

Luminescent solutions and films of new europium complexes with chelating ligands

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ABSTRACT

Abstract: The development of new complexes of rare earth elements (REE) with chelating organic ligands opens up the possibility of purposeful alteration in the composition and structure of the complexes, and therefore tuning their optical properties. New ligands possessing two pyridine rings in their structure were synthesized to improve coordination properties and photophysical characteristics of REE compounds. Complexes of trivalent europium with novel chelating ligands were investigated using luminescence and absorption spectroscopy, as well as atomic force microscopy. Luminescence properties of new compounds were studied both for solutions and films deposited on the solid support. All complexes exhibit the characteristic red luminescence of Eu (III) ion with the absolute luminescence quantum yield in polar acetonitrile solution varying from 0.21 to 1.45 % and emission lifetime ranged from 0.1 to 1 ms. Excitation spectra of Eu coordination complexes correspond with absorption bands of chelating ligand. The energy levels of the triplet state of the new ligands were determined from the phosphorescence at 77 K of the corresponding Gd (III) complexes. The morphology of films of europium complexes with different substituents in the organic ligands was investigated by atomic force microscopy (AFM). It strongly depends both on the type of substituent in the organic ligand, and the rotation speed of the spin-coater. New europium complexes with chelating ligands containing additional pyridine fragments represent outstanding candidates for phosphors with improved luminescence properties.

Keywords: luminescence, absorbance, atomic force microscopy, rare earth elements, coordination complexes.

1. INTRODUCTION

Nanotechnology is one of the most rapidly growing fields in all of science. Novel nanoscale materials can be exploited for both bioimaging and drug delivery for prospective theragnostics.¹⁻³ Synthesis of new phosphors with improved characteristics is an important task of development nanoconjugates for biomedical research to improve nanoparticles imaging techniques and other applications.⁴⁻⁷ One of the most promising classes of phosphors are coordination compounds of rare-earth elements (REE) due to their high brightness and long live luminescence. The intensities of the emission are in close relation with the symmetry of the coordination environment. Therefore the efficiency of energy transfer depends on both the nature of the ligand and REE ion. In the last three decades many inorganic and organometallic REE complexes have been synthesized, but the correlations between their structures and photophysical properties are still unclear. Because of that the search for new REE complexes with organic ligands providing high quantum yields of the luminescence opens up the possibility of purposeful changes in the composition and structure of the complexes, and therefore tuning their optical properties. However, there are no suitable compounds which simultaneously possess high stability and good solubility, as well as intense luminescence high yield and long emission lifetime in the millisecond range. In general, the establishment of unambiguous correlation between the composition, coordinating and emission properties of optical materials based on organometallic complexes are a challenging task.

Chelating ligands with two pyridine rings in their structure provide increased coordination of the ligand to the REE ions. In this study such ligands were synthesized to improve complexing and photophysical characteristics of REE compounds. Complexes of REE ions with diamides of 2,2'-bipyridin-6,6'-dicarboxylic acid can be readily soluble in organic solvents and exhibit photoluminescence both in solutions and as the films deposited on the solid support. They

might be outstanding candidates for phosphors which allow the preparation of new optical materials with enhanced luminescence properties.

1.1. Luminescence of coordination complexes of rare earth elements

Luminescence of lanthanides (III) coordination compounds is characteristic and is related to the f-f transitions. Exchanging the central ion of the lanthanide (III) the emission wavelength of luminescence can be varied throughout the entire range of the electromagnetic spectrum from UV to IR. However because f-f transitions are theoretically forbidden, low molar extinction coefficients do not provide an effective luminescence yields upon direct excitation of REE ions. To solve the problem it is possible to use coordination compounds of lanthanides which allows indirect excitation of the REE ion emission. In the lanthanide coordination complexes luminescence is produced by the light absorption performed by the organic ligand and emission of narrow spectral lines by the REE ion. The process takes place in three stages: the light absorption by the ligand, then energy transfer to the metal ion via the triplet state of the ligand and the emission of characteristic radiation of the lanthanide ion.⁸ Simplified scheme of energy transfer that is usually considered for lanthanide's coordination compounds is the following: $^1S^*$ (ligand) – $^3T^*$ (ligand) – Ln*. Intramolecular energy transfer efficiency is determined mainly by tuning the energy gap between $^3T^*$ and the resonance level of the lanthanide ion. Because the position the triplet level depends on the nature of the organic ligand, it is possible to alter the luminescence properties of the complex due to the changing nature of the ligand. For efficient energy transfer to the europium ion (III) the difference between the triplet state of the organic ligand and the resonance 5D_0 level of europium ΔE should lie in the range from 2500 to 3500 cm^{-1} .

For europium (III) complexes all emissions are radiated from the 5D_0 level. The strongest emissions are observed in the 7F_1 (593 nm) and 7F_2 (618 nm) transition regions, and the $^5D_0 - ^7F_4$ emission frequently has lower intensity.⁹ The $^5D_0 - ^7F_0$ emission is generally observed to be relatively weak, its intensity is quite sensitive to the ligand environment. It is possible to observe emissions from the 5D_1 and 5D_2 levels when excitation wavelength is shorter 523 or 465 nm, correspondingly.¹⁰ The number, energy spacings and relative intensities of those emission lines can provide detailed information about the symmetry and structure of the europium (III) coordination site. The luminescence lifetime of the 5D_0 emitting state of europium (III) complexes in solutions generally falls in the 0.1-1.0-ms range.

