

Sensitized Luminescence of Trivalent Lanthanide Complexes Eu^{3+} /Quinaldinic Acid and Eu^{3+} /1,4-Dihydro-Oxo-Chinoline-3-Carboxylic Acid

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Abstract Studies of the luminescence of Eu^{3+} /quinaldinic acid sodium $[\text{Eu}(\text{QA})_3]$ and Eu^{3+} /1,4-dihydro-4-oxo-quinoline-carboxylic acid sodium $[\text{Eu}(\text{DOQCA})_3]$, both in solid form and in aqueous solution, are presented in room temperature. The energy transfer to the emitting levels of the lanthanide ions are discussed on the basis of the emission spectra and lifetime data of $^5\text{D}_0$ and $^5\text{D}_1$ levels of Eu^{3+} . In the aquated $\text{Eu}(\text{QA})_3$ complex, the most intense spectral band belongs to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition (592 nm) and not to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (616 nm), which otherwise occurs usually. In the cases of the $\text{Eu}(\text{DOQCA})_3$ complex the hypersensitive transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ is the most intense as so far was reported for various Eu^{3+} chelates.

Keywords Europium · Luminescence · Energy transfer

Introduction

Spectroscopic properties of trivalent lanthanide ions have continuous interest, especially when they are chelated with appropriate organic ligands. The lanthanide chelates have been widely used for many applications such as laser materials or luminescent labels in clinical chemistry and molecular biology [1–6].

The specific physical and chemical properties of the lanthanides which make them useful in the studies of biological systems [7] are the consequence of their electronic structure. The electron transitions in the 4f shells are responsible for the characteristic absorption and luminescence spectra of very narrow bands. The lanthanides' emission has long lifetime and lies spectrally far from the emission of the ligands. On the basis of energy level and quantum yield considerations, the Eu^{3+} can be considered as one of the best lanthanide ion for sensitized luminescence.

The mechanism of this photosensitization process involve both inter- and intra-molecular energy transfer. In addition to this energy transfer, radiative and non-radiative relaxation of the singlet excited states of the ligand to the ground level, different quenching and shielding effects influence the yield of the whole energy circle [8–10].

One challenge in these complex investigations is to produce emission intensity as high as possible by testing different kinds of ligands [11, 12] and lanthanides and also by using surfactants and different solvents in the solutions.

In this paper, the luminescence properties of the complexes $\text{Eu}(\text{QA})_3$ and $\text{Eu}(\text{DOQCA})_3$ both in powder form and in aqueous solution are reported.

Experimental details

Reagents

Analytical grade quinaldinic acid (QA) and Eu^{3+} -nitrate was purchased from Aldrich Co. and used as received. The solid $\text{Eu}(\text{QA})_3$ was prepared from neutralized aqueous solution of QA and Eu^{3+} -nitrate. The 1,4-dihydro-4-oxoquinoline-2-carboxylic acid (DOQCA) was prepared in

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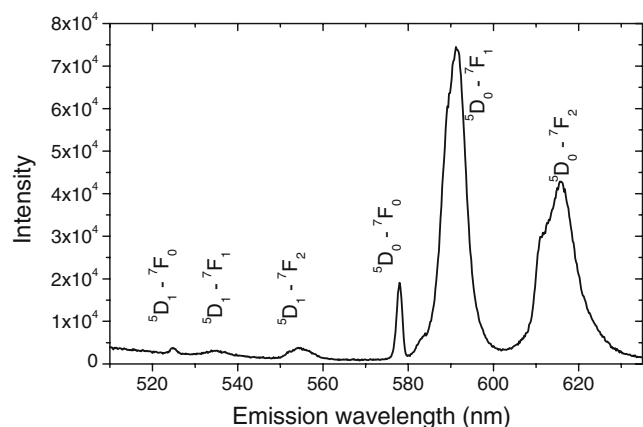


Fig. 1 Steady-state spectrum of Eu/(QA)₃ in aqueous solution. $\lambda_{\text{ex}} = 320$ nm

our laboratory [13] and the structure of the compound was determined by elemental analysis. The solid Eu/(DOQCA)₃ compound was prepared from aqueous solution of sodium salt of DOQCA and Eu³⁺-nitrate in proper molar rate. Working solutions were prepared by dilution of aqueous solutions with bidistilled water.

