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The influence of the counterion type on the luminescent properties of organo-soluble europium complexes

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ABSTRACT

In this work, the luminescence properties of three europium complexes with ligands based on 2,2'-bipyridyldicarboxylic acid with various counterions (TFA, NO₃, Cl) were studied in the form of powders and acetonitrile solutions. Their luminescence spectra were recorded at room temperature and in liquid nitrogen. We obtained and calculated the following luminescence characteristics: luminescence lifetime, relative intensities of each luminescence peak, asymmetry coefficient, radiative lifetime, internal quantum yield, luminescence quantum yield, and the effectiveness of sensitization.

Keywords: luminescence, europium complexes, counterions, luminescence lifetime, asymmetry coefficient, quantum yield, the effectiveness of sensitization.

1 INTRODUCTION

Due to such properties as intense luminescence, long luminescence lifetime, good solubility in water and organic liquids, as well as a high degree of stability, complexes of rare earth metals can be used in many fields of optics, biophysics, and medicine. Europium complexes soluble in organic solvents potentially can be used to create various optoelectronic devices: organic light-emitting devices, photoelectronic multipliers, lasers, and waveguide amplifiers¹. The nearest environment of the rare earth ion and the complex as a whole strongly affects its luminescence, therefore, the study of the dependence of the luminescent properties on the type of counterion is an actual task². Without studying the effect of solvents, ligands, and counterions on the photophysical properties of rare-earth element complexes, it is impossible to interpret correctly the results of studies of spectral-luminescent characteristics³.

The nearest environment of the europium ion has a strong effect on the spectral-luminescent properties of coordination compounds. The reason for the change in the luminescent properties can be a change in the structure of the ligand or the type of counterion⁴⁻⁶. The work aimed to study the effect of the counterion type on the spectral-luminescent properties of europium complexes with ligands based on 2,2'-bipyridyldicarboxylic acid.

2 OBJECTS AND METHODS

2.1 Europium complexes

We investigated spectral-luminescence properties of organo-soluble europium complexes with ligands based on 2,2'-bipyridyldicarboxylic acid without substituents with various counterions: (1) Bipy H Eu(TFA), (2) Bipy H Eu(NO₃), (3) Bipy H Eu(Cl) (Fig.1). The synthesis of complexes of this type was described in the article⁷. These complexes were studied in a solid state, both at room temperature and at liquid nitrogen temperature. Additionally, solutions of these complexes in acetonitrile were examined at room temperature^{8,9}.

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Figure 1. Structure of studied europium complexes with ligand based on 2,2'-bipyridyldicarboxylic acid (counterion $X = \text{CF}_3\text{CO}_2$ (1), NO_3 (2), Cl (3)).

2.2 Spectral-luminescent measurements

Absorption spectra of europium complexes in acetonitrile were measured in the spectral range 200-500 nm using spectrophotometers Hitachi U-1900 and Solar PB 2201 at room temperature. Emission, excitation luminescence spectra, and luminescence kinetics were recorded using Hitachi F-7000 and Solar CM2203 spectrometers. The emission spectra were obtained in the spectral range 350-800 nm and the excitation wavelength was set as 320 nm. The excitation spectra were recorded at emission wavelength of 618 nm while the spectral range of the excitation wavelength was 250-600 nm.

We corrected the luminescence spectra in accordance with the formula: $I = I_0 \cdot 10^{\frac{D_{ex} + D_{em}}{2}}$, where I_0 – uncorrected luminescence intensity, D_{ex} and D_{em} – optical density at the excitation and emission wavelength respectively.

3 RESULTS AND DISCUSSION

3.1 Absorption spectra

Solutions of investigated complexes (1)-(3) have a similar form of absorption spectra and differ in absorbance values (Fig. 2). It means that the shape of the absorption spectra depends on the ligand type, and there is no dependence between absorption spectra and the type of counterion.

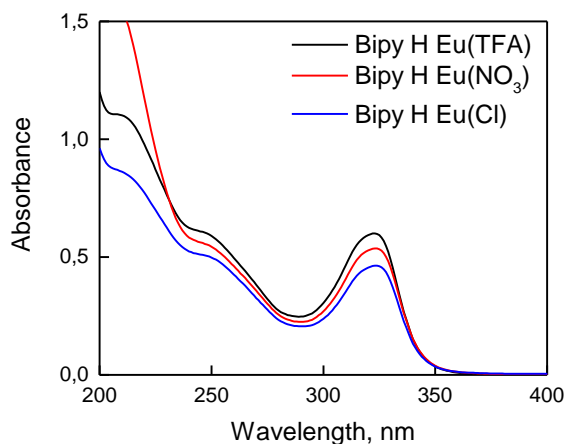


Figure 2. Absorption spectra of europium complexes (1)-(3) in acetonitrile, $C = 3 \cdot 10^{-5} \text{ mol/l}$

Maximum in the absorption spectra is observed at a wavelength 323 nm. Therefore, the position of the singlet energy level of the ligand does not depend on the kind of counterion and is determined only by the type of the ligand.

