The anomalous influence of water on the intensity and lifetime of fluorescence in tris(benzoyltrifluoroacetonate)europium(III)

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Addition of H_2O (D_2O) to a Eu(btfa)$_3$ toluene solution enhances the luminescence intensity and lifetime of Eu(btfa)$_3$, a phenomenon due to the formation of associates Eu(btfa)$_3 \cdot n H_2O$ [Eu(btfa)$_3 \cdot n D_2O$].

It is well known that water and other hydroxyl-containing molecules effectively quench the fluorescence of rare-earth ions. The quenching occurs through the exchange of rare-earth ion electronic excitation energy with the high-frequency vibrational overtones of the O–H bond. The quenching efficiency is sharply decreased upon deuteration of the O–H bond.[1]

However, we have observed that addition of water to toluene solutions of fluorinated europium β-diketonate Eu(fod)$_3$ (fod = [C$_3$F$_7$COCHCOCF$_3$]$^-$) enhances the fluorescence quantum yield and lifetime of this complex. This unexpected result was explained by assuming that outer-sphere associates are formed between water and fluorine atoms in the chelate ligand.[2]

Here we report results on the influence of water on the photoluminescence of tris(benzoyltrifluoroacetonate)europium(III), Eu(btfa)$_3$, toluene solutions.

Complex Eu(btfa)$_3$ was prepared according to the literature.[3] Toluene was dried by boiling over metallic sodium for 4 h and distilled. Fluorescence spectra and intensity of Eu(btfa)$_3$ were recorded on a MPF-4 'Hitachi' spectrofluorimeter after excitation with radiation $\lambda = 390$ nm in the temperature range 60–80 °C. Fluorescence lifetime was measured with a laser impulse fluorimeter LIF-200 at 65 °C. The fluorescence quantum yield of Eu(btfa)$_3$ in toluene was determined relative to Eu(TTA)$_3 \cdot$phen (10^{-4} M in toluene).

Addition of H_2O (D_2O) to a toluene solution of Eu(btfa)$_3$ leads to formation of an emulsion. However, in a short period of time (5 min) the drops of the emulsion are transformed into crystals and then a rather lengthy process of dissolution of these crystals takes place (20–30 min). All measurements were carried out for optically homogeneous solutions in which all transformations had finished.

Addition of H_2O (D_2O) enhances the photoluminescence intensity and lifetime of Eu(btfa)$_3$ upon excitation into the absorption band of the ligand (Figures 1 and 2). In our experimental conditions, when the water concentration was one order of magnitude greater than that of Eu(btfa)$_3$, we obtained inner-sphere complexes between H_2O (D_2O) and Eu(btfa)$_3$ at each water concentration studied, since in solvents with low donor number, such as toluene, water molecules coordinate to the rare-earth ion in the inner coordination sphere.[4]