2. OBJECTS AND METHODS

2.1. Compounds synthesis and films preparation

The ligands were prepared by acylation of the secondary amine series by dichloride 2,2'-bipyridyl-6,6'-dicarboxylic dichloride as we propose earlier¹¹ (Figure 1).

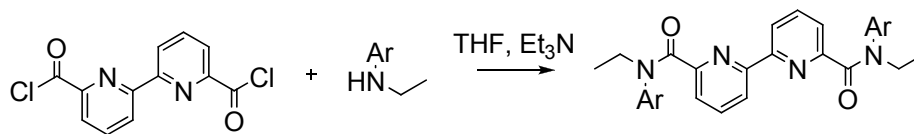


Figure 1. Scheme of ligands synthesis via acylation of the secondary amine series dichloride 2,2'-bipyridyl-6,6'-dicarboxylic acid.

Synthesis of dicarboxylic acid diamides (general procedure). The 2,2'-bipyridyl-6,6'-dicarboxylic acid was refluxed in thionyl chloride (5 mL of SOCl_2 per 1 g of the acid), adding dimethylformamide (0.5 mL) for 2.5 h. Then thionyl chloride was evaporated and the residue was dried in a vacuum and dissolved in anhydrous tetrahydrofuran (10 ml of THF per 1 g of the starting acid). The obtained solution was portionwise added with stirring to a solution of 2.1 equivalents of amine and 10 equivalents of triethylamine in anhydrous tetrahydrofuran (10 mL of THF per 1 g of the amine). After the end of addition, the reaction mixture was protected from moisture with a CaCl_2 -tube, stirred for 4–5 h at 40–50°C, and stirred overnight at room temperature. The reaction mixture was twice diluted with water and the organic layer was separated. Aqueous layer was extracted with diethyl ether three times. The combined organic fractions were washed with water and dried over anhydrous sodium sulfate. After the solvents were evaporated, crude solid was treated with a minimal amount of ethyl acetate. The precipitate formed was washed by cold ethyl acetate and dried in air.

The yields of the diamides were 65—80%. The physicochemical characteristics of the diamides and their yields are given in Table 1.

Interaction of synthesized compounds with nitrates of europium or gadolinium in boiling acetonitrile leads to the formation of the complexes **BiPyLn** in high yields of 50-90% depending on the structure of the ligand as we reported for the related compounds¹² (see Figure 2).

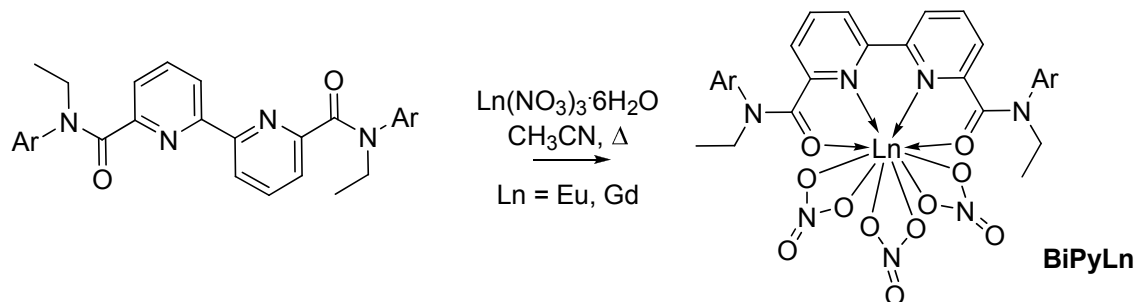


Figure 2. Formation of the salt complexes of Ligand 1:1.

Synthesis of europium complexes with dicarboxylic acid diamides (general procedure). The mixture of the ligand and equal amounts of hexahydrate europium trinitrate in dry acetonitrile (25 ml per 100 mg of a ligand) was boiled for 7-8 hours and slowly cooled to room temperature (for a complete precipitation of the product reaction mixtures were leave to stand overnight). White or pale brown precipitate was filtered under vacuum, washed with a small amount of cold acetonitrile and dried in air. The yields of and spectral characteristics of compounds are given in Table 2.

2.2. Spectral measurements

Spectral measurements were performed for europium complexes in acetonitrile at concentration of $3\text{-}7 \cdot 10^{-5}$ mol/l. The films of europium complexes on solid support were obtained by spin-coating method from ethyl acetate solutions of complexes **Bipy Hex Eu** and **Bipy Et Eu** in a concentration of $2.24 \cdot 10^{-4}$ and $1.79 \cdot 10^{-4}$ mol/l respectively. As solid substrates we used quartz plates either polyethylene terephthalate plates coated with indium tin oxide (ITO) with resistivity of $60 \Omega/\text{cm}^2$.

The absorption spectra of solutions and films deposited on quartz plates were recorded by a spectrophotometer Hitachi U-1900. The emission and excitation luminescence spectra, as well as luminescence lifetimes were measured using a luminescence spectrometer Hitachi F-7000. Solutions of europium complexes in acetonitrile were placed in quartz cuvettes and the luminescence properties were measured at 90-degree geometry. For the films deposited on solid substrates luminescence characteristics were measured at reflection geometry.