Apparatus

The steady-state luminescence measurements (emission and excitation spectra) were carried out with a Jobin–Yvon Fluorolog Tau3 spectrofluorometer working in photon counting mode at room temperature. The time-resolved spectra and the luminescence decays of the Eu³⁺ in the complexes were obtained using a laser pulsed fluorometer, where the samples were excited by a N₂ laser ($\lambda = 337.1$ nm, $\Delta t = 1.0$ ns). The data were measured by a Stanford Research System SR250 boxcar unit. The control of the monochromator, gating of the boxcar unit and the data processing was managed by a PC through RS232-C interface module.

The fluorescence of the organic molecules, Raman bands of the solvent and the scattered light of the source radiation are

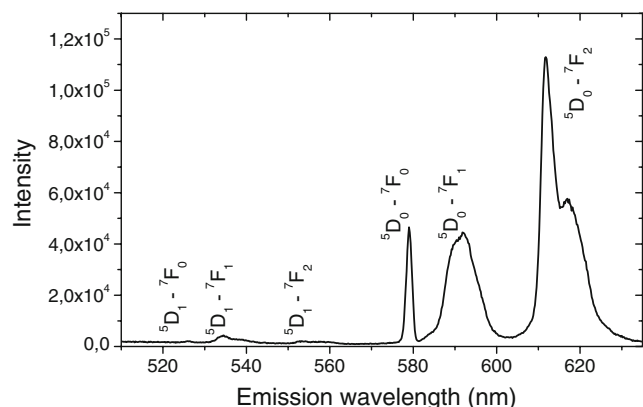


Fig. 2 Steady-state spectrum of Eu/(DOQCA)₃ in aqueous solution. $\lambda_{\text{ex}} = 320$ nm

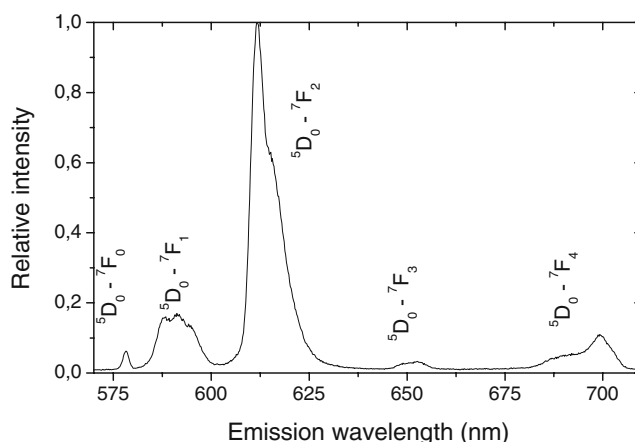


Fig. 3 Steady-state spectrum of Eu/(QA)₃ in solid powder. $\lambda_{\text{ex}} = 318$ nm

the major obstacles to the luminescence measurements. The organic compounds have relatively very short lifetimes compared to Eu³⁺. Unwanted signals mentioned before can be suppressed sometimes by using filters or/and by selecting appropriate delay of the sampling gate from the laser pulse.

Results and discussions

Steady spectra

The 4f electrons of the lanthanides and their trivalent ions are shielded by electrons from higher shells (5s, 5p) and thus are mostly protected from the influence of the environment. Owing to this, lanthanides in different combinations show the same spectroscopic properties (related to the 4f transitions) as their free ions in gas state.

