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Solvent quenching of the $^5D_0 \rightarrow {}^7F_2$ emission of Eu(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate)$_3$

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Abstract

Quenching of luminescence of Eu(fod)$_3$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5 octanedionate) has been studied in different solvents (i.e., acetonitrile, ethanol, methanol, *n*-butanol, 2-propanol, bencylic alcohol, chloroform, dichloromethane, 1,1-dichloroethane, 1,2-dichloroethane, carbon tetrachloride, benzene, toluene, *m*- and *p*-xilene, acetone, ciclohexanone, methylethylketone, methylpropylketone (iso), fluorobenzene, chlorobenzene, bromobenzene, ethyl ether, dioxane and tetrahydrofurane, and deuterated solvents acetonitrile (d_3), ethanol (d_1), methanol (d_4), benzene (d_6), acetone (d_6) and chloroform (d)). Absorption and emission spectra of the complex in the different solvents, their luminescence lifetimes at room temperature and at the boiling temperature of liquid air, so as in solid phase were measured. Evidences of different mechanisms for quenching of the luminescence is presented and discussed.

Keywords: Europium(III); Luminescence quenching; Solvent effects

1. Introduction

Lanthanide chelates have attracted a large interest since they may be used for many applications such as solvent extraction agents, NMR shift reagents and laser materials [1,2]. Their luminescent properties have been useful to use them as replacements for radioactivity, alternatives to standard fluorescent dyes and donors in energy transfer experiments [3]. Quenching of their emission by solvents have received attention since the sixties. Most of the studies were carried out in aqueous or alcoholic solutions and the effect of deuterated solvents has been considered [4–7]. It was well established that an efficient radiationless decay channel is coupling with the high-frequency O–H oscillators [8–10]. This mechanism has also been considered as operative when C–H [11] or N–H [12,13] were the oscillators available to withdraw the energy from the f–f excited state. In dichloromethane [2] and benzene [14] the lifetime of Eu complexes decreases as compared with solid state, however no attempt was made to explain the deactivation mechanism. In the present paper a research about the luminescence of Eu(fod)$_3$ in several solvents is reported and evidence is presented to support the existence of different mechanism depending on the solvent type.

2. Experimental details

2.1. Materials

The Eu(fod)$_3$ complex from Aldrich Chem. was used as received. The following solvents, acetonitrile, ethanol, methanol, *n*-butanol, 2-propanol, bencylic alcohol, chloroform, dichloromethane, 1,1-dichloroethane, 1,2-dichloroethane, carbon tetrachloride, benzene, toluene, *m*- and *p*-xilene, acetone, ciclohexanone, methylethylketone, methylpropylketone (iso), fluorobenzene, chlorobenzene, bromobenzene, ethyl ether, dioxane and tetrahydrofurane were Merck reagent grade. The deuterated solvents acetonitrile (d_3), ethanol (d_1), methanol (d_4), benzene (d_6), acetone (d_6) were Merck reagent grade and chloroform (d) was Fluka Chem. Fabrik. Acetonitrile, alcohols and ethers were previously dried on molecular sieves. Other solvents were used as received without further purification.

Dissociation constant data are not available for the systems studied. However, absorption of Eu(fod)$_3$ solutions in the

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more polar solvents (acetonitrile, methanol) follow the Lambert–Beer Law in the concentration range used in this work. Although, acetonitrile solutions showed a very small increase in conductivity with complex concentration indicating some dissociation, previous reports [15] showed that acetonate complexes of Eu in methanol solutions do not present any variation of the emission quantum yield with concentration indicating that essentially only one chelate species was present.

2.2. Equipments and procedures

UV–visible spectra were recorded on a CARY 3 spectrophotometer. Luminescence spectra were taken with an SLM 4800 (Aminco) spectrofluorometer.

The instrumentation for the time-resolved luminescence measurements has been described elsewhere [16]. Lifetime measurements were made at room-temperature and at the boiling temperature of liquid air using a pulsed nitrogen laser with excitation at 337 nm and monitoring the signal at different wavelengths between 560 and 750 nm for the Europium (III) compound. A modified 1P28 photomultiplier tube circuit with ca. 1 ns response time was used as the detector for the red emission dispersed through a monochromator. The signal was directly measured on a fast digitizing oscilloscope (Hewlett-Packard Instruments) and the temporal resolution of the overall system was ca. 2 μs.

Lifetime measurements were carried out on fresh solutions of the europium (III) compound in the above mentioned solvents without deaereation. Low temperature experiments were done using solutions of the europium (III) compound in a mixture of ethanol and methanol (4:1 volume ratio). Measurements in other solvents, i.e., CH_2Cl_2, CH_3CN, C_6H_6, etc., not amenable to the formation of glasses, were carried out only at room temperature.

