

# Photo- and electroluminescent properties europium complexes using bistriazole ligands

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## ABSTRACT

Luminescent properties of two heteroleptic dibenzoylmethanate europium(III) complexes with 1,3-bis(5-pyridin-2-yl-1,2,4-triazol-3-yl)propane ( $H_2L^1$ ) and 1,4-bis(5-pyridin-2-yl-1,2,4-triazol-3-yl)butane ( $H_2L^2$ ) as ancillary ligands are described. The two double-layer-type electroluminescent cells with the structures: (1) ITO/NPB(40 nm)/Eu(DBM)<sub>2</sub>HL<sup>1</sup> (40 nm)/LiF (1 nm)/Al (100 nm) and (2) ITO/NPB(40 nm)/Eu(DBM)<sub>2</sub>HL<sup>2</sup> (40 nm)/LiF (1 nm)/Al (100 nm) emit red light originating from the europium complexes. The device 2 gives the maximum brightness of 455 cd/m<sup>2</sup> at 19.2 V.

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## 1. Introduction

The search for new materials for organic light-emitting diodes (OLEDs) is one of the actual problems of both chemistry and materials science [1–3]. Despite the significant progress achieved in this field for the last decade, the production of brightness luminescent materials that can be used as active layers in OLEDs remains important. There are three main classes of luminophore that are most suitable for producing of electroluminescent devices: rigid organic molecules, d-metals complexes, and lanthanide complexes [1,4–6]. Until now first two classes are more popular as electroluminophore due to very high quantum efficiency of luminescence, high chemical stability and electronic conductivity. However, despite all the advantages, obtaining the luminescence spectrum with a small half-width at half-maximum remains an open issue for the phosphor of this type. In contrast lanthanide complexes with organic ligands can provide potential solutions for such issue due to the central lanthanide metal ions exhibit extremely sharp emission bands as results of their specific electronic structure. Unfortunately till now the most efficient Ln(III) phosphors doesn't show high

electroefficiency. One of the important reasons is the poor carrier transporting properties (especially electron-transporting) of these complexes [7]. Unbalanced injection and transport of charge carriers would cause their recombination at locations other than the emitting layer, leading to low OLEDs efficiency and reduced lifetime. There are two main approaches to improve carrier-transporting properties of the europium complexes. The first is doping europium complexes into polymers or small molecular compounds with high hole or electron mobility. The second one is grafting hole- or electron-transporting units on ligands. It is well known that 1,3,4-oxadiazole and 1,2,4-triazole derivatives are the most widely employed as electron-transporting and hole-blocking materials [8]. Several groups have been focused on the design and synthesis of oxadiazole-functionalized  $\beta$ -diketonate ligands and corresponding lanthanide complexes. The literature contains several interesting results which show the effectiveness of such direction of investigation for improving carrier transporting properties of Eu(III) complexes [9–11]. However, we could not find any mention about employing triazole derivatives as ligands for design luminescent europium complexes. Recently we reported about new pyridyltriazole ancillary ligands which effectively enhance photoluminescence of Eu(III) with respect to Eu(DBM)<sub>3</sub>·2H<sub>2</sub>O (HDBM – dibenzoylmethane) [12]. Here we give detailed description of photo- and electroluminescent properties of europium complexes based on bis(pyridyltriazolyl)alkanes and DBM<sup>−</sup> presented in Fig. 1.

