Novel Eu$^{3+}$ complex based on β – diketonate ligand for OLED application

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Abstract. It was demonstrated that bonding Eu$^{3+}$ ion to β – diketonate ligand as main ligand and 4,7-Diphenyl-1,10-phenanthroline (bathophenanthroline) as ancillary ligand leads to a significant increase of extinction and luminescence intensity. To order the potential of this complex to OLED application, we fabricated and investigated the electroluminescent device based on this compound. We achieved a high value of photoluminescence quantum yield (56 %) and external quantum efficiency value of 1% at 12 V.

1. Introduction
A promising direction for the development of new light sources is the creation of organic light-emitting diodes. As a rule, such light-emitting structures are created on the basis of iridium complexes, which play the role of radiative recombination centers [1]. However, these materials are expensive. Moreover, the fabrication process is difficult. In this regard, there was a need to develop a new class of luminophors that would provide the same performance characteristics as the iridium complexes, but with a lower production cost [2].

Lanthanide complexes with various organic ligands could be good candidates for efficient and stable luminescent materials [3-5]. They demonstrate remarkable luminescent properties due to the «antenna» effect [6]. The luminescence efficiency is governed by the processes of energy transfer from the ligand environment to the central ion, as well as by the excitation quenching. The transfer mechanism efficiency depends on the energy difference between the ligand triplet level and the resonant level of the given ion. According to the Latva–rule optimal energy difference is found in the range of 2000 – 2500 cm$^{-1}$ for Eu$^{3+}$ ion [7]. There is a way to decrease the probability of nonradiative processes by replacing the CH bonds with CF ones. It is also important to remove the solvent molecules from the inner coordination sphere of the ion since they can cause additional quenching. This is achieved by the employment of ancillary ligands as bathophenanthroline [8-9]. Moreover, this ligand is an additional electronic excitation «antenna» due to suitable triplet energy.

In present work we investigated photo- and electroluminescent potential of novel (1-(1,3-Dimethyl-1H-pyrazol-4-yl)-4,4,4-trifluorobutane-1,3-dionato)(4,7-diphenyl-1,10-phenanthroline) europium (III) complex with 4,7-Diphenyl-1,10-phenanthroline (bathophenanthroline) ancillary ligand.

2. Experimental part
2.1. Spectroscopy study
Optical absorption spectra were recorded at ambient temperature with the use of a Specord M40 spectrophotometer operating within 200–800 nm. The experiments were carried out for the complexes and corresponding neat ligand bathophenanthroline in the solutions poured into 1-cm-pathlength quartz optical cells. Photoluminescence (PL) spectra were obtained at ambient temperature with an Ocean Optics Maya 2000 Pro CCD spectrometer sensitive within 450–800 nm. The measurements were carried out at ambient temperature. The samples in quartz cells were placed near the center of the sphere. An emission-standard 45W quartz tungsten-halogen lamp (Oriel) was employed to measure the instrument response function.

2.2. OLEDs fabrication and characterization
Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) hole injection material, 2,2’-Dimethyl-N,N’-di-[(1-naphthyl)-N,N’-diphenyl]-1,1’-biphenyl-4,4’-diamine (α-NPD) hole transport material, 4,4’-Bis(N-carbazolyl)-1,1’-biphenyl (CBP) host layer material, 1,3,5-tris[N-(phenyl)benzimidazole]-benzene (TPBi) electron transport material as well as LiF and Al cathode materials were purchased from Luminescence Technology Corp. and used without further purification.

The luminance of the OLED samples was measured by a TKA-PKM luminance meter produced by TKA Scientific Instruments. Current voltage characteristics were obtained using an automated setup involving a Keitley 6485 picammeter, Agilent 34401A voltmeter, and a Motech 2019 power supply. OLED optical power was determined using a Coherent FieldMaxII Laser Power Meter with a calibrated photodiode head. Electroluminescence (EL) spectra were obtained with an Ocean Optics Maya 2000 Pro CCD spectrometer.

3. Results and discussions

3.1. Spectroscopy
Optical absorption spectra of the neat bath ligand and the complex with the bath ancillary ligand and main ligand are presented in Figure 1. The absorption spectrum of the investigated complex (Figure 1, curve 1) reveals several bands. These bands maxima are located at 220, 240, 290 and 320 nm. Comparison of the spectrum of complex and neat ligands spectra allowed to conclude, that two absorption maxima at 220 and 280 nm are associated with the absorption of the bath ligand. Absorption maxima at 320 nm are associated with both ligands, and broadband at wavelength range 330 – 360 nm is a feature of the main β – diketone ligand.

