Experimental determination of energy transfer in Eu(III) complexes, based on pyrazole substituted 1,3-diketones

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Abstract. We succeeded in synthesis of the novel Eu-based luminophore with almost 100% efficiency of energy transfer from ligands to the lanthanide ion. The luminophores with β-diketonate ligands were characterized by means of optical spectroscopy. Impact of different types of β-diketonates on the quantum yield of luminescence was revealed. A β-diketonate complex exhibiting the highest luminescence quantum yield and prospective for OLED applications was determined. The reasons for decreasing quantum efficiencies for other types of investigated ligands are discussed.

1. Introduction
Lanthanides have characteristic luminescence spectral lines corresponding to transitions inside the partially filled 4f-shell. Screening by the filled 5s\textsuperscript{2}5p\textsuperscript{6} shell leads to narrow luminescence bands of the lanthanides. Moreover, these materials can be an excellent substitute for iridium in the production of organic light-emitting diodes (OLED) as the lanthanides technology is by far less expensive. This fact inspires intensive research to find new types of lanthanide luminophores with high quantum efficiencies.

Effective luminescence of lanthanides is limited by weak light absorption due to forbidden f-f transitions. Combining lanthanide ion with organic ligands having broad absorption bands strongly increases a probability to absorb photons with the transition to the first excited singlet state and subsequent intersystem crossing of the ligands to the triplet state. To make an energy transfer from the ligand to the ion possible, the triplet level of the ligand should be just above the excited level of the ion. The correct matching of the ligands allows us to observe effective luminescence of lanthanides. The process of transfer of absorbed energy from ligands to an emission center is called “antenna effect”. Furthermore, ligands also influence its luminescence spectrum by means of developing the electric field which leads to a redistribution of the intensity of different transitions bands and their splitting [1].

We synthesized europium complexes based on a new set of β-diketonates ligands containing a pyrazole groups (figure 1). The production of these luminophores is relatively straightforward and it...
can be manufactured on a commercial scale. We measured energy of the triplet states of the \( \beta \)-diketonates ligands and researched their influence on the quantum yield of luminescence of the europium complexes. We found out a complex exhibiting a high quantum yield due to efficient energy transfer of electronic excitation from the ligands to the europium ion.

![Chemical structures of complexes](image)

**Figure 1.** The chemical structure of complexes (a) Eu(L\(^1\))\(_3\)Phen; (b) Eu(L\(^2\))\(_3\)Phen and (c) Eu(L\(^3\))\(_3\)Phen.

2. **Quantum yield**

The luminescence quantum yield is the ratio of the number of emitted photons per absorbed photons. To describe the luminescence of lanthanide complexes it is essential to introduce two types of quantum yields: an overall \( Q_{\text{Ln}}^L \) and an intrinsic \( Q_{\text{Ln}}^{\text{in}} \) quantum yields. The overall quantum yield is related to the intrinsic one by the following equation:

\[
Q_{\text{Ln}}^L = \eta_{\text{sens}} Q_{\text{Ln}}^{\text{in}},
\]

where coefficient \( \eta_{\text{sens}} \) is the sensitization efficiency [2].

The intrinsic quantum efficiency can be calculated with the use of radiative \( A_{\text{rad}} \) and nonradiative \( A_{\text{nonrad}} \) rate constants:

\[
Q = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nonrad}}},
\]

This calculation requires evaluating the rate constant of a transition between an initial state \( \Psi_{J_i} \) and a final state \( \Psi_{J_f} \). Taking into account only the dipole magnetic and electric transitions, this rate can be expressed as

\[
A(\Psi_{J_i}, \Psi_{J_f}) = \frac{64\pi^4\nu^3}{3h(2J+1)} \left[ n^3D_{MD} + \frac{n(n^2 + 2)^2}{9} D_{ED} \right],
\]

where \( \nu \) is energy of the transition in \( \text{cm}^{-1} \), \( h \) is Planck’s constant, \( n \) is the refractive index, \( 2J+1 \) is the degeneracy of the initial state, \( D_{ED} \) and \( D_{MD} \) are the electric and magnetic dipole strengths in \( \text{esu}^2 \text{cm}^2 \), respectively [3]. Forbidden electric dipole f-f transitions become partially allowed due to influence of the ligand field which leads to the mixing of electronic states of opposite parity. These transitions called induced electric dipole transitions [4] are much weaker than the conventional electric dipole transitions.

To find out the intrinsic quantum yield using (2) it is required to determine electric and magnetic dipole strengths which are quite difficult to calculate. The europium spectra, in contrast to other rare
earth complexes have unique features giving a way to avoid these complicated calculations. As the transition $^5D_0 \rightarrow ^7F_1$ has only magnetic dipole nature, its intensity does not depend on the ion’s field environment. Thus radiative rate $A_{01}$ for this transition behave as constant equal to $14.65 \text{ s}^{-1}$. This value is used as an intensity gauge for the calculation of the intrinsic quantum yield. The overall radiative rate constant can be calculated by

$$A_{\text{rad}} = A_{01} n^3 \frac{I_{\text{rad}}}{I_{01}},$$

where $I_{\text{rad}}$ is the integrated emission from the $^5D_0$ to the $^7F_J$ ($J = 0–6$), $I_{01}$ is the integrated intensity of the magnetic dipole transition.

The nonradiative rate constant $A_{\text{nrad}}$ can be determined from the luminescence decay measurements. The observed lifetime is related to the radiative and nonradiative rate constant by the following equation:

$$\tau = \left( A_{\text{rad}} + A_{\text{nrad}} \right)^{-1}.$$

Thus, the intrinsic quantum efficiency is given by

$$Q_{\text{in}} = A_{\text{rad}} \tau,$$

where $A_{\text{rad}}$ is determined from (3) [4].