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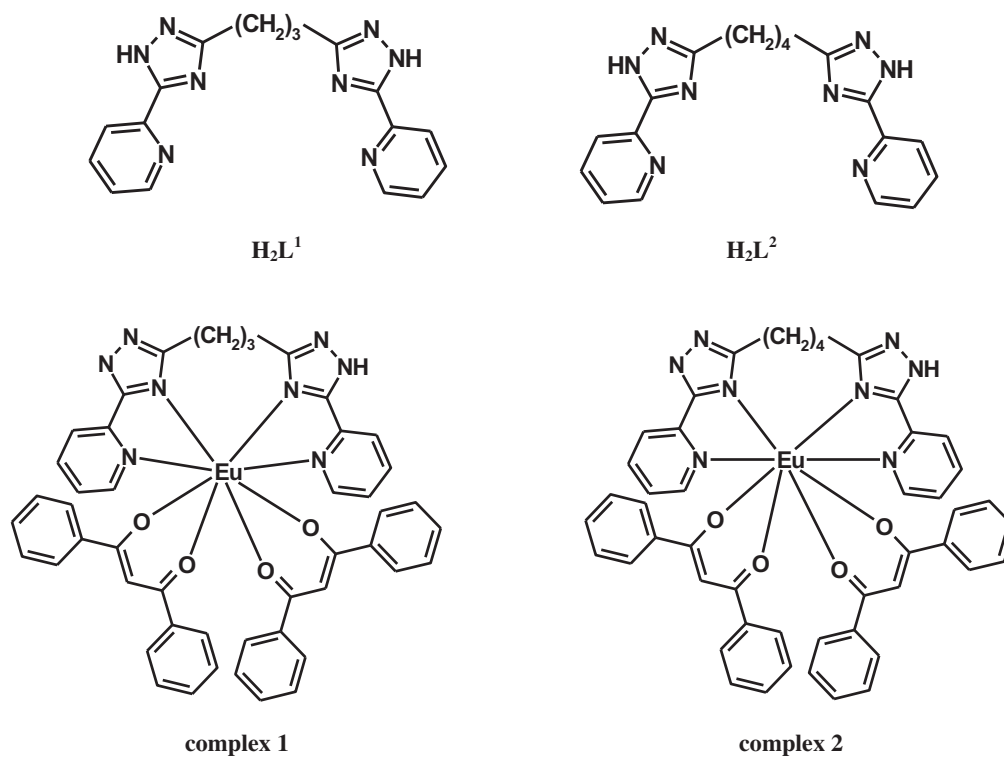


Fig. 1. Drawing of the bis(pyridyltriazolyl)alkanes and Eu complexes.

## 2. Experimental

### 2.1. General information and instrumentation

Chemicals and reagents were obtained from commercial sources, and used without further purification unless otherwise noted. Synthesis of title complexes (unsolvated form) and molecular structure of  $\text{Eu}(\text{DBM})_2 \cdot \text{HL}^1$  (as solvate with two benzene molecules) we described in our previous paper [12]. Absorption spectra were recorded on a Perkin-Elmer Lambda-9 UV/VIS/NIR spectrophotometer. Solid-state excitation and photoluminescence spectra were recorded on a Horiba Jobin-Yvon Fluorolog FL-3-22 spectrofluorometer equipped with a 450 W Xe lamp, quantum yields were determined under ligand excitation on the same instrument, and using absolute method using a home-modified integrating sphere. Lifetime measurements were performed on a Horiba Fluorocube lifetime instrument by a time-correlated single-photon counting method using a 365 nm LED excitation source. The current density–luminance–voltage characteristics of the OLEDs were measured by Keithley source measurement unit with a calibrated silicon photodiode. Electroluminescence spectra were taken by an multichannel S2000 Ocean Optics spectrometer. All measurements were carried out in ambient atmosphere at room temperature.

### 2.2. Fabrication OLED devices

The double-layer-type OLED devices with structure (1) ITO/NPB(40 nm)/ $\text{Eu}(\text{DBM})_2 \cdot \text{HL}^1$  (40 nm)/LiF (1 nm)/Al (100 nm) and (2) ITO/NPB(40 nm)/ $\text{Eu}(\text{DBM})_2 \cdot \text{HL}^2$  (40 nm)/LiF (1 nm)/Al (100 nm) were fabricated on glass substrates with 100 nm thickness ITO. *N'*-Diphenyl-*N*,*N'*-bis(1-naphthyl)(1,1'-biphenyl)-4,4'-diamine–NPB was used as hole-transporting materials. Organic layers were sequentially deposited at a rate in the range of 0.1–0.3 nm/s onto the substrates by high-vacuum ( $10^{-5}$  mbar)

thermal evaporation techniques. The shadow mask with 5 mm × 5 mm openings was used to define the cathodes. The evaporating speeds and thickness were monitored by quartz oscillators. All of the measurements were carried out in ambient atmosphere at room temperature after vacuum break.