Absolute luminescence quantum yields for solutions of europium complexes in acetonitrile were calculated from absorbance values and fluorescence intensities using classical approach¹³ and solution of Rhodamine as a reference.

The energy levels of the triplet state of ligands were determined from the phosphorescence spectra of Gd (III) complexes with the same ligands measured at 77 K.

2.3. Atomic force microscopy

The morphology of films of europium complexes with different substituents in the organic ligands was investigated by atomic force microscopy (AFM). AFM measurements were performed with a scanning probe microscope SMENA-A, Platform «Solver» company NT-MDT. Scanning was performed with a silicon cantilevers DCP-11 with a resonance frequency of 178.6 kHz in the semi-contact (tapping mode). When operating in this mode, the cantilever is excited near resonance with amplitude of the order of 10 - 100 nm. The cantilever is brought to the surface so that the lower half-period oscillations occurred touching the sample surface. We also used the method of phase imaging. The AFM images were processed using the software «NOVA» for two-dimensional (2D) and three-dimensional (3D) data.

3. RESULTS AND DISCUSSION

3.1. Physicochemical properties of the chemical compounds

All of the prepared compounds, both ligands and their complexes were analyzed by several spectral techniques, which supports structure, composition and purity of the compounds. The mass-spectrometry and NMR spectroscopy confirm the structure of the ligands; the yields, ¹H NMR and mass-spectra are represented in Table 1.

Table 1. Physicochemical properties of the ligands.

Ar	Yield, %	¹ H NMR	Mass-spectra, (m/Z)
Ph	79	7.62 (t, 6 H, J = 7.32), 7.12 (br.m, 10H), 4.02 (q, 4 H, J = 6.97), 1.24 (t, 6 H, J = 6.97)	450
2-F-C ₆ H ₄	74	7.72 (d, 2H, J=7.72), 7.62 (m, 2H), 7.50 (d, 2H, J=7.12), 126.85-7.12 (br.m, 8H), 3.94 (q, 4H, J=6.93), 1.24 (t, 6H, J=6.93)	486
3-F-C ₆ H ₄	78	7.67 (m, 6 H); 7.12 (td 2 H, J = 7.95, J = 6.60), 6.89 (d, 2 H, J = 9.78), 6.87 (t, 4 H, J = 6.60). 4.01 (q, 4 H, J = 7.09), 1.28 (t, 6 H, J = 7.09)	486
4-F-C ₆ H ₄	67	7.65 (m, 4 H); 7.57 (br.t, 2 H, J = 7.15); 7.04 (m, 4 H); 6.87 (t, 4 H, J = 7.15) 3.96 (q, 4 H, J = 7.03) 1.25 (t, 6 H, J = 7.03)	486
4- <i>n</i> -Hex-C ₆ H ₄	72	7.61 (m, 6 H); 6.98); (br.m, 8 H), 3.99 (q, 4 H, J = 7.05); 2.47 (t, 4 H, J = 7.83); 1.47 (tt, 4 H J = 6.93, J = 7.09); 1.27 (m, 18 H); 0.97 (t, 6 H, J = 6.97).	618
4-Et-C ₆ H ₄	76	7.59 (m, 6H), 6.97 (m, 8H), 3.97 (q, 4H, J=6.50), 2.48 (q, 4H, J=7.25), 1.23 (t, 6H, J=6.50), 1.06 (t, 6H, J=7.25)	506
4- <i>i</i> -Pr-C ₆ H ₄	73	7.60 (m, 4H), 7.42 (m, 2H), 6.96 (m, 8H), 3.98 (q, 4H, J=6.97), 2.72 (m, 2H), 1.23 (t, 6H, J=6.97), 1.05 (d, 12H, J=6.97)	534
2,4- diMe-C ₆ H ₃	64	7.64(m, 6H, H _{Py}); 6.95(m, 2H, H _{Ar}), 6.89(c, 2H, H _{Ar}), 6.84(d, 2H, J=7.34, H _{Ar}), 4.22(m, 2H, CH ₂), 3.55(m, 2H, CH ₂), 2.18(c, 12H, CH ₃) 1.26(t, 6H, J=7.09, CH ₂ -CH ₂)	506
3,4- diMe-C ₆ H ₃	82	7.62(t, 2H, J=8.07, H _{Py}), 7.51(d, 2H, J=7.19, H _{Py}), 7.67(d, 2H, J=7.34, H _{Py}); 6.96(c, 1H, H _{Ar}), , 6.94(c, 1H, H _{Ar}), 6.90(t, 2H, J=7.41, H _{Ar}), 6.82(d, 2H, J=7.34, H _{Ar}) 4.15(m, 2H, CH ₂), 3.63(m, 2H, CH ₂), 2.20(c, 6H, CH ₃), 2.10(d, 6H, J=13.42, CH ₃), 1.25(t, 6H, J=6.93, CH ₃)	506
2,5-diMe-C ₆ H ₃	62	7.61(m, 6H, H _{Py}) 6.94(m, 2H, H _{Ar}), 6.86(d 2H, J=6.85, H _{Ar}), 6.73(d, 2H, J=5.87, H _{Ar}), 3.99(m, 4H, CH ₂), 2.10(2c, 12H, CH ₃) 1.25(t, 6H, J=6.24, CH ₃).	506
4-EtO-C ₆ H ₄	84	7.55 (m 6H), 6.96 (d 4 H, J=6.90), 6.67 (d 4 H, J=6.90) 3.93 (m 8 H) 1.25 (m, 12 H)	538
2-COOMe-C ₆ H ₄	57	7.73 (m, 2H), 7.68 (m, 2H), 7.55 (m, 2H), 7.35 (br. m., 6H), 7.14 (m, 2H), 4.16 (m, 2H), 3.75 (m, 8H), 1.23 (m, 6H)	566
6-Me-2-pyridyl	59	7.74 (dd, 2H, J=0.97, J=7.58), 7.62 (t, 2H, J=7.83), 7.49 d, 2H, J=7.83), 7.28 (t, 2H, J=7.80), 6.78 (d, 2H, J=7.70), 6.63 (d, 2H, J=7.43), 4.15 (d, 4H, J=4.11), 2.38 (c, 6H), 1.24 (t, 6H, J=7.12)	480