The observed increase in fluorescence intensity and lifetime of Eu(btfa)$_3$ could not be explained by the generally accepted point of view of the strong quenching effect of H_2O on the luminescence of rare-earth ions. The suggestion that Eu(btfa)$_3$ undergoes hydrolysis on addition of water was rejected based on the similarity of the Eu(btfa)$_3$ luminescence spectra obtained in the absence and in the presence of H_2O (D_2O) in the concentration range of H_2O (D_2O) studied (10^{-2}–5×10^{-2} M), although it is known that hydrolysis of chelates is accompanied by a change in the fluorescence spectra and usually leads to a decrease in the fluorescence intensity of the rare-earth ion.
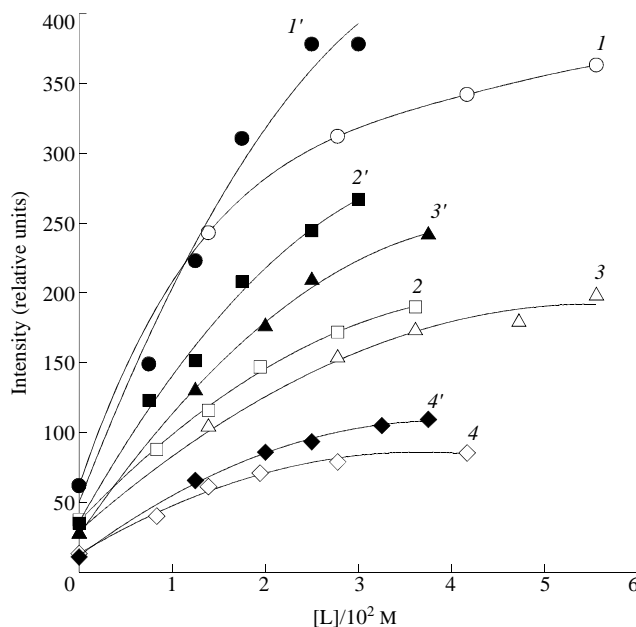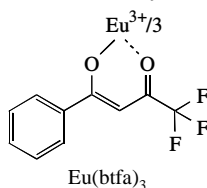
Figure 1 Dependence of 10^{-3} M Eu(btfa)$_3$ photoluminescence on concentration of H_2O (*1–4*) and D_2O (*1'–4'*) at 60 °C (*1, 1'*), 65 °C (*2, 2'*), 70 °C (*3, 3'*), 80 °C (*4, 4'*).

The addition of water results in a slight decrease of the optical density at 390 nm in the absorption spectrum of Eu(btfa)$_3$ which could not explain the observed increase in fluorescence intensity.

The luminescence decay of Eu(btfa)$_3$ in the presence of water was non-exponential, consisting of two parts with different lifetimes: τ_1 and τ_2, where τ_2 was 2–4 times greater than τ_1. However, recording of τ_2 was impossible because of the small luminescence yield (5–10% of the total luminescence), causing a large error in the measurement of τ_2. For this reason the following conclusions were drawn by considering the dependence of luminescence with lifetime τ_1 on the concentration of H_2O (D_2O). τ_1 is subsequently abbreviated as τ.

We assume that the increase in fluorescence intensity and lifetime of Eu(btfa)$_3$ is caused by the associates Eu(btfa)$_3 \cdot n H_2O$ [Eu(btfa)$_3 \cdot n D_2O$] formed through hydrogen bonds arising between the fluorine atoms or aryl substituent present in the ligand and hydrogen or deuterium atoms in water.†

The formation of complexes between molecules able to form hydrogen bonds (HF, HCl, H_2O, H_2S, NH_3) and aromatic molecules (serving as H acceptor) is well established.[5] This process is accompanied by significant redistribution of electronic charge.[5] We should therefore expect that the Eu^{3+}–O bond in

Eu(btfa)$_3$

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† Evidence for associate formation involving the aryl substituent in the chelate can be found in ref. 1 where the authors observed that addition of D_2O to a cyclohexane solution of europium benzoylacetonate [Eu(CH$_3$COCHCOPh)$_3$] enhances the fluorescence lifetime of this complex. Although the authors gave no explanation for this phenomenon we think that it is caused by the formation of associates similar to those discussed in this paper.
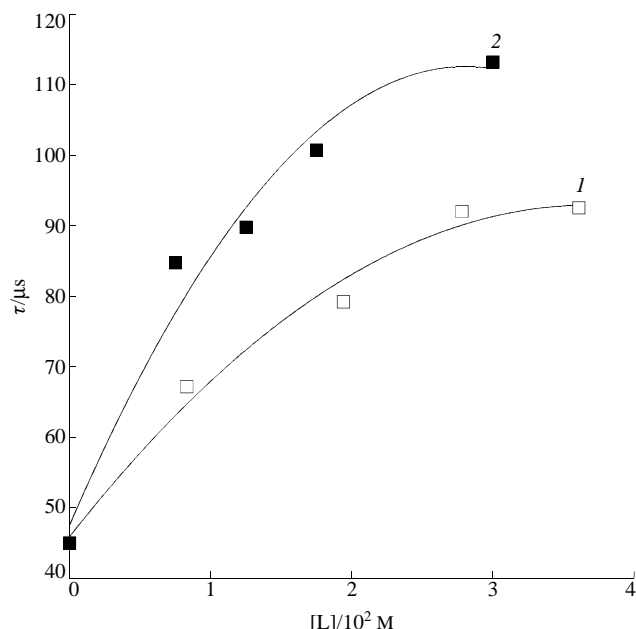
Figure 2 Dependence of 10^{-3} M Eu(btfa)$_3$ photoluminescence lifetime on the concentration of water at 65 °C: *1*, H$_2$O; *2*, D$_2$O.