3. Experimental part

We investigated polycrystalline samples of the different $\beta$-diketonate europium complexes. To determine the intrinsic quantum yield, we carried out two experiments. In the first experiment, we observed luminescence spectra when the sample was excited at the wavelength corresponding to absorption of the europium ion. It gave us an opportunity to determine correctly the intrinsic quantum efficiency of the ion, taking into account the influence of the ligand environment, which did not participate directly in light absorption. The radiative rate constants were evaluated from this spectrum by (3). In the second experiment, we evaluated time constants from luminescence intensity decay measurements. All the luminescent experiments were carried out with the use of SDL-1 double monochromator.

The experimental setup for measurement of luminescence spectrum is shown in the figure 2.

![Experimental Setup](image)

**Figure 2.** The experimental setup for measuring the luminescence spectra.

Selective excitation of the europium ions of the sample placed in the cuvette was performed with laser diode emission at a wavelength of 470 nm. Two gratings with 600 grooves per mm were installed...
in the monochromator. The luminescence was detected with a Hamamatsu H8259-01 photomultiplier. The measured spectra were corrected taking into account detector sensitivity and monochromator transmission functions and saved in a computer.

When measuring decays, the excitation of the sample was performed with 355 nm emission from a YAG:Nd\textsuperscript{3+} pulse laser with 12 Hz repetition frequency and 20 mJ average energy. As the pulse duration (6 ns) is much smaller than the luminescence decay time it does not affect the measurement results. The monochromator (figure 3) was tuned to the wavelength 615 nm corresponding to the maximum intensity of the europium luminescence spectrum. The luminescence signal was detected with photodiode and then amplified with Stanford Research SR570 current amplifier. The amplified signal was directed to an oscilloscope which averaged over 1000 decay curves for different laser shots. This averaging technique significantly increased signal-to-noise ratio and provided a way to obtain more accurate results for decay times.

Measurements of the overall quantum yield were carried out using an integrating sphere [5].

4. Results and discussions

For β-diketonate ligands using in the study the energy of triplet states was measured [6]. The results represent in the table 1. The excited level of europium \( \text{^5D}_0 \) is about 17300 cm\(^{-1}\).

| Ligand | L\(^1\) | L\(^2\) | L\(^3\) |
|--------|--------|--------|--------|
| Energy of triplet level, cm\(^{-1}\) | 21276 | 19638 | 19764 |

The measured luminescence spectra of the complexes are shown in the figure 4. Lifetime, radiative and nonradiative rate constants, overall and intrinsic quantum yields and sensitization efficiency calculated from the experimental for the investigated europium complexes are given in the table 2. The error of measurement of the quantum yields did not exceed 10%.

The highest luminescence quantum yield was achieved for Eu(L\(^3\))\textsubscript{3}Phen. Moreover, this complex demonstrated the highest sensitization efficiency - almost all the energy absorbed by ligand was transferred to the europium ion.

Complexes with ligands L\(^1\) and L\(^2\) exhibited low quantum yields. For complex Eu(L\(^1\))\textsubscript{3}Phen decrease of the quantum yield possibly emerges from the large differences in energy between the triplet levels of the ligands and the resonance level of the lanthanide ion (table 1). Triplet levels of ligands L\(^2\) and L\(^1\) have nearly the same energy but the quantum yield of complex Eu(L\(^2\))\textsubscript{3}Phen is by an order of magnitude less than the quantum yield of complex Eu(L\(^1\))\textsubscript{3}Phen. This difference can be caused by multiphonon relaxation of energy on the C-H vibrations in the complex Eu(L\(^2\))\textsubscript{3}Phen. The replacement of the C-H vibrations by C-F vibrations (figure 1) reduces nonradiative deactivation of
the exited state of the europium ion. In addition, the fluorine in the inner coordination sphere screens the ion from the Van-der-Waals forces leading to the quenching of luminescence.

Figure 4. The luminescence spectra of complexes (a) Eu(L\(_1\))\(_3\)Phen; (b) Eu(L\(_2\))\(_3\)Phen and (c) Eu(L\(_3\))\(_3\)Phen.

Table 2. The experimental value of the lifetime (\(\tau\)), radiative (\(A_{rad}\)) and nonradiative (\(A_{nrad}\)) rate constants, overall (\(Q_{Ln}^{L}\)) and intrinsic (\(Q_{Ln}^{Ln}\)) quantum yields and sensitization efficiency (\(\eta_{sens}\)) for \(\beta\)-diketonate europium complexes.

| Complex         | \(\tau\), mks | \(A_{rad}\), s\(^{-1}\) | \(A_{nrad}\), s\(^{-1}\) | \(Q_{Ln}^{L}\), % | \(Q_{Ln}^{Ln}\), % | \(\eta_{sens}\), % |
|-----------------|----------------|-----------------|----------------|-----------------|----------------|------------------|
| Eu(L\(_1\))Phen | 279            | 1011            | 2573           | 28              | 6              | 21               |
| Eu(L\(_2\))Phen | 243            | 873             | 3243           | 21              | 4              | 19               |
| Eu(L\(_3\))Phen | 754            | 558             | 769            | 42              | 40             | 96               |

5. Conclusion
For a number of \(\beta\)-diketonates europium complexes investigated in this work we found how efficiencies of energy transfer from ligands to the europium ion depends on the ion environment. Complex Eu(L\(_3\))Phen was proved to exhibit the highest quantum yield due to the almost 100% sensitization efficiency. It gives a possibility to use it as an efficient luminophore in organic light emitting diodes.
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