![Figure 1. Optical absorption spectra for investigated complex (1), neat bath ligand (2) and neat main ligand (3) dissolved in acetonitrile.](image-url)
Photoluminescence spectra of the neat main ligand and complex in solid phase are shown in Figure 2. The PL spectrum of the neat ligand (curve 1 in Figure 2) has a complex structure with a maximum at 470 nm and a shoulder ranging up to 700 nm, while the PL of complex exhibits multiple peaks within 580 – 605 nm, 610 – 620 nm, 650 – 660 nm and 680 – 710 nm (curve 2 in Figure 2). The observed narrow emission bands with maxima at 583 nm, 588 nm, 615 nm, 655 nm, and 680 nm are assigned to the $^5D_0 - ^7F_0$, $^5D_0 - ^7F_1$, $^5D_0 - ^7F_2$, $^5D_0 - ^7F_3$ and $^5D_0 - ^7F_4$, respectively. For ligand, the broad PL peaks are extended with a shoulder in the red spectral region. However, the broad luminescence band of ligand doesn’t observe in PL spectra of the complex. It indicates that energy transfer from the ligand environment to a metal ion is complete (efficiency $\approx 99\%$).

![Figure 2. Photoluminescence spectra of neat main ligand (1) and complexes (2) of Eu$^{3+}$ ion.](image)

In order to investigate the potential of our complex of Eu$^{3+}$, we measured his absolute quantum yield (QY). It was demonstrated, that QY of the compound is 56% and doesn’t depend on the excitation wavelength.

3.2. Electroluminescence

We developed and examined ITO/PEDOT:PPSS/α–NPD/Eu complex:CBP/TPBI/LiF/Al (see Figure 3). The average thickness of the obtained composite Eu complex:CBP active layers did not exceed 40 nm. The OLED cell consists of a glass substrate coated with transparent a conductive layer of indium tin oxide (ITO), performing the role of the anode. A layer of a hole-conducting material (HTL) is applied to it, then an emission layer of an organic complex (EML), an electrically-conductive layer (ETL) and a metal film acting as the cathode. Charge carriers (electrons and holes) are injected into the conducting layers (ETL and HTL) from the cathode and anode. Then at the heterointerface, charges are knitted into excitons, which recombine in the active radiating layer (EML).

![Figure 3. Typical structure of fabricated devices (left) and AFM photo of the active layer (right).](image)
Electroluminescent (EL) spectra of fabricated OLED are showed in Fig. 4. The EL spectrum of OLED device exhibit pronounced peaks corresponding to radiation transition $^5D_0 - ^7F_1$ in Eu$^{3+}$ ion. The other transitions $^5D_0 - ^7F_j$ ($j = 0, 2, 3, 4$) are also observed with small intensities. The additional subtle peak corresponding to $^5D_1 - ^7F_1$ detected at 540 nm. In the blue region of the spectrum for OLED characteristic the presence of a broad luminescence band that cannot be matched with ion Eu$^{3+}$ radiation. This PL band cannot be related to the luminescence of OLED’s layers or Eu$^{3+}$ ion emission. PL spectra of CBP material qualitatively resemble the regarded EL band (see Figure 4, curve 2).

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Electroluminescence spectrum at 12 V (1) obtained for ITO/PEDOT:PPSS/α–NPD/Eu complex:CBP/TPBI/LiF/Al OLED; PL spectrum for Eu$^{3+}$ complex (2) and CBP transport material (3) measured under 365 nm excitation.

Increasing the bias leads to an increase in the emission contribution of the CBP material. CBP emission appears at 10 V, and it has non-uniform growth as can be seen in Figure 5.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Electroluminescence spectra at different voltages.

EL of the investigated device appears at 4.5 V. This value of turn-on voltage is comparable to the ones reported for analogous OLED devices. The highest achieved external quantum efficiency was 1% at 12 V.

4. Conclusion

Thus, photophysical properties of the novel metal-organic compound were investigated. The organic light - emitting diode based on the investigated complex was studied as well. The maximum of his
absolute quantum yield 56 % was achieved for complex with the quantum efficiency of the corresponding OLED being 1%. These results can be employed in the design of the lanthanide complexes with highly efficient luminescence.

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