## 3. Results and discussion

### 3.1. Photophysical properties

In our previous paper [12] we demonstrated only general features of the photoluminescence of europium complexes with  $\text{DBM}^-$  and  $\text{HL}^-$  anions with an indication possibility of using europium complexes with triazole ligands for creating electroluminescent cells. In this article we focused on detailed description of the opti-cophysical properties of title complexes and characterization of electroluminescent cells based on its.

It is well known that for high luminescence efficiency lanthanide–ligand pair should meet the following conditions, energy of the resonance level of Ln(III) should be lower than the energy of the triplet level ligands. To substantiate abilities of title bistriazoles to enhance luminescence of europium complexes the lowest triplet state energy level of the ligands were determined firstly. Phosphorescence spectra for solid samples of the Gd(III) complexes with the ligands  $\text{H}_2\text{L}^1$  and  $\text{H}_2\text{L}^2$  were measured at 77 K. Gd(III) complexes show broad phosphorescence with maximum at 433 and 435 nm for  $\text{H}_2\text{L}^1$  and  $\text{H}_2\text{L}^2$  complexes respectively. These data give the values of the triplet levels of ligands as 22,989 and 23,095  $\text{cm}^{-1}$  respectively. According to Latva's empirical rule, an optimal ligand-to-metal transfer process for Eu(III) needs energy gaps  $>2500 \text{ cm}^{-1}$  [13]; therefore, the ligand-to-metal transfer processes are effective for both ancillary triazole ligands. The most probable stepwise energy transfer from pyridyltriazole ligands to Dbm (20,400  $\text{cm}^{-1}$ ) and further the emitting level of the europium ion.