3. Results

3.1. Absorption spectra

Absorption spectra of Eu(fod)$_3$ recorded in different solvents show an intense band in the UV region with a maximum between 290 and 294 nm and a set of very week and narrow bands between 500 and 600 nm superimposed to the tail of the intense band of the UV region. (Fig. 1 and Table 1).

3.2. Emission spectra

When solutions of Eu(fod)$_3$ are irradiated at the UV band an intense red emission can be seen. The emission spectra of the complex ($\lambda_{ex}=337$ nm) were monitored in different solvents. The observed emission spectra are shown in Fig. 2. In all the experiments, five narrow emission bands can be observed, with band maxima at 580, 595, 613, 652 and 702 nm. These band maxima are nearly independent on the solvent. The emission band at 613 nm is the most intense of the five ones.

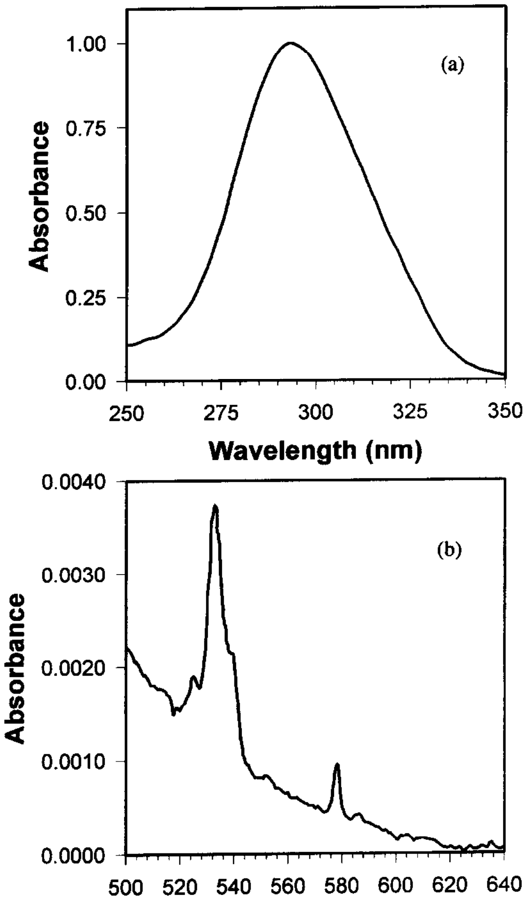

Fig. 1. Absorption spectra of Eu(fod)$_3$ in acetonitrile. (a) shows the intraligand absorption band and (b) shows the f–f absorptions of Eu(III) superimposed to the tail of the intraligand absorption band.

Table 1
Absorption band maxima of Eu(fod)$_3$ in different solvents

Solvent	λ_{max}/nm
Methanol	293
Ethanol	291
2-Propanol	289
Dioxane	294
Acetonitrile	293
Dichloromethane	294
Chloroform	294
Carbon Tetrachloride	293

3.3. Lifetime measurements

Monochromatic laser flash irradiations ($\lambda_{ex}=337$ nm) of Eu(fod)$_3$ in various solvents were used to perform a time-resolved study of the respective luminescence. The corresponding decay of the emissions, followed at 610, 615 and 620 nm, can be fitted, without appreciable deviations, to a single exponential (Fig. 3), Eq. (1):