The structure of obtained complexes is also confirmed by mass spectrometry and NMR spectroscopy. The main peaks in the MALDI-TOF mass spectrum are corresponding to the ion clusters which are formed by the elimination of the nitrate

ion from the original complexes (see Table 2). Mass-spectra show the characteristic peak clusters of the main daughters of the complexes (see Figure 3).

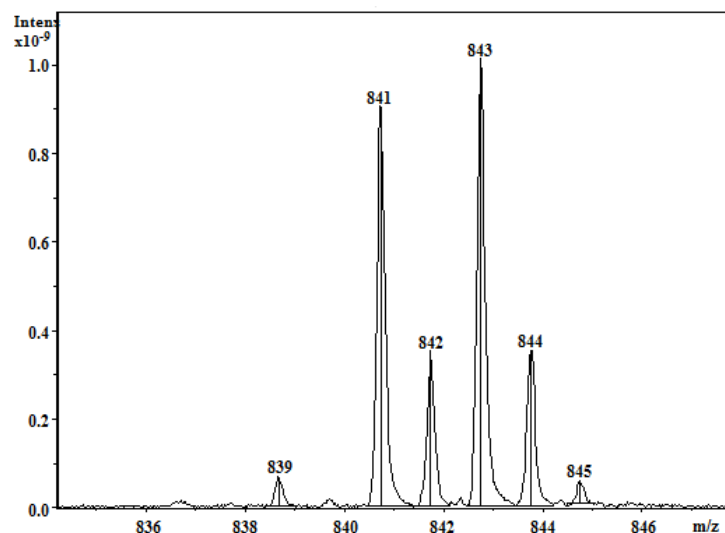


Figure 3. MALDI-TOF peak cluster for the ion $[\text{BiPyCOOMeEu-NO}_3]^+$ which is typical for the investigated complexes.

Table 2. Physicochemical properties of the europium complexes.

	Ar	Yield, %	Mass-spectra (m/z)
BiPy Eu	Ph	65	727 $[\text{M-NO}_3]^+$
BiPy oF Eu	2-F-C ₆ H ₄	49	761 $[\text{M-NO}_3]^+$
BiPy mF Eu	3-F-C ₆ H ₄	73	761 $[\text{M-NO}_3]^+$
BiPy pF Eu	4-F-C ₆ H ₄	82	761 $[\text{M-NO}_3]^+$
BiPy Hex Eu	4-n-Hex-C ₆ H ₄	69	816 (100%) $[\text{M-NO}_3]^+$
BiPy Et Eu	4-Et-C ₆ H ₄	76	783 (100%) $[\text{M-NO}_3]^+$
BiPy iPr Eu	4-i-Pr-C ₆ H ₄	59	811 (100%) $[\text{M-NO}_3]^+$
BiPy 2,4-DiMe Eu	2,4- diMe-C ₆ H ₃	87.5	816 (100%) $[\text{M-NO}_3]^+$
BiPy 3,4-DiMe Eu	3,4- diMe-C ₆ H ₃	89	816 (100%) $[\text{M-NO}_3]^+$
BiPy 2,5-DiMe Eu	2,5-diMe-C ₆ H ₃	84	816 (100%) $[\text{M-NO}_3]^+$
BiPy OEt Eu	4-EtO-C ₆ H ₄	69	814 (100%) $[\text{M-NO}_3]^+$
BiPy COOMe Eu	2-COOMe-C ₆ H ₄	55	842 (100%) $[\text{M-NO}_3]^+$
BiPy 6Me2Py Eu	6-Me-2-pyridyl	55	756 $[\text{M-NO}_3]^+$

3.2. Atomic-force microscopy

The film morphology of the Eu (III) complexes with diamides of dicarboxylic acids strongly depends on the type of substituent in the organic ligand, and the rotation speed of the spin-coater. Films received by the drip method without rotation of the support of **BiPy Hex Eu** or **BiPy Et Eu** provide a structure of long and thick interwoven filaments.

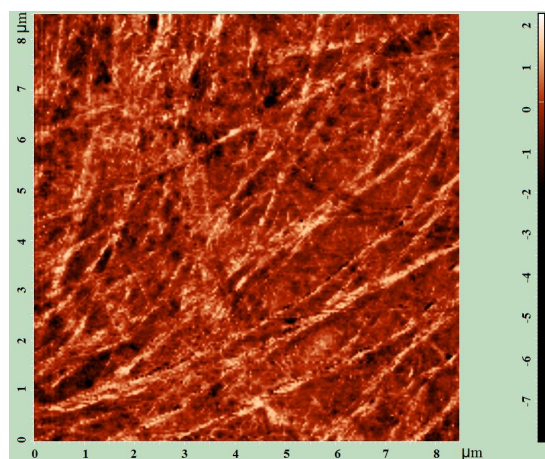


Figure 4. Phase AFM-picture of film with complex of **BiPy Hex Eu**, obtained without rotation.