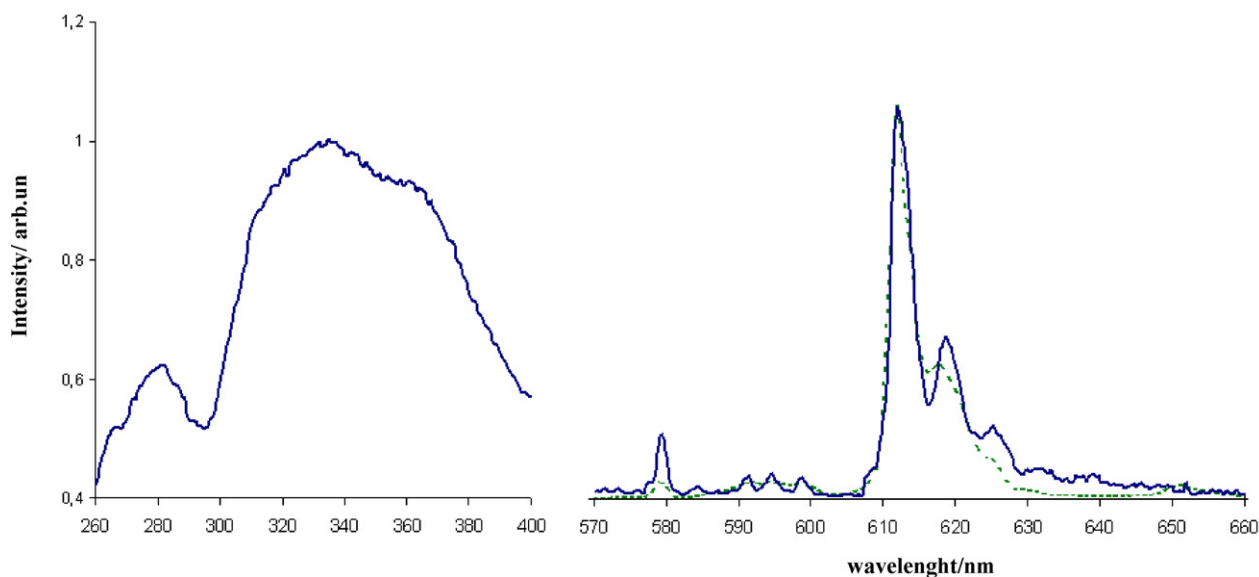


Fig. 2. Excitation (left) and emission spectra (right) of complex 1 in solid state (solid line) and in DMSO solution (dotted line) at 298 K.

Emission spectra for ligands  $H_2L^1$  and  $H_2L^2$  upon excitation at 250 nm show the one blue emission band centered at 403 and 452 nm respectively. The excitation spectra both of 1 and 2 in the solid state were measured in the range of 260–400 nm from the emission of the hypersensitive  $^5D_0 \rightarrow ^7F_2$  transition (HTS) at 612 nm. The excitation spectra showed two excitation bands: one is located at 268–296 nm mainly due to bistriazole ligands absorption, and another centered at 340 nm is very intense and is contributed by the  $DBM^-$  ligands. The excitation and emission spectra for the solids and DMSO solutions of complexes 1 and 2 are shown in Figs. 2 and 3.

For each of the two complexes the photoluminescence spectrum of the solid shows better resolved emission features than the solution, implying that the energy transfer from the anionic ligands to the Eu(III) is more efficient in the solid state than in solution. The profiles of the emission spectra of 1 and 2 are similar because the ligands coordinated to Eu(III) ion are in identical manner and the coordination surroundings of Eu(III) ion in 1 and 2 are also analogous.

The luminescence spectra display typical pattern of europium  $^5D_0 \rightarrow ^7F_j$  ( $J = 1-4$ ) emissive transitions with the most prominent band at 612 nm assigned to the  $^5D_0 \rightarrow ^7F_2$  hypersensitive transition. It is well known that the electronic dipole transition  $^5D_0 \rightarrow ^7F_2$  is sensitive to the symmetry of the coordination environment [14]. It is clearly see from Figs. 2 and 3 that HTS band are extremely split on several components centered at 612, 619 and 624 nm. Only one sharp band of symmetry-forbidden emission of  $^5D_0 \rightarrow ^7F_0$  at 580 nm and three Stark components ( $2J+1$ ) for the  $^5D_0 \rightarrow ^7F_1$  transition are observed. The resulting features of the luminescence spectra indicate that there is only one symmetry site of the Eu(III) ions which is consistent with the crystal structure analyses [12].

For evaluating the efficiency of the luminescence of the complexes quantum yield of luminescence was measured. The solid state absolute quantum yields of the complexes 1 and 2 were found to be 29.7% and 32.1% respectively. The quantum yield in solution [12] is slightly less than the calculated quantum in solid state. Such differences may be associated with different polymethylene chain mobility in the crystal and in solution. Greater mobility in