the associates Eu(btfa)$_3$·H$_2$O [Eu(btfa)$_3$·D$_2$O] will be much more ionic than in free Eu(btfa)$_3$, since less electron density will be donated from the aryl substituent to the oxygens of the ligand. Taking into account the fact that enhancement of the ionic character of that bond results in lower nonradiative degradation of the electronic excitation of Eu^{3+} through the vibrational overtones of the surrounding molecules[6] we obtain a reasonable explanation for the observed 'anomalous' influence of water on the luminescent properties of Eu(btfa)$_3$.

An alternative explanation for the observed phenomenon might be an increase in the energy of the triplet level of the ligand caused by the formation of associates. This would result in diminished radiationless losses of energy from the resonant excited $^5D_0$ level of Eu^{3+} through the triplet level of the ligand. However, the observed activation energy of the temperature dependence of the Eu^{3+} luminescence intensity in Eu(btfa)$_3$ $E_a = 4.5\pm0.7$ kcal mol^{-1} coincides with the value of the energy gap between the $^5D_1$ and $^5D_0$ levels of europium ($\Delta E = 4.9$ kcal mol^{-1}). Apparently the deactivation of the resonant excited $^5D_0$ level of Eu^{3+} in Eu(btfa)$_3$ takes place through the population of the higher lying $^5D_1$ level of Eu^{3+} but not through the triplet level of the ligand.

The formation of associates is further proved by the fact that water does not enhance the luminescence intensity or lifetime of another β-diketonate, Eu(dpm)$_3$ (dpm = [Bu^{t}COCHCOBu^t]$^-$), which contains neither fluorine atoms nor aryl groups.[2]

With an increase in the H$_2$O (D$_2$O) concentration the fluorescence lifetime (τ) and intensity (I) reach a maximum value (Figures 1 and 2). These dependences were linearised in the inverse coordinates [H$_2$O^{-1} (D$_2$O^{-1}) *vs.* I^{-1} or τ^{-1}]. This empirical approach does not reflect the complicated processes involved in associate formation with more than one molecule of water taking place in the system. It does nevertheless permit the determination of the maximum values of Eu^{3+} luminescence

Table 1 Maximum values for the relative increase of Eu(btfa)$_3$ photoluminescence intensity (I_{max}/I_0) and lifetime (τ_{max}/τ_0) in the presence of H$_2$O (D$_2$O).[a]

T/K	$\tau_0/\mu s$	I_{max}/I_0 H$_2$O	τ_{max}/τ_0 H$_2$O	I_{max}/I_0 D$_2$O	τ_{max}/τ_0 D$_2$O
333		7.0		16	
338	42	7.7	2.2	12	2.9
343		10.0		16	
353		10.0		15	

[a]I_0 and τ_0 are the photoluminescence intensity and lifetime of a Eu(btfa)$_3$ anhydrous toluene solution. Errors of measurement of I and τ are 5% and 10%, respectively.

Table 2 Photophysical constants for Eu(btfa)$_3$ toluene solutions: (ϕ_0, k_{em}^0, k_d^0) and in the presence of H$_2$O (D$_2$O) (ϕ_{max}, k_{em}, k_d) at 65 °C.[a]

ϕ_0 (%)	k_{em}^0/s^{-1}	k_d^0/s^{-1}	ϕ_{max} H$_2$O	k_{em} H$_2$O	k_d H$_2$O	ϕ_{max} D$_2$O	k_{em} D$_2$O	k_d D$_2$O
2.7	640	23000	21	2000	7700	32	2700	5400

[a]Errors in the calculation of the photophysical constants are 30%.

intensity and lifetime. From the intercepts on the I^{-1} or τ^{-1} axes the maximum values for I and τ were obtained (I_{max} and τ_{max}, respectively, Table 1).