Eu³⁺ has a regular ⁷F as ground multiplet followed by a ⁵D multiplet and the ⁵L₆ level [14]. This ion exhibits two resonance levels, one at 17,267 cm⁻¹ (⁵D₀) and a second at 19,030 cm⁻¹ (⁵D₁) which provide a suitable gap between

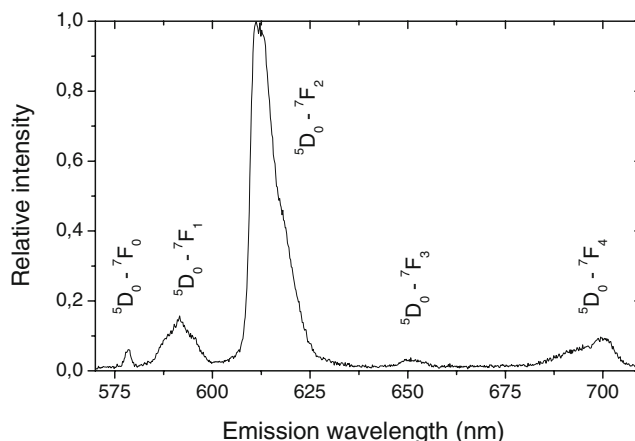


Fig. 4 Steady-state spectrum of Eu/(DOQCA)₃ in solid powder. $\lambda_{\text{ex}} = 328$ nm

Table 1 Emission intensities of Eu/(QA)₃ complex in aqueous solution

| Transitions: ⁵ D _i → ⁷ F _j | Wavelength (nm) | Relative intensity |
|--|-----------------|--------------------|
| ⁵ D ₁ → ⁷ F ₀ | 524.7 | 0.017 |
| ⁵ D ₁ → ⁷ F ₁ | 534.6 | 0.014 |
| ⁵ D ₁ → ⁷ F ₂ | 554.6 | 0.035 |
| ⁵ D ₀ → ⁷ F ₀ | 578.0 | 0.237 |
| ⁵ D ₁ → ⁷ F ₃ | 583.0 | 0.013 |
| ⁵ D ₀ → ⁷ F ₁ | 591.4 | 1.000 |
| ⁵ D ₀ → ⁷ F ₂ | 611.7 | 0.113 |
| | 615.8 | 0.550 |
| ⁵ D ₀ → ⁷ F ₃ | 649.1 | 0.027 |
| ⁵ D ₀ → ⁷ F ₄ | 687.1 | 0.072 |
| | 690.4 | 0.079 |
| | 693.8 | 0.133 |
| | 697.7 | 0.293 |

the lowest emission level and the ground state. The emission spectra of Eu³⁺ reveals bands related to the ⁵D_i→⁷F_j (i=0, 1; j=0–4) transitions. All the transitions producing intense emission originate from the ⁵D₀ level.

Emission spectra of Eu/(QA)₃ and Eu³⁺/DOQCA complexes

The emission spectrum of Eu/(QA)₃ complex in aqueous solution reveals transitions ⁵D₀→⁷F_{0,1,2,3,4}. In addition to the these transitions, the ⁵D₁→⁷F_{0, 1, 2} transitions can also be resolved (Fig. 1).

The same transitions can be identified in the emission spectrum of Eu/(DOQCA)₃ complex in aqueous solution. In this case, transitions from ⁵D₁ level produce lower emission intensities (Fig. 2).

In the solid form of the these Eu³⁺ complexes the ⁵D₁→⁷F_{0, 1, 2} transitions are practically absent (Figs. 3 and 4).