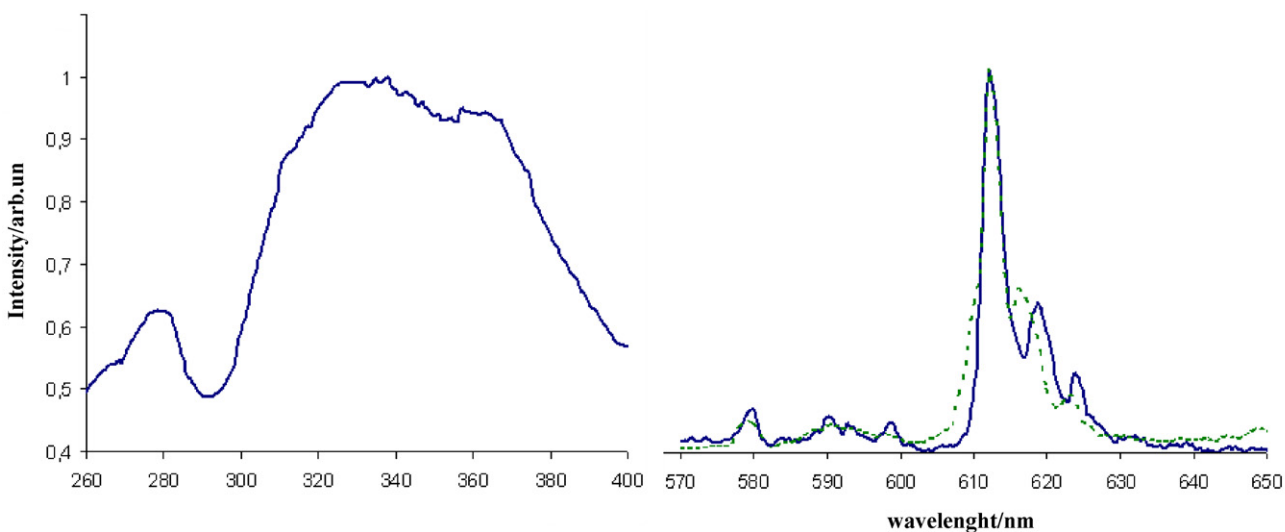


Fig. 3. Excitation (left) and emission spectra (right) of complex 2 in solid state (solid line) and in DMSO solution (dotted line) at 298 K.

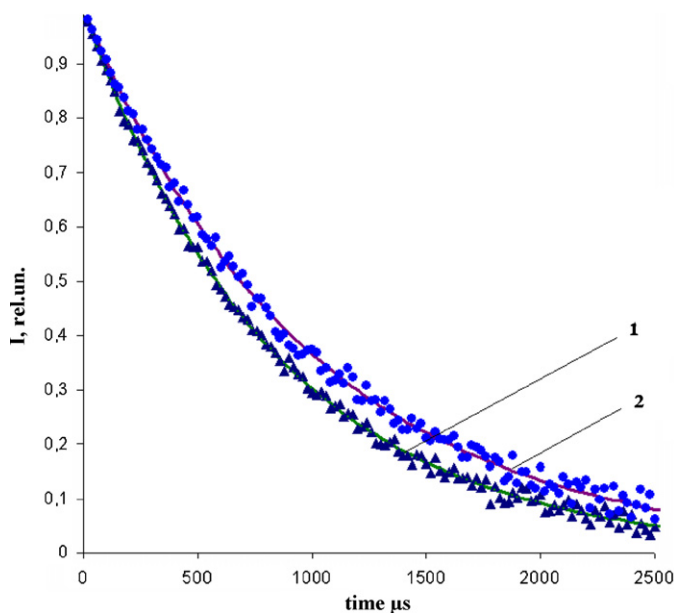


Fig. 4. Photoluminescence lifetime decay measurement of 1 and 2 in solid state 298 K (experimental and best-fit line).

solution leads to an increase in nonradiative energy losses and reduce the quantum yield. High photoluminescence enhancement might also be due to low symmetry of the coordination sphere around the Eu(III) complex, which makes f–f transitions more allowed.

Luminescence lifetimes of solid samples were investigated for both Eu(III) complexes. Luminescence decay curves were obtained at 298 K by monitoring the  $^5D_0 \rightarrow ^7F_2$  transition (612 nm) and are depicted in Fig. 4. Decay curves for the both complexes could be good fitted with a single exponential, indicating only one chemical microenvironment around where the Eu(III) ion existed [15] and it was in agreement with the result of only one  $^5D_0 \rightarrow ^7F_0$  line in the emission spectrum. The lifetime values were found to be 837 and 995  $\mu\text{s}$  for 1 and 2, respectively. This value are much longer than the previously reported value (318  $\mu\text{s}$ ) Eu(DBM)<sub>3</sub>Phen [16]. Quite long lifetime of title complexes is consistent with the good shield the Eu(III) ion from coordination of solvating molecules, which prevents a potential non-radiative decay path.