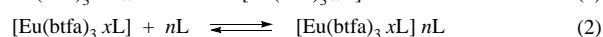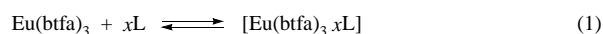The quantum yield for Eu(btfa)$_3$·H$_2$O [Eu(btfa)$_3$·D$_2$O] ϕ_{max} corresponding to I_{max} was obtained from the equation $\phi_{max} = \phi_0(I_{max}/I_0)^{-1}$ where ϕ_0 and I_0 are the photoluminescence quantum yield and intensity for an anhydrous toluene solution of Eu(btfa)$_3$.

Using ϕ_{max} and τ_{max} we calculated the values of radiative and non-radiative decay rate constants (k_{em} and k_d, respectively) for the associates from equations $k_{em} = \phi_{max}\tau_{max}^{-1}$ and $k_d = (1 - \phi_{max})\tau_{max}^{-1}$ (Table 2).

As can be seen from Figures 1 and 2 the increase of fluorescence intensity and lifetime of Eu(btfa)$_3$ for D$_2$O is much larger than for H$_2$O. This fact is in accordance with the theory of radiationless energy transfer.[1] The observed isotope effect clearly shows that in the system consisting of europium chelate containing potential H-accepting groups in the ligand and in water, two opposing effects exist. The first is quenching of rare-earth ion luminescence by the water molecules coordinated in the inner sphere of Eu^{3+}; and the second is a luminescence increase due to the formation of outer-sphere associates between water and the chelate ligand.

Assuming that H$_2$O and D$_2$O form similar associates we can estimate the average number of water molecules coordinated in the inner sphere of Eu^{3+} in the presence of water. The difference between non-radiative decay rate constants for Eu(btfa)$_3$·nH$_2$O and Eu(btfa)$_3$·nD$_2$O is 2300 s^{-1}. Taking into account the fact that the rate constant for quenching of the $^5D_0$ excited state of Eu^{3+} by a single O–H bond[7] is 450–650 s^{-1} we deduce that 2 or 3 molecules of H$_2$O (D$_2$O) are present in the inner coordination sphere of Eu^{3+} in the presence of water (4 or 6 O–H bonds, respectively). This is a reasonable estimate because the coordination number for Eu^{3+} is 8–9 and only 6 coordination sites are occupied in the tris-β-diketonates of Eu^{3+}.

The reactions for associate formation can thus be represented by Scheme 1:

Eu(btfa)$_3$ + xL ⇌ [Eu(btfa)$_3$ xL]   (1)

[Eu(btfa)$_3$ xL] + nL ⇌ [Eu(btfa)$_3$ xL] nL   (2)

Scheme 1

where L = H$_2$O (D$_2$O), reaction (1) represents formation of an inner-sphere complex ($x = 2$ or 3) and reaction (2) represents formation of outer-sphere associates.

The larger increase of quantum yield for Eu(btfa)$_3$ ($\phi_{max}/\phi_0 = 10$–15) compared to Eu(fod)$_3$ ($\phi_{max}/\phi_0 = 2$–4)[2] can be explained by considering that besides fluorine atoms the (btfa) ligand also contains an aryl substituent. The aryl substituent (being the chromophore) and the H-accepting group form a system of conjugated bonds in the β-diketonate which helps the redistribution of the electronic density caused by the formation of associates.

Thus, based on these and previous[2] results we should expect that addition of water to a rare-earth β-diketonate containing H-accepting groups in the ligand will lead to an 'anomalous' influence of water on the fluorescence intensity and lifetime of the rare-earth β-diketonate. The same influence on the luminescence of rare-earth β-diketonates should be expected from other compounds able to form hydrogen bonds, *e.g.* alcohols.

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