The films with the same complexes obtained by spin-coating at different rotation speeds (1000 and 2000 rot/min) give a continuous film on the surface of the plate. These kinds of films manifest honeycomb-type structure in the case of **BiPy Et Eu** and randomly spaced rod-shaped particles in the case of **BiPy Hex Eu**.

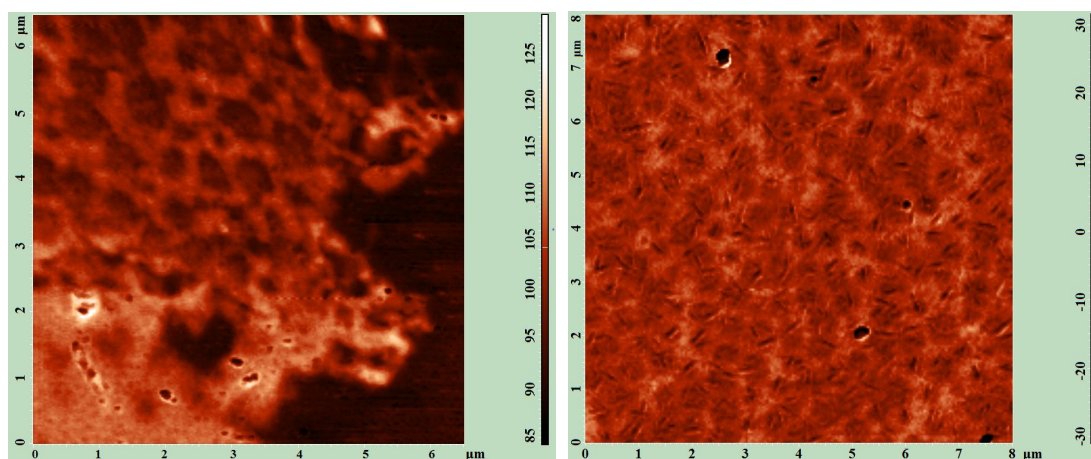


Figure 5. Phase AFM-picture of film with complex **BiPy Et Eu** (left) and **BiPy Hex Eu** (right), obtained with rotation (2000 rot/min).

Diameter of the pores and the size of particles at the surface of films depends on the speed of spin-coater rotation during the production of the films. Films **BiPy Et Eu**, deposited on a substrate at a rotation speed of 1000 r/min, take the form of a mesh grid with fairly regularly spaced pores with a diameter of about 0.5 microns and a depth of 5 nm. More uniform films with rarely disposition of "craters" with the same size as the pores in the mesh grid were obtained by increasing the rotational speed of 2000 r/min. For films **BiPy Hex Eu**, fabricated at a speed of 1000 r/min, the length of the "rod" is equal to approximately 0.8 microns. The increasing of the rotational speed of 2000 r/min shorter "sticks" length to 0.3 microns and a height to 2-3 nm.

3.3. Absorption spectra

The Figure 6 shows the absorption spectra of solutions of europium complexes in acetonitrile. The solution has the short-wavelength maximum centered the range 320-330 nm. The absorbance values for the complexes in solutions follow the

Burger-Lambert-Beer law. The absorption band of Eu complexes in the UV region for films on quartz substrates were red-shifted in 2 nm compared to that of solutions.

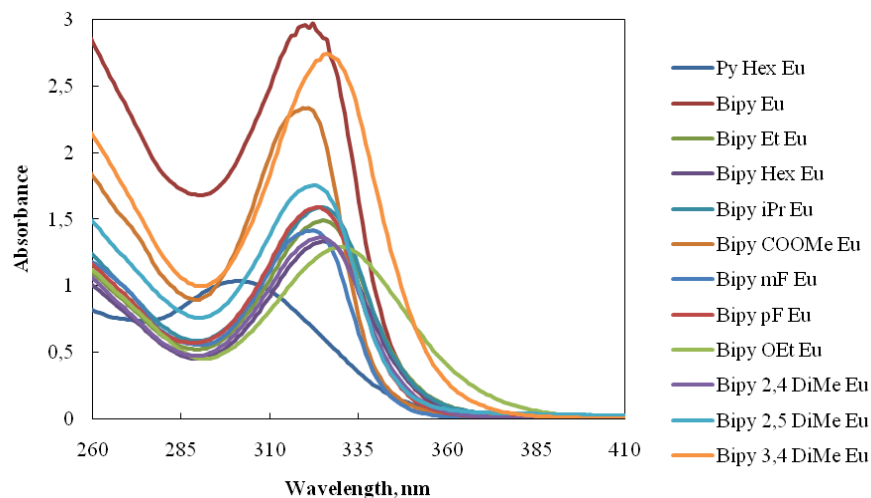


Figure 6. Absorbance spectra of europium (III) complexes in acetonitrile solutions.