### 3.2. Electroluminescent properties

Investigation of photoluminescence of Eu(III) complexes 1 and 2 have shown high efficiency in the solid state. It is known that there is a correlation between the intensity of luminescence in powders and thin films of OLED device, so title complexes are good candidates for creating electroluminescent diodes.

Considering the low electronic conductivity of coordination compounds of lanthanides emitting layer in the OLED is usually located between two additional layers with electron- and hole-conductivity respectively. Pyridyltriazole derivatives established themselves as excellent materials with electron transport properties [17]. The presence of pyridyltriazole fragment in the structure of the title complexes is expected to increase allows the electronic conductivity of the compounds and eliminates the need to use one of the additional layers in the OLED. We created two double-layer-type electroluminescent cell 1-ITO/NPB(40 nm)/Eu(DBM)<sub>2</sub>-HL<sup>1</sup> (40 nm)/LiF (1 nm)/Al (100 nm) and 2-ITO/NPB(40 nm)/Eu(DBM)<sub>2</sub>-HL<sup>2</sup> (40 nm)/LiF (1 nm)/Al (100 nm) with only hole-transporting additional layer. Fig. 5 shows the EL spectra of the resulting device 2 at 16 V.

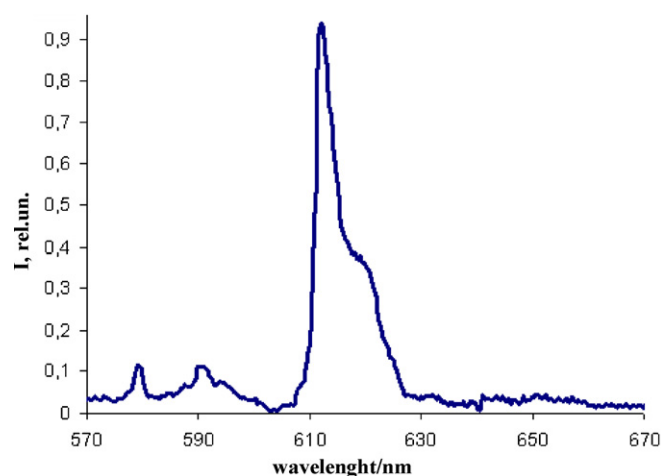


Fig. 5. Electroluminescence of complex 2 at 16 V.

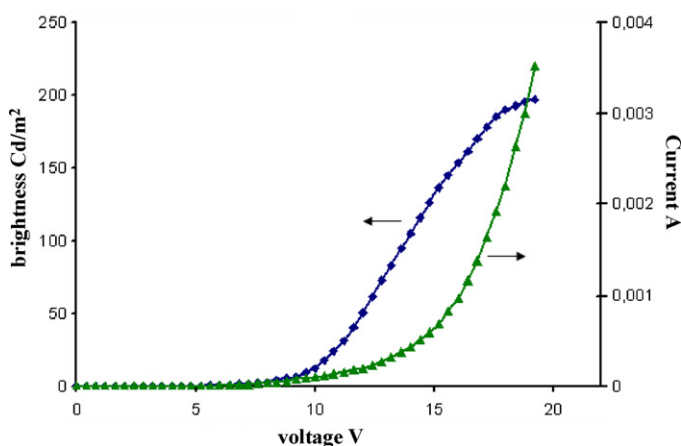


Fig. 6. Current density–voltage–luminescence characteristics of OLED devices 1.

It can be seen that the EL spectrum is identical to the photoluminescent spectrum, indicating that the electroluminescent emission at 612 nm originates from the Eu(III) ion in compound. The luminescence–current density–voltage characteristics of a double-layer-type EL cells 1 and 2 are shown in Figs. 6 and 7 respectively.

It shows that the luminescence increases with increasing injection current as well as bias voltage. Pure red emission was observed