$$I(\lambda)=I_0(\lambda)\times\exp(-t/\tau) \quad (1)$$

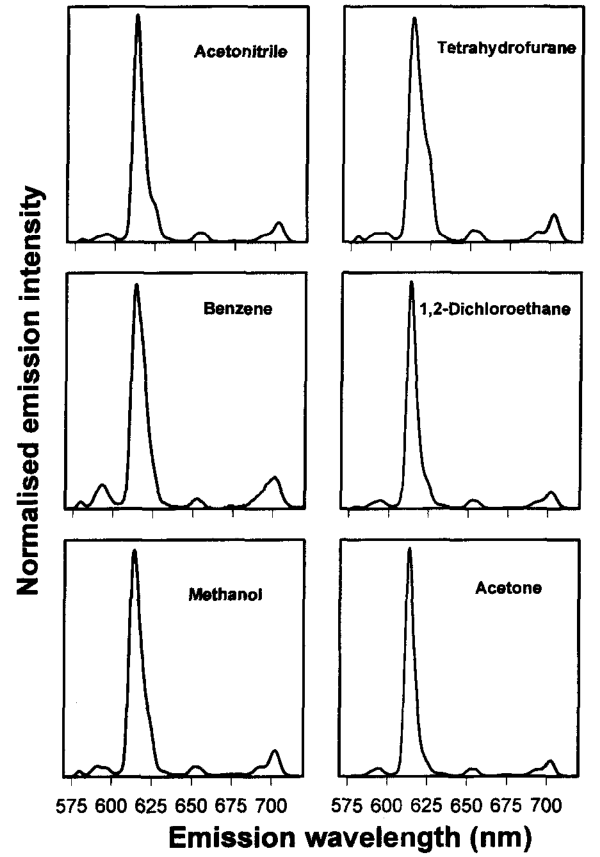

Fig. 2. Normalised emission spectra of Eu(fod)$_3$ recorded at room temperature in several solvents.

where $I(\lambda)$ represents the emission intensity at time t monitored at λ, after the laser pulse; $I_0(\lambda)$ represents the emission intensity at time $t=0$ monitored at the same wavelength and τ the observed lifetime for the luminescence decay (i.e., the time for the diminish of the emission intensity to $1/e$ of its initial value) which is independent of the monitoring wavelength.

When extrapolating to $t=0$ the exponential behaviour of the luminescence decay, the spectra obtained with the $I_0(\lambda)$ values is very close to those obtained under steady state irradiations.

Comparison of the spectra obtained by the extrapolation procedure at room temperature and at the boiling temperature of liquid air in ethanol–methanol mixtures (4:1 v/v) shows nearly independence of the lifetime with lowering the temperature and a blue shift of the spectrum (Fig. 4).

The luminescence lifetime for the Eu(fod)$_3$ in the solid state (powder) was also measured giving a value of 0.62 ms.

The observed values of τ in different solvents are shown in Table 2.

4. Discussion

4.1. Absorption and emission spectra

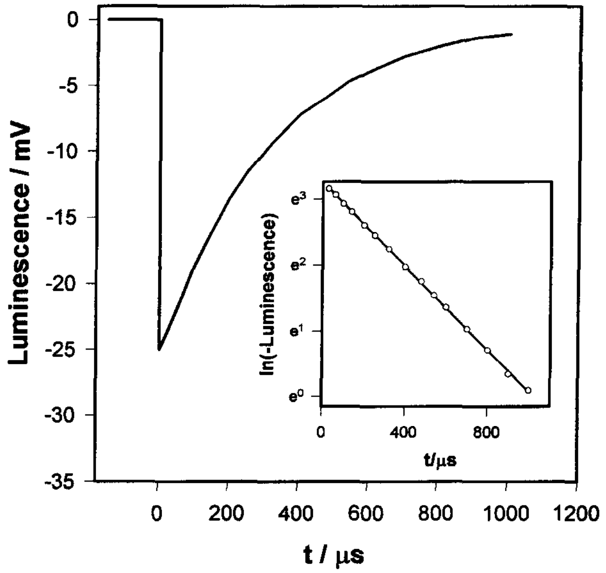

Fig. 3. Typical trace for the luminescence decay of Eu(fod)$_3$. Inset shows a semilogarithmic plot of luminescence vs. time.

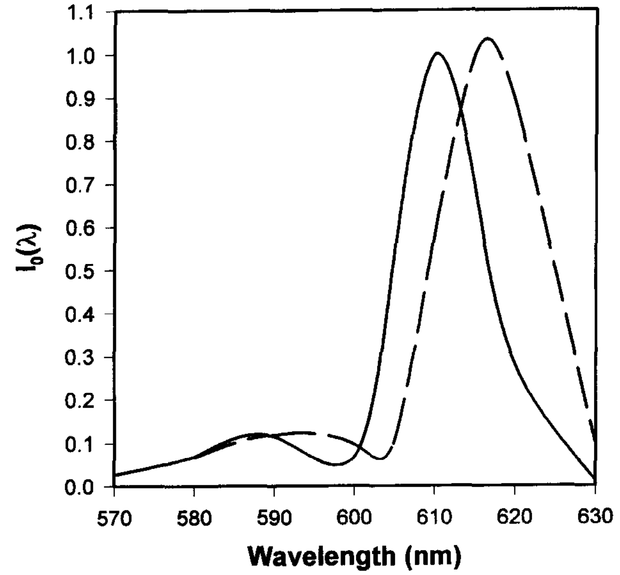

Fig. 4. Comparison of the emission spectra obtained by the extrapolation procedure at room temperature (dashed line) and at the boiling point temperature of liquid air (solid line) in ethanol–methanol mixtures (see text for details).