3.4. Luminescence spectra, quantum yield and emission lifetimes

The studied compounds exhibit luminescence emission lines characteristic for the REE binded in the complex, and excitation spectra related to absorption bands of the ligands. Luminescence intensity strongly depends on the type of the ligand. Typical luminescence spectrum of europium complexes has two main maxima: centered at 592 nm, corresponding to the transition $^5D_0 - ^7F_1$, and at 618 nm, corresponding to the transition $^5D_0 - ^7F_2$. The latter is the most intense maximum.

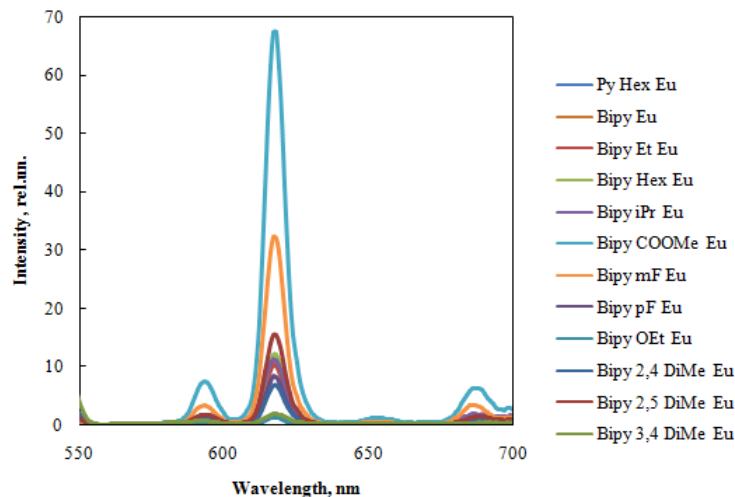


Figure 7. Fluorescence spectra of europium (III) complexes in acetonitrile solutions.

The films of europium complexes deposited on solid substrates exhibit luminescence similar to that for solutions with a main peak emission centered at 618 nm and a lifetime about 1 ms. The band in excitation spectra with emission at 618 nm depended on the way of film preparation. For instance, for the films obtained without spin-coating the wavelength of

the UV excitation peak was shorter (322 nm for **BiPy Hex Eu** and 329 nm for **BiPy Et Eu**) than that for films deposited by spin-coating (333 nm for both ligands regardless of the rotation speed). The difference in the position of maximum in the excitation spectrum can be explained by the decrease in film thickness and size of the aggregates of complexes due to rotation of the substrate.

The absolute luminescence quantum yield QY for studied europium complexes measured in relation to Rhodamine solution varied from 0.21 to 1.45 %. The largest yield was found for complexes **BiPy mF Eu** (1.23%) and **BiPy pF Eu** (1.45%), the smallest one for **BiPy OEt Eu** (0.1%). The characteristic emission lifetime for all of Eu complexes ranged from 0.1 to 1 ms in acetonitrile solutions at room temperature.

Table 3. Spectral characteristics of studied europium complexes.

Complex	Absorption wavelength maximum, nm	Absolute luminescence quantum yield, %	Emission lifetime, ms
Py Hex Eu	301	0.95	0.27
BiPy Eu	322	0.45	0.74
BiPy Et Eu	325	0.53	1.01
BiPy Hex Eu	325	0.59	1.06
BiPy iPr Eu	325	0.55	1.00
BiPy COOMe Eu	319	0.98	0.62
BiPy mF Eu	322	1.23	0.68
BiPy pF Eu	323	1.45	0.73
BiPy OEt Eu	330	0.10	0.65
BiPy 2,4 DiMe Eu	324	0.29	0.37
BiPy 2,5 DiMe Eu	322	0.39	0.89
BiPy 3,4 DiMe Eu	326	0.21	0.10

The overall luminescence quantum yield of the lanthanide coordination complexes is a production of quantum yield resulting from indirect excitation and the efficiency of energy transfer from the antenna ligand to the centered ion. Although a number of sensitized lanthanide complexes have been reported, energy-transfer pathways have not been fully understood for the sensitization of the lanthanide ions. To understand better the process of photoexcitation of europium emission we have studied triplet levels of ligands and compared them with the resonance level of europium ion

3.5. Triplet levels of the ligands and dependence $\Delta E(QY)$

The phosphorescence spectra of Gd (III) complexes measured at 77 K are shown in Figure 8.