Tables 1, 2, 3 and 4. summarize the relative intensities of spectral bands of both complexes in aqueous solution and in solid form. The Eu³⁺ ions receive energy from triplet

Table 2 Emission intensities of Eu/(QA)₃ complex in solid form

| Transitions: ⁵ D _i → ⁷ F _j | Wavelength (nm) | Relative intensity |
|--|-----------------|--------------------|
| ⁵ D ₀ → ⁷ F ₀ | 578.2 | 0.060 |
| ⁵ D ₀ → ⁷ F ₁ | 588.0 | 0.158 |
| | 591.2 | 0.168 |
| | 594.0 | 0.120 |
| ⁵ D ₀ → ⁷ F ₂ | 611.7 | 1.000 |
| | 615.8 | 0.597 |
| ⁵ D ₀ → ⁷ F ₃ | 648.7 | 0.010 |
| | 652.6 | 0.02 |
| ⁵ D ₀ → ⁷ F ₄ | 690.2 | 0.04 |
| | 699.1 | 0.09 |

Table 3 Emission intensities of Eu/(DOQCA)₃ complex in aqueous solution

| Transitions: ⁵ D _i → ⁷ F _j | Wavelength (nm) | Relative intensity |
|--|-----------------|--------------------|
| ⁵ D ₁ → ⁷ F ₀ | 525.2 | 0.0015 |
| ⁵ D ₁ → ⁷ F ₁ | 535.3 | 0.0077 |
| ⁵ D ₁ → ⁷ F ₂ | 556.0 | 0.0031 |
| ⁵ D ₀ → ⁷ F ₀ | 578.8 | 0.26 |
| ⁵ D ₀ → ⁷ F ₁ | 588.7 | 0.164 |
| | 592.4 | 0.20 |
| ⁵ D ₀ → ⁷ F ₂ | 611.0 | 1.00 |
| | 616.5 | 0.29 |
| | 620.7 | 0.15 |
| ⁵ D ₀ → ⁷ F ₃ | 649.6 | 0.021 |
| | 653.3 | 0.0093 |
| ⁵ D ₀ → ⁷ F ₄ | 690.7 | 0.04 |
| | 699.4 | 0.21 |

state ligands, thus the fluorescence of the ligand (a singlet–singlet transition) is practically not influenced by the presence of Eu³⁺. Thus, intensities of ⁵D_i→⁷F_j transitions were calculated by subtracting the spectra of the pure ligand’s solution from the spectra of the complex. Deconvolution of the spectra gives distinct peaks originating from the splitting of the Eu³⁺ levels by the ligand field. The intensities of sub-bands were determined by deconvolving the main bands. Excellent fits were made using Lorentzian shapes (see an example on Fig. 5).

The most extreme spectrum is shown on the Fig. 1. displaying that in case of Eu/(QA)₃ in aqueous solution the ⁵D₀→⁷F₁ transition gives far the most intense spectral band, which is quite rare among the Eu³⁺ complexes. It can be stated, that in aqueous solution of Eu/(QA)₃ the ⁵D₁→⁷F_{0,2}, ⁵D₀→⁷F₁ transitions are the favoured ones (compare data of Tables 1 and 3). In case of Eu/(QA)₃ in solid form and Eu/(DOQCA)₃ in both aqueous solution and solid form, the ⁵D₀→⁷F₂ transition is the most intense one.

Considering the intensities of the transitions, the odd parity transitions seem to be more favoured in the Eu/(QA)₃ complexes in contrast to the Eu/(DOQCA)₃ com-

Table 4 Emission intensities of Eu/(DOQCA)₃ complex in solid form

| Transitions: ⁵ D _i → ⁷ F _j | Wavelength | Relative intensity |
|--|------------|--------------------|
| ⁵ D ₀ → ⁷ F ₀ | 578.5 | 0.048 |
| ⁵ D ₀ → ⁷ F ₁ | 592.4 | 0.143 |
| ⁵ D ₀ → ⁷ F ₂ | 611.0 | 1.000 |
| | 616.5 | 0.665 |
| | 620.7 | 0.020 |
| ⁵ D ₀ → ⁷ F ₃ | 649.6 | 0.019 |
| | 653.3 | 0.012 |
| ⁵ D ₀ → ⁷ F ₄ | 690.7 | 0.052 |
| | 699.4 | 0.085 |