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Table 1. Characteristics of the absorption spectra of the investigated europium complexes (1)-(3)

Complex	Wavelength of absorption maximum, nm	Extinction coefficient, $10^3 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$
Bipy H Eu(TFA)	323	19.9 ± 0.6
Bipy H Eu(NO ₃)	323	17.7 ± 0.3
Bipy H EuCl	323	15.36 ± 0.18

3.2 Luminescence emission and excitation spectra

There are five bands in each emission spectrum corresponding to the transitions $^5D_0 \rightarrow ^7F_J$, $J = 0 - 4$. The transitions $^5D_0 \rightarrow ^7F_5$ and $^5D_0 \rightarrow ^7F_6$ were not detected since these peaks are outside the sensitivity range of the detector. The Stark structure of the band is clearly visible, which appears due to the influence of the crystal field of the nearest environment of the europium ion for all three complexes (Fig. 3).

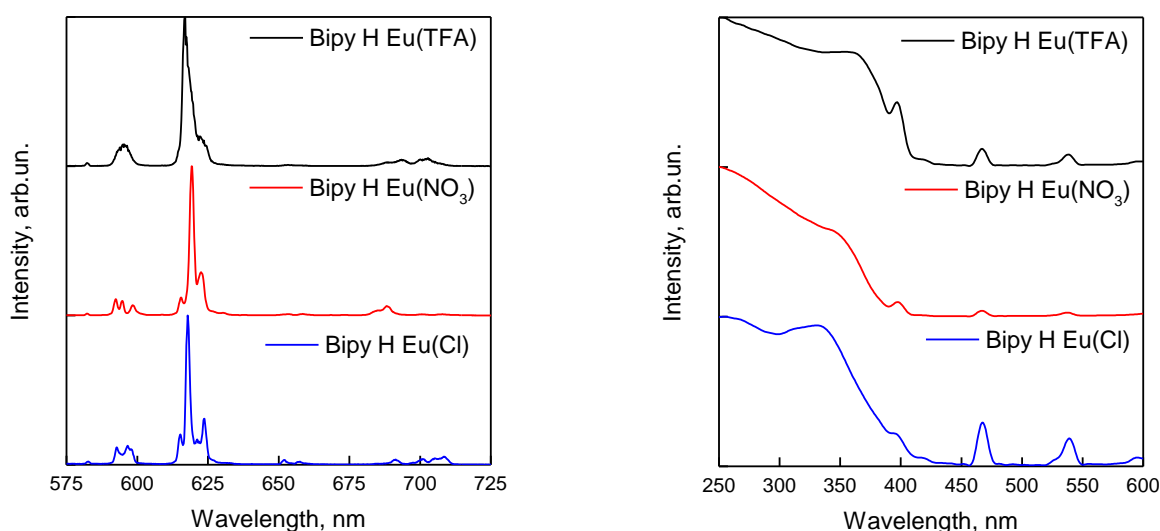


Figure 3. Emission spectra of europium complexes (1)-(3), $\lambda_{ex} = 320 \text{ nm}$, $T = 77 \text{ K}$ (left panel), excitation spectra of europium complexes (1)-(3), $\lambda_{em} = 618 \text{ nm}$, $T = 300 \text{ K}$ (right panel).

In the excitation spectra (Fig.3, right panel) the broad bands in the UV-range correspond to excitation of the ligand and the narrow peaks in the visible region there are typical for direct excitation of luminescence of the europium ion. The excitation spectra depend on the type of counterion if the complex is in a solid state.

3.3 Luminescence properties

Using luminescence kinetics, the luminescence lifetime was calculated. The lifetime was almost the same, $1.42 \pm 0.10 \text{ ms}$, for three studied complexes when measuring complexes in the form of powders in liquid nitrogen, the lifetime equaled $1.27 \pm 0.07 \text{ ms}$ when measuring solutions of complexes in acetonitrile. The luminescence lifetime is changing significantly when measuring complexes in the form of powders at room temperature. The shortest luminescence lifetime was obtained for BipyHEu(TFA) $0.70 \pm 0.02 \text{ ms}$. The luminescence lifetime equaled $1.20 \pm 0.02 \text{ ms}$ and $1.41 \pm 0.01 \text{ ms}$ for Bipy H EuCl and Bipy H Eu(NO₃) complexes respectively.

We decomposed the luminescence emission bands of europium complexes measured at the temperature of liquid nitrogen into several components of the Gaussian form. According to the obtained data, energy diagrams of the electric

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levels were constructed (Fig. 4). The fine structure of the electric levels of europium ions was different for all complexes with various counterions. Consequently, counterion penetrates in the nearest surrounding of the europium ion, and the distance between europium and the nearby atoms changes.