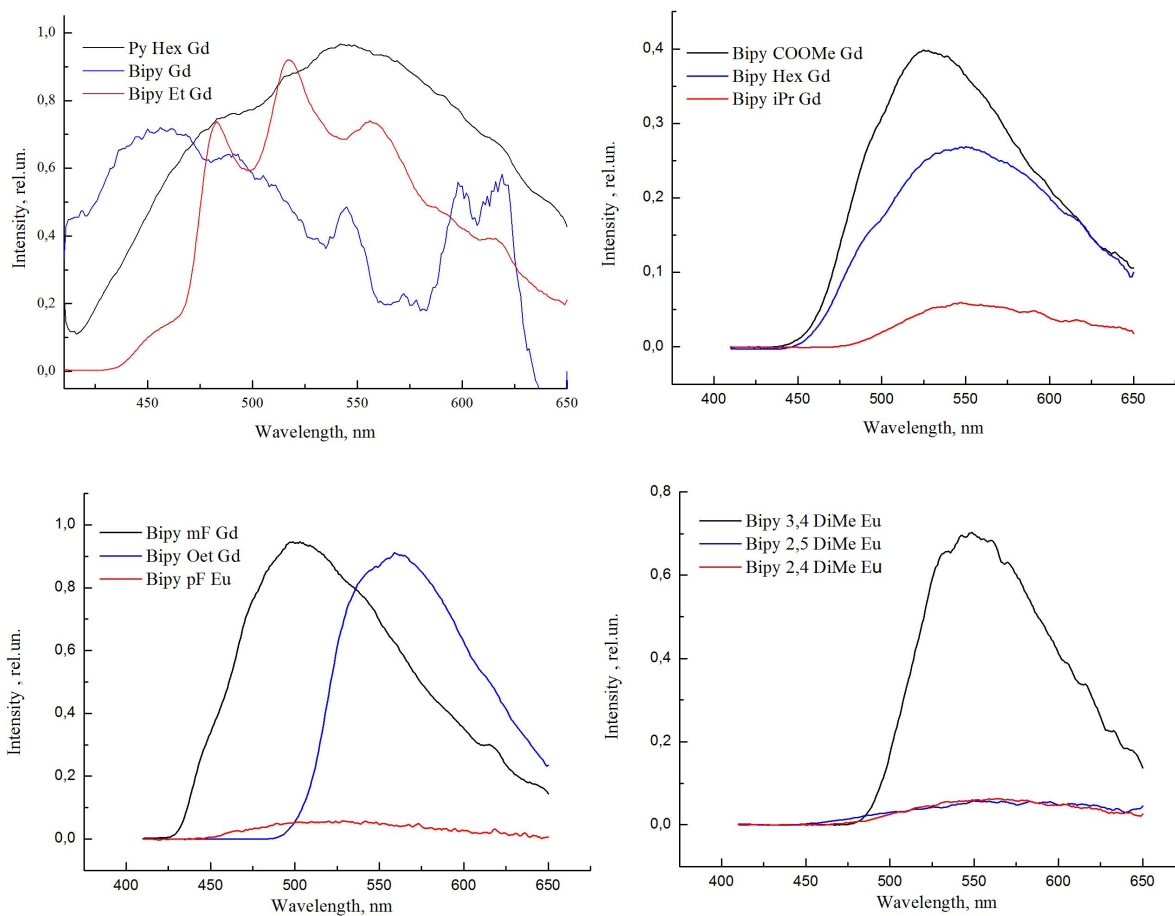


Figure 8. Phosphorescence spectra of gadolinium (III) complexes.

The energy levels of the triplet state $E(\text{Tr})$ of the new ligands were determined from the phosphorescence spectra of Gd (III) complexes with appropriate ligands, they are given in the Table 4.

Table 4. The energy levels of the triplet state $E(\text{Tr})$ of the new ligands and the difference between the triplet level of the ligand and the resonance level of the europium ion $\Delta E(\text{Tr}-^5\text{D}_0)$

Complex	$E(\text{Tr}), \text{cm}^{-1}$	$\Delta E(\text{Tr}-^5\text{D}_0), \text{cm}^{-1}$
Py Hex Gd	21160	3896
Bipy Gd	21969	4705
Bipy Et Gd	21645	4381
Bipy Hex Gd	20664	3400
Bipy iPr Gd	18743	1479
Bipy COOMe Gd	20591	3327
Bipy mF Gd	22409	5145
Bipy pF Gd	21459	4195

Bipy OEt Gd	18800	1536
Bipy 2,4 DiMe Gd	19819	2116
Bipy 2,5 DiMe Gd	20408	3144
Bipy 3,4 DiMe Gd	18349	1085

Triplet levels of the ligands were compared with the efficiency of the luminescence of the Eu complexes. From those data we conclude the dependence of the quantum yield of the luminescence on difference (ΔE , cm^{-1}) between the triplet level of the ligand and the resonance level of the europium ion $\Delta E(\text{Tr}-^5\text{D}_0)$ (see Table 4).

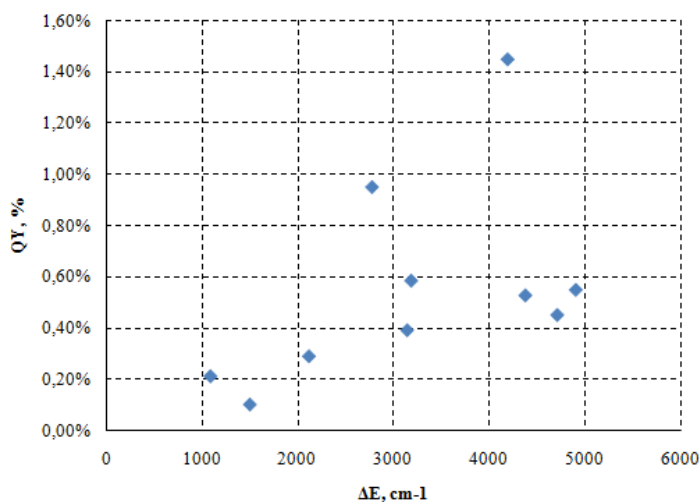


Figure 9. The dependence of the absolute luminescence quantum yield (QY) of europium complexes on the energy difference of the triplet level of the ligand and the resonance level of the europium ion (ΔE).

