cannot be neglected since the ϕ_{CL} enhancement is ~ 2 times lower than the enhancement of ϕ (Table 1). If intracomplex route was negligible one would expect $\phi(\text{H}_2\text{O})/\phi$ and $\phi_{\text{CL}}(\text{H}_2\text{O})/\phi_{\text{CL}}$ values to be equal. The quenching by water of Sm^{3+} chemiluminescence at low chelate concentrations (Fig. 6) is due to the quenching of monomer luminescence [34].

4. Conclusions

Water enhances photoluminescence quantum yields of Eu^{3+} , Tb^{3+} and Sm^{3+} β -diketonates in concentrated ($>10^{-4} \text{ M}$) toluene solutions due to dissociation of weakly luminescent dimers, and by decreasing energy losses through

a LMCT state (for Eu^{3+}). The influence of water on chemiluminescence of Ln^{3+} is dependent on its chemiexcitation mechanism. In the case of intracomplex chemiexcitation water always quenches CL intensity of Ln^{3+} independent of change of ϕ . In the case of intermolecular chemiexcitation, enhancement of ϕ by water may result in the enhancement of ϕ_{CL} , e.g. BTFA and TTA chelates of Eu^{3+} and Sm^{3+} .

References

- [1] G.F. De Sa, O.L. Malta, C. De M. Donega, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. Da Silva Jr., *Coord. Chem. Rev.* 196 (2000) 165.
- [2] S.B. Meshkova, Z.M. Topilova, D.V. Bolshoy, S.V. Beltyukova, M.P. Tsvirko, V.Y. Venchikov, *Acta Phys. Polon. A* 95 (1999) 983.
- [3] H.F. Brito, C.A.A. Carvalho, O.L. Malta, J.J. Passos, J.F.S. Menezes, R.D. Sinisterra, *Spectrochim. Acta A* 55 (1999) 2403.
- [4] M.H.V. Werts, M.A. Duin, J.W. Hofstra, J.W. Verhoeven, *Chem. Commun.* (1999) 799.
- [5] L.S. Villata, E. Wolcan, M.R. Feliz, A.L. Capparelli, *J. Phys. Chem. A* 103 (1999) 5661.
- [6] W. Streck, J. Sokolnicki, J. Legendziewicz, K. Maruszewski, R. Reisfeld, T. Pavich, *Opt. Mater.* 13 (1999) 41.
- [7] H.H. Li, S. Inoue, K. Machida, G. Adachi, *Chem. Mater.* 11 (1999) 3171.
- [8] J.L. Yuan, K. Matsumoto, H. Kimura, *Anal. Chem.* 70 (1998) 596.
- [9] O.A. Serra, E.J. Nassar, C.A. Kodaira, C.R. Neri, P.S. Calefi, I.L.V. Rosa, *Spectrochim. Acta A* 54 (1998) 2077.
- [10] L.C. Thompson, F.W. Atchison, V.G. Young, *J. Alloys Compounds* 275–277 (1998) 765.
- [11] V.A. Belyakov, R.F. Vasilev, G.F. Fedorova, *Russ. Chem. Bull.* 45 (1996) 1596.
- [12] M.T. Berry, P.S. May, H. Xu, *J. Phys. Chem.* 100 (1996) 9216.
- [13] S.T. Frey, M.L. Gong, W. De W. Horrocks Jr., *Inorg. Chem.* 33 (1994) 3229.
- [14] G.D.R. Napier, J.D. Neilson, T.M. Shepherd, *Chem. Phys. Lett.* 31 (1975) 328.
- [15] C.J. Liang, Z.R. Hong, X.Y. Liu, D.X. Zhao, D. Zhao, W.L. Li, J.B. Peng, J.Q. Yu, C.S. Lee, S.T. Lee, *Thin Solid Films* 359 (2000) 14.
- [16] Y. Kawamura, Y. Wada, Y. Hasegawa, M. Iwamuro, T. Kitamura, S. Yanagida, *Appl. Phys. Lett.* 74 (1999) 3245.
- [17] X.C. Gao, H. Cao, C.H. Huang, B.G. Li, K. Ibrahim, F.Q. Liu, S. Umitani, *Chem. Phys. Lett.* 297 (1998) 530.
- [18] V.E. Karasev, A.V. Gerasimenko, A.G. Mirochnik, I.N. Botova, N.V. Polyakova, *Koord. Khim.* 25 (1999) 945.
- [19] A.B. Yusov, *Radiokhimiya* 35 (1993) 3.
- [20] X.F. Chen, S.H. Liu, C.Y. Duan, Y.H. Xu, X.Z. You, M. Jing, N.B. Min, *Polyhedron* 17 (1998) 1883.
- [21] N. Takada, J. Sugiyama, R. Katoh, N. Minami, S. Hieda, *Synthetic Met.* 91 (1997) 351.
- [22] L.M. Sweeting, A.L. Rheingold, *J. Am. Chem. Soc.* 109 (1987) 2652.
- [23] M.M. Richter, A.J. Bard, *Anal. Chem.* 68 (1996) 2641.
- [24] M. Elbanowski, B. Makowska, K. Staninski, M. Kaczmarek, *J. Photochem. Photobiol. A* 130 (2000) 75.
- [25] A.I. Voloshin, N.M. Shavaleev, V.P. Kazakov, *J. Lumin.* 91 (2000) 49.
- [26] A.I. Voloshin, N.M. Shavaleev, V.P. Kazakov, *J. Photochem. Photobiol. A* 131 (2000) 61.
- [27] V.P. Kazakov, A.I. Voloshin, N.M. Shavaleev, *J. Photochem. Photobiol. A* 119 (1998) 177.
- [28] G.L. Sharipov, A.I. Voloshin, V.P. Kazakov, G.A. Tolstikov, *Dokl. Akad. Nauk SSSR* 315 (1990) 425.
- [29] A. Beeby, I.M. Clarkson, R.S. Dickins, S. Faulkner, D. Parker, L. Royle, A.S. de Sousa, J.A.G. Williams, M. Woods, J.C.S. Perkin *Trans. 2* (1999) 493.
- [30] V.L. Ermolaev, E.B. Sveshnikova, *Russ. Chem. Rev.* 63 (1994) 905.
- [31] S. Lis, G.R. Choppin, *Anal. Chem.* 63 (1991) 2542.
- [32] V.P. Kazakov, A.I. Voloshin, S.S. Ostakhov, N.M. Shavaleev, *Mendeleev Commun.* (1998) 47.
- [33] S.S. Ostakhov, A.I. Voloshin, V.P. Kazakov, N.M. Shavaleev, *Russ. Chem. Bull.* 47 (1998) 1466.
- [34] A.I. Voloshin, N.M. Shavaleev, V.P. Kazakov, *J. Photochem. Photobiol. A* 134 (2000) 111.
- [35] T. Ala-Kleme, K. Haapakka, M. Latva, *Anal. Chim. Acta* 395 (1999) 205.
- [36] G.B. Schuster, N.J. Turro, H.-C. Steinmetzer, A.P. Schaap, G. Faler, W. Adam, J.C. Liu, *J. Am. Chem. Soc.* 97 (1975) 7110.
- [37] Y. Haas, G. Stein, *Chem. Phys. Lett.* 8 (1971) 366.
- [38] B. Marciniak, G.L. Hug, *J. Photochem. Photobiol. A* 78 (1994) 7.