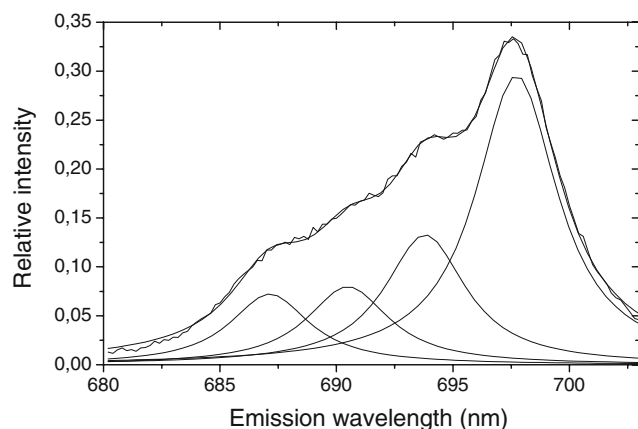


Fig. 5 Steady-state spectrum of Eu/(QA)₃ in aqueous solution. $\lambda_{\text{ex}}=320$ nm. For sub-band-intensities see Table 1, $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition

plexes which show relatively more intense even parity transitions.

In earlier works of other authors, the hypersensitive transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ remained the most intense as so far reported for various Eu^{3+} chelates. In the investigations of Richardson [5] for Eu^{3+} chelated by ethylene-diamine in DMSO the inversion of the relative intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ were observed for certain concentration of the ligand. He associated this phenomenon with the change of Eu^{3+} from a weaker ligand field of pure solvent to a stronger ligand field of ethylene-diamine.

Missing of spectral bands corresponding to $^5\text{D}_1 \rightarrow ^7\text{F}_j$ transitions in solid powder form means that in case of close proximity of complex molecules to each other, the $^5\text{D}_1 \rightarrow ^5\text{D}_0$ relaxation is much more effective than in aqueous solution.

Time resolved spectra and the relaxation of the europium

Detailed analysis of decay curves and spectra were done, the decay parameters are summarized in Tables 5 and 6. Luminescence decay from $^5\text{D}_0$ state is practically one-exponential (Fig. 6). In case of $^5\text{D}_1 \rightarrow ^7\text{F}_j$ transitions in solution two- or three-exponential fits are adequate. This reflects that the $^5\text{D}_1$ level has a transitional position in the energy transfer chain (Fig. 7).

Table 5 Decay times of Eu/(QA)₃ complexes

| Sample | In solution | | In solid form | |
|----------|------------------------|----------------------------|------------------------|------------------------|
| | Wavelength (nm) | 592 | 616 | 592 |
| Lifetime | $\tau=142 \mu\text{s}$ | Biexponential (unresolved) | $\tau=326 \mu\text{s}$ | $\tau=320 \mu\text{s}$ |

Table 6 Decay times of Eu/(DOQCA)₃ complexes

| Sample | In solution | | In solid form | |
|----------|------------------------|---|------------------------|------------------------|
| | Wavelength (nm) | 616 | 616 | 592 |
| Lifetime | $\tau=189 \mu\text{s}$ | $\tau_1 < 5 \text{ ns}$ $\tau_2=0.689 \mu\text{s}$ $\tau_3=3.1 \mu\text{s}$ $A_1 > 20$ $A_2=0.87$ $A_3=0.43$ | $\tau=313 \mu\text{s}$ | $\tau=336 \mu\text{s}$ |

The rising part of the $^5\text{D}_0$ decay indicates clearly that the energy transfer from the ligand occurs to levels above the $^5\text{D}_0$ level, most probably to $^5\text{D}_1$ level, which limits the rate of the transfer to the $^5\text{D}_0$ level.

Following the pulse excitation at 337 nm, the luminescence from the $^5\text{D}_0$ state at 592 nm increase concomitantly with the decay of the $^5\text{D}_1$ state and decays with longer lifetime. This result also indicate that the energy transfer from the ligand occurs selectively to the $^5\text{D}_1$ of the Eu^{3+} , followed by luminescence from this state or relaxation to the $^5\text{D}_0$ state and luminescence from this later.