Absorption spectra of Eu(fod)$_3$ is dominated by an intense band, with a maximum near 290 nm, the position of which is mostly independent of the solvent (Fig. 1a and Table 1). This strong absorption is characteristic of the organic ligand and is referred as an intra-ligand transition (IL) [17]. Though an overimposed charge transfer transition cannot be excluded. Besides, absorptions corresponding to the f–f excited states of Eu(III) are also shown in Fig. 1b, where two very weak peaks, λ_{max} at 579 and 532 nm, appear superimposed to the tail of the IL band. These lines correspond to the population of the $^5D_0$ level from the $^7F_0$ and the $^5D_1$ from the $^7F_1$ level of the Eu(III), respectively. A weaker line is also present at 525 nm corresponding to the transition $^7F_0 \rightarrow {}^5D_1$ [18,19].

Table 2
Luminescence lifetime of Eu(fod)$_3$ in different solvents

Solvent	τ/ms
Alcohols	
Methanol	0.45
Ethanol	0.45
2-Propanol	0.43
n-Butanol	0.43
Bencylic alcohol	0.37
Chloroalkanes	
Dichloromethane	0.30
Chloroform	0.33
1,2-Dichloroethane	0.32
1,1- Dichloroethane	0.31
Carbon tetrachloride	0.30
Arenes	
Toluene	0.25
m-Xilene	0.34
p-Xilene	0.19
Benzene	0.35
Halobenzenes	
Chlorobenzene	0.24
Bromobenzene	0.20
Fluorobenzene	0.18
Ethers	
Dioxane	0.56
Tetrahydrofurane	0.67
Ethyl ether	0.42
Ketones	
Acetone	0.58
Cyclohexanone	0.59
Methyl ethyl ketone	0.54
Methyl propyl ketone (iso)	0.57
Deuterated solvents	
Ethanol-d$_1$	0.84
Methanol-d$_4$	0.93
Acetonitrile-d$_3$	0.57
Benzene-d$_6$	0.23
Acetone-d$_6$	0.74
Chloroform-d	0.15
Other solvents	
Acetonitrile	0.64
Ethanol–methanol (4:1 v/v) (room temperature)	0.47
Ethanol–methanol (4:1 v/v) (liquid air boiling temperature)	0.50
Acetonitrile–H_2O (9:1 v/v)	0.49
Acetonitrile–D_2O (9:1 v/v)	0.82

After excitation of the Eu(III) chelate to a vibrational level of the first excited singlet state, the molecule undergoes rapid internal conversion to lower vibrational levels through interaction with the solvent matrix. This excited singlet state can be deactivated radiatively (fluorescence), or undergoes intersystem crossing to the triplet system, which by internal conversion reaches the lowest triplet state. This state can combine radiatively with the ground state by means of a spin-forbidden transition giving rise to a typical long-lived molecular phosphorescence. Alternatively, the molecule can undergo a non-radiative transition from the triplet system to a low lying f→f excited states. After this indirect excitation by energy transfer, the excited Eu(III) reaches the ground state by radiative or radiationless deactivation.

Emission spectra shown in Fig. 2 correspond to the radiative deactivation of the $^5D_0$ excited state to ground states $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$ and $^7F_4$ respectively. Although the position of these lines is independent on the solvent, changes in relative intensities can be seen in Fig. 2. For instance, for benzene lines at 595 ($^5D_0 \rightarrow {}^7F_1$) and 702 nm ($^5D_0 \rightarrow {}^7F_4$) relative to the line of 613 nm ($^5D_0 \rightarrow {}^7F_2$) are more intense than for other solvents.

4.2. Emission lifetimes

The decay curves of the luminescence emission were single exponential. The values of the lifetimes for different solvents are given in Table 2. Temperature seems not to have any effect on the luminescence lifetimes as the values obtained in ethanol–methanol mixtures are nearly the same at room temperature and in the glassy state. It is well-known [4–7] that an efficient radiationless decay channel for many Eu(III) complexes in H_2O solution is coupling with the high-frequency O–H oscillators as has been shown by an increase in the lifetime when H_2O is replaced by D_2O. It is also known that, for other Eu(III) compounds, the decrease in the emission lifetime with increasing temperature is caused by a thermally activated nonradiative pathway via a LMCT excited state [20,21]. In this case, Eu(fod)$_3$, the emission lifetime present nearly the same value (between 0.43 to 0.45 ms) for all the aliphatic alcohols used as solvents. When CD_3OD or CH_3CH_2OD are the solvents the lifetime increases indicating that the O–H high energy vibration could be responsible for quenching the f–f excited state. This, vibronic deexcitation pathway becoming much less efficient when deuterated solvents are used, led Horrocks et al. [8–10] to show that for Eu(III) complexes the number of coordinated water molecules, q, is given, within an estimated uncertainty of 0.5, by the Eq. (2) where k_H and k_D are