4. CONCLUSIONS

Luminescence characteristics were studied for a series of newly synthesized complexes with diamides of dicarboxylic acids, both for compound dissolved in acetonitrile and as thin films deposited on the solid support. All complexes exhibit the characteristic red luminescence of Eu (III) ion with the absolute luminescence quantum yield in solution varying from 0.21 to 1.45 %. The largest yield was found for complexes **Bipy mF Eu** (1.23%) and **Bipy pF Eu** (1.45%), the smallest one for **Bipy OEt Eu** (0.1%). The characteristic emission lifetime for all of Eu complexes ranged from 0.1 to 1 ms in acetonitrile solutions at room temperature.

The morphology of films of europium complexes with different substituent in the organic ligands was investigated by atomic force microscopy. It strongly depends both on the type of substituent in the organic ligand, and the rotation speed of the spin-coater. The films of europium complexes deposited on the solid support exhibited luminescence similar in emission wavelength and lifetime to that for solutions. However the UV band in excitation spectra depended on the way of film preparation and its maximum position could vary in few nanometers due to different film thickness.

The energy levels of the triplet state of the new ligands were determined from the phosphorescence of their Gd (III) complexes measured at 77 K. The triplet states of some ligands fitted well the emission level of Eu (III) ion giving rise in several times of absolute luminescence quantum yield. This finding allows fabrication of new optical materials with enhanced luminescence properties.

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REFERENCES

- [1] Shenderova, O., Hens, S., Vlasov, I., Turner, S., Lu, Y.-G., Van Tendeloo, G., Schrand, A., Burikov, S. A. and Dolenko, T. A., "Carbon-Dot-Decorated Nanodiamonds," *Part. Part. Syst. Charact.* 31, 580–590 (2014).
- [2] Von Haartman, E., Jiang, H., Khomich, A.A., Zhang, J., Burikov, S.A., Dolenko, T.A., Ruokolainen, J., Gu, H., Shenderova, O.A., Vlasov, I.I., Rosenholm, J.M., "Core-shell designs of photoluminescent nanodiamonds with porous silica coatings for bioimaging and drug delivery I: Fabrication," *J. of Materials Chemistry B* 1, 18, 2358-2366 (2013).
- [3] Prabhakar, N., Nareoja, T., von Haartman, E., Karaman, D., Jiang, H., Koho, S., Dolenko, T., Hanninen, P., Vlasov, D., Ralchenko, V., Hosomi, S., Vlasov, I., Sahlgren, C., and Rosenholm, J., "Core-shell designs of photoluminescent nanodiamonds with porous silica coatings for bioimaging and drug delivery II: Application," *Nanoscale* 5, 9, 3713–3722 (2013).
- [4] Mikami, M., Watanabe, H., Uheda, K., Shimooka, S., Shimomura, Y., Kurushima, T., Kijima, N., "New Phosphors for white LEDs: Material Design Concepts," *IOP Conf. Series: Materials Science and Engineering* 1, 012002, 1-10 (2009).
- [5] Roesky, P.W., [Molecular Catalysis of Rare-Earth Elements, Structure and Bonding], "Springer, Berlin, Heidelberg," (2010).
- [6] Gai, Y.L., Jiang, F.L., Chen, L., Bu, Y., Su, K.Z., Al-Thabaiti, S.A., Hong, M.C., "Photophysical Studies of Europium Coordination Polymers Based on a Tetracarboxylate Ligand," *Inorg. Chem* 52 (13), 7658-7665 (2013).
- [7] Li, T., Kaercher, S., Roesky, P.W., "Synthesis, structure and reactivity of rare earth metal complexes containing anionic phosphorus ligands," *Chem. Soc. Rev.* 43, 42-57 (2014).
- [8] Crosby, G.A., Whan, R.E., Freeman, J.J., "Spectroscopic studies of rare earth chelates," *J. Phys. Chem.* 66, 2493-2499 (1962).
- [9] Li, Q., Li, T., Wu, J., "Luminescence of Europium(III) and Terbium(III) Complexes Incorporated in Poly (Vinyl Pyrrolidone) Matrix," *J. Phys. Chem.*, 105, 12293-12296 (2001).
- [10] Richardson, F.S. "Terbium(III) and Europium(III) Ions as Luminescent Probes and Stains for Biomolecular Systems," *Chem. Rev.* 82, 541-552 (1982).
- [11] Kirsanov, D.O., Borisova, N.E., Reshetova, M.D., Ivanov, A.V., Korotkov, L.A., Eliseev, I.I., Alyapyshev, M.Y., Spiridonov, I.G., Legin, A.V., Vlasov, Y.G., Babain, V.A., "Novel diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid: synthesis, coordination properties, and possibilities of use in electrochemical sensors and liquid extraction," *Russian Chemical Bulletin* 61, 881-890 (2012).
- [12] Borisova, N.E., Kostin, A.A., Eroshkina, E.A., Reshetova, M.D., Lyssenko, K.A., Spodine, E.N., Puntus, L.N., "Lanthanide Complexes with Tetradentate N,N',O,O'-Dipyridyl-Based Ligands: Structure, Stability, and Photophysical Properties," *European Journal of Inorganic Chemistry*, 2219-2229 (2014).
- [13] Lakowicz, J.R., [Principles of Fluorescence Spectroscopy], "Edition: 3rd Springer Science+Business Media, NY," (2006).