The radiationless deactivation of the $^5\text{D}_0$ level in solution by the O–H vibration of water (quenching effect) reduces the decay time of the Eu^{3+} compared to that one in the solid form.

Time-resolved spectra (Figs. 8 and 9) illustrate very well the temporal evolution of emission of the complex and the steps of the energy transfer processes (see below).

Energy transfer process

The intramolecular energy transfer (IMET) in the europium complexes enhances the luminescence of the Eu^{3+} ions.

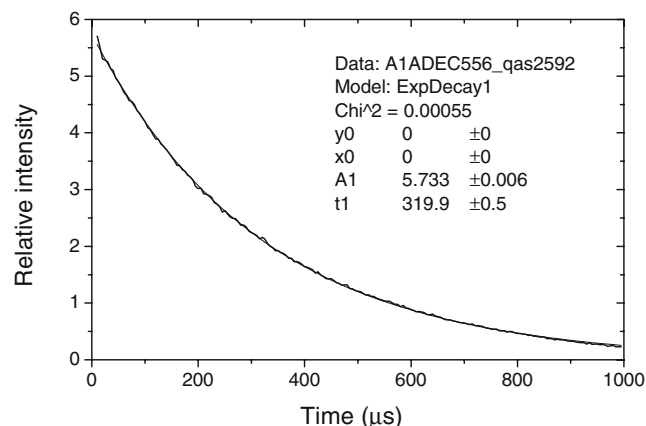


Fig. 6 Luminescence decay of Eu/(QA)₃ in solid powder. $\lambda_{\text{ex}}=337$ nm, $\lambda_{\text{em}}=592$ nm. See also Table 5

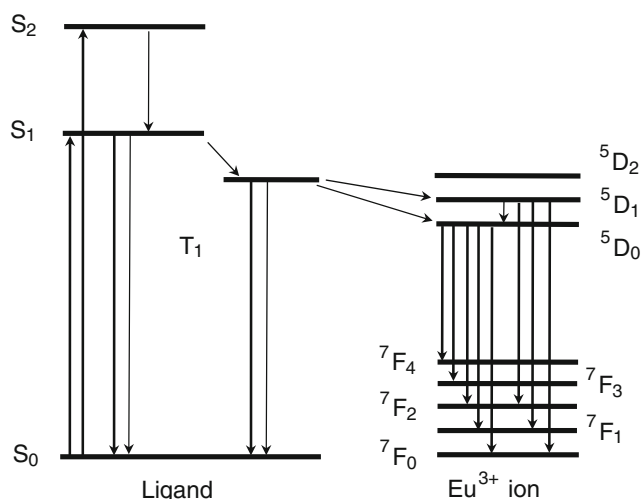


Fig. 7 Energy transfer scheme

This enhancement is due to the intense and broad absorption peaks of the ligands in the UV and to the high quantum yield of the Eu^{3+} ions. The IMET involves the participation of the first singlet (S_1) and triplet (T_1) states of the ligand. The electromagnetic energy is then transferred to the lanthanide ions from that excited triplet states which is in best resonance with the 5D_1 (Eu^{3+}) states (Fig. 7). The latter are long lived states and emit in the visible part of the spectrum.

This photophysical process can be handled in four step mechanism:

- Ground singlet absorption in the UV region to the excited singlet states of the ligand
- Radiationless intersystem-crossing from the excited singlet state to the low lying triplet states
- Transfer of energy to the chelated lanthanide ion
- Characteristic ionic luminescence emission in visible region