$$q = 1.05(k_H - k_D) \qquad (2)$$

the reciprocal (in ms^{-1}) of the experimental excited-state lifetimes in H_2O and D_2O solutions. Experiments carried out in mixtures of acetonitrile and H_2O/D_2O give $q = 0.86$, i.e., one molecule of water is in the inner coordination sphere. Assuming that the same equation can be applied to alcohols we find values of q between 1.1 and 1.2. As the number of O–H oscillators per water molecule is twice the number of OH oscillators per alcohol molecule, this indicates that there must be two alcohol molecules bound to, or at least closely associated with, the metal, on average. Moreover, fractional numbers of solvent molecules can arise from: (a) the ±0.5 uncertainty in Eq. (2); (b) the existence of two species with different number of solvent molecules in a faster exchange than the lanthanide lifetime, and (c) bound solvent molecules in the outer coordination sphere with a reduced nonradiative deexcitation efficiency compared to the inner-coordinated solvent molecules. (taking into account that some amount of the complex could be dissociated, cause (b) might be considered in order to explain those q values 10 to 20% higher than unity). In bencyl alcohol, the observed lifetime is between the values obtained for benzene and alifatic alcohols and surprisingly, the observed lifetimes in deuterated benzene and chloroform are smaller than in the normal solvents. These facts would indicate that the C–H vibrations are not responsible [12,13] for the deactivation of the luminescence in those solvents as the vibrational frequencies in deuterated solvents have lower values than in the hydrogenated ones. Similar anomaly has been observed previously when the emission of a europium complex with a polyamine ligand was quenched with water or heavy water [22].

Eu(fod)$_3$ has been used as a Lewis acid partner to form adducts with AreneCr(CO)$_3$ [17] complexes. Spectroscopic evidence was found that support the adduct formation. Moreover, the presence of the europium complex alters the photosubstitution in the cromiun arene. On the other hand arene are well known to form charge transfer complexes [23]. In the present case, though the UV–visible spectra in arene solvents do no show any evidence of interaction between Eu(fod)$_3$ and the solvent, the emission spectrum in benzene, for instance, shows differences with those spectra taken in other solvents. The changes in the emission spectra on changing the first coordination sphere, although very small compared to those observed for d-transition-metal ions, are very specific, especially when the relative intensities and the splitting patterns of the bands are concerned [22]. The interactions of the arene solvent with lanthanide complexes can be identified as second sphere donor–acceptor (SSDA) one [18,19]. Weak SSDA interaction involving the complex as a Lewis acid has been invoked to account for solvent effects on some ammine complexes [24]. In consequence, the shorter lifetimes observed in arene solvents can be attributed to a charge transfer interaction with the complex.

Emission lifetimes in acetonitrile, ketones, dioxane and tetrahydrofurane have nearly the same values that the one found for Eu(fod)$_3$ in powder.

Emission lifetimes measured in halocarbon solvents show values longer than those obtained in arene solvent though shorter than in alifatic alcohols. No significant differences are observed between those having C–H bonds and those totally chlorinated. Besides deuterated chloroform appears as a better quencher. It suggests that deactivation via weak vibronic coupling with the vibrational states of the high frequency C–H oscillators can be discarded. Also a heavy atom effect inducing spin–orbit coupling which allows mixing of states having different multiplicities should not be considered because in lanthanide complexes a high spin–orbit coupling already exists. As atom transfer could be excluded because the ligands that constitute the coordination sphere of the complex are quite inert we thus have to remain with electron-transfer as a possible quenching mechanism. The occurrence of electron-transfer is in agreement with flash and steady state photolysis experimental observations [25] that indicate Eu(II) formation.[3] Finally, it can be said that for ketones energy transfer involving C–H vibrations could be the deactivation mechanism. Though for acetonitrile similar lifetimes are observed in CH_3CN and CD_3CN, i.e., within the experimental error. Since energy transfer is strongly dependent on distance, and $\nu_{C\equiv N}$ is not so much lower than ν_{C-H}, it is probable that the deactivation here is determined primarily by energy transfer to the C≡N bond which in this case is directly bound to the metal, in contrast to the more distant C–H bonds.

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[3] Studies underway in our laboratory showed the formation of Eu(II) in steady state photolysis of Eu(fod)$_3$.