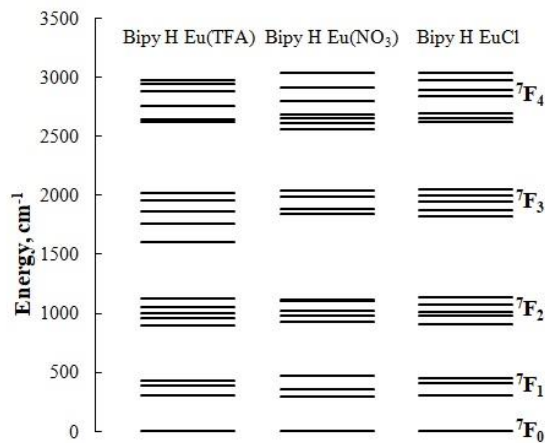


Figure 4. Energy levels in europium complexes with different counterions showing splitting of the level 7F_1 ($J=0-4$) due to the Stark effect.

The relative intensities of luminescence peaks corresponding to energy transitions ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0 - 4$) were calculated (Table 2). The most intense peak was the transition to 7F_2 or hypersensitive transition. However, the integral intensity increased to 70% europium complexes in the form of powder and to 80% for complexes dissolved in acetonitrile. This is explained by the fact, that ligand prevents the interaction of water molecules and other luminescence quenchers with europium ion.

Table 2. The relative luminescence intensities for the peaks corresponding to energy transitions ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0 - 4$) of europium complexes (1)-(3), $(I({}^5D_0 \rightarrow {}^7F_J)/I_{int}, \%)$

Complex	J=0	J=1	J=2	J=3	J=4
Bipy H Eu(TFA)	0.6	12.2	73.6	2.5	11.1
Bipy H Eu(NO ₃)	0.5	12.8	73.9	3.3	9.4
Bipy H EuCl	0.8	13.9	67.6	4.3	13.4

The asymmetry coefficient was found the lowest for the complex Bipy H EuCl in a powder form: 4.9 at room temperature and 4.3 when measured in liquid nitrogen. The asymmetry coefficient was 6.0 and 5.0 respectively for the complex Bipy H Eu(TFA), 6.2 and 5.9 for complex Bipy H Eu(NO₃). It means that the type of counterion influences this coefficient. When the complexes were dissolved in acetonitrile, the asymmetry coefficient for all complexes increased about 2 times, which indicates that the acetonitrile molecules lead to a strong increase in the deviation of europium from the inverse center.

The values of a radiative lifetime and internal quantum yields were calculated. The complexes had the greatest radiative lifetime when measured at the temperature of liquid nitrogen, it was equal to 2.49, 2.25, and 2.64 ms for the complexes Bipy H Eu(TFA), Bipy H Eu (NO₃), and Bipy H EuCl, respectively. At the room temperature, the radiative lifetime decreased for all complexes and was equal to 2.23, 2.24, and 2.25 ms, respectively, when measuring in the form of powders. And the radiative lifetimes of solutions were 2.19, 2.18, and 2.11 ms. Therefore, the radiative lifetime of europium complex with NO₃ counterion is less sensitive to alteration of experimental conditions.

The BipyH Eu(NO₃) complex had the highest value of the internal quantum yield, 65% at 77K and 63% at 300K. Solutions of europium complexes in acetonitrile had almost the same internal quantum yield, equal to 57% for Bipy H

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Eu(TFA) and 59% for Bipy H Eu (NO₃) and Bipy H EuCl. The luminescence quantum yield determined for solutions of europium complexes in acetonitrile was almost independent on the type of counterion and was equal to (6±2) %, (6±3) %, and (5±2) % for Bipy H Eu (TFA), Bipy H Eu (NO₃), and Bipy H EuCl, respectively. The effectiveness of sensitization was weakly dependent on the type of counterion and was equal to (11±4) %, (11±3) % and (9±3) % for Bipy H Eu (TFA), Bipy H Eu (NO₃), and Bipy H EuCl, respectively. Therefore, the luminescence quantum yield and the efficiency of sensitization are weakly dependent on the type of counterion.

4 CONCLUSION

Luminescence properties of three organo-soluble europium complexes with ligands based on 2,2'-bipyridyl dicarboxamides with various counterions were studied. We conclude that there is no dependence between absorption spectra and the type of counterion, and between the position of the singlet energy level of ligand and the kind of counterion either. Only the type and shape of the ligand affect these properties. We infer that the type of counterion influences the asymmetry coefficient, and acetonitrile increases the deviation of the europium ion from the centrally symmetric position compared to the complex in the solid state form. The radiation lifetime of the europium complex with counterion NO₃ is less sensitive to environmental changes compared to other complexes studied in this work. In addition, the luminescence quantum yield and the efficiency of sensitization are weakly dependent on the type of counterion.

ACKNOWLEDGEMENTS

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