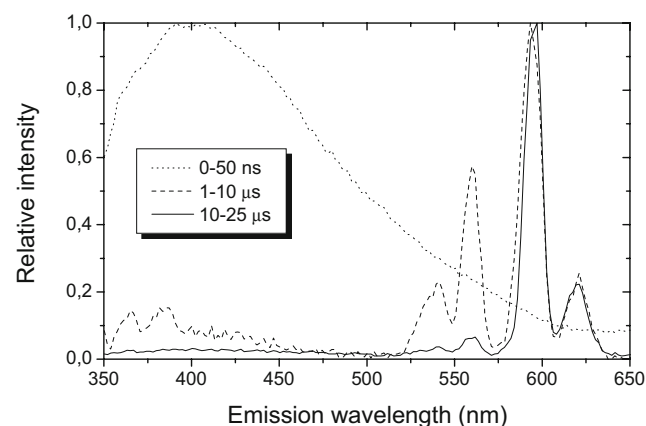


Fig. 8 Time-resolved spectra of $\text{Eu}/(\text{QA})_3$ in aqueous solution. $\lambda_{\text{ex}} = 337 \text{ nm}$

This IMET scheme is based on the observation that sensitized lanthanide emission occurs for chelates whose triplet states lies above the emitting lanthanide level. The probability of excitation of the triplet states (T_n) of the ligand due to direct optical absorption from the ground state is extremely small if not impossible. Intersystem crossing (typically $S_1 \rightarrow T_1$) is expected to be efficient.

Conclusions

Eu^{3+} shows a remarkable luminescence quantum yield at room temperature upon ligand excitation and a long 5D_0 lifetime (in the order of sub-millisecond range), which makes it a promising light-conversion molecular device. Energy transfer processes play a major role in determining the dynamics of excited molecular systems and enable the understanding of the photophysical properties of complex molecules. In this paper the following statements were established:

- (1) The ratio of intensities $I({}^5D_0 \rightarrow {}^7F_1)/I({}^5D_0 \rightarrow {}^7F_2)$ is higher in solution than in solid powder form.
- (2) $I({}^5D_0 \rightarrow {}^7F_1)/I({}^5D_0 \rightarrow {}^7F_2)$ is even higher than one in case of $\text{Eu}/(\text{QA})_3$ solution.
- (3) The odd parity transitions are more favoured in the $\text{Eu}/(\text{QA})_3$ complexes in contrast to the $\text{Eu}/(\text{DOQCA})_3$ complexes which show relatively more intense even parity transitions.
- (4) Decay of ${}^5D_1 \rightarrow {}^7F_j$ is multiexponential, reflecting that the energy transfer from the ligand occurs to 5D_1 state and the next step is the ${}^5D_1 \rightarrow {}^5D_0$ relaxation.
- (5) ${}^5D_1 \rightarrow {}^5D_0$ relaxation is much faster in solid powder than in solution. This is proved by (a) the absence of ${}^5D_1 \rightarrow {}^7F_j$ transitions from the spectra of solid powders, and (b) the faster decaying of 5D_1 (not resolved with the measuring system).

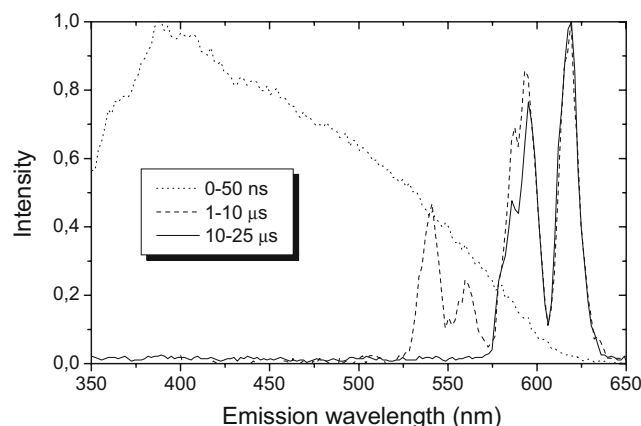


Fig. 9 Time-resolved spectra of $\text{Eu}/(\text{DOQCA})_3$ in aqueous solution. $\lambda_{\text{ex}} = 337 \text{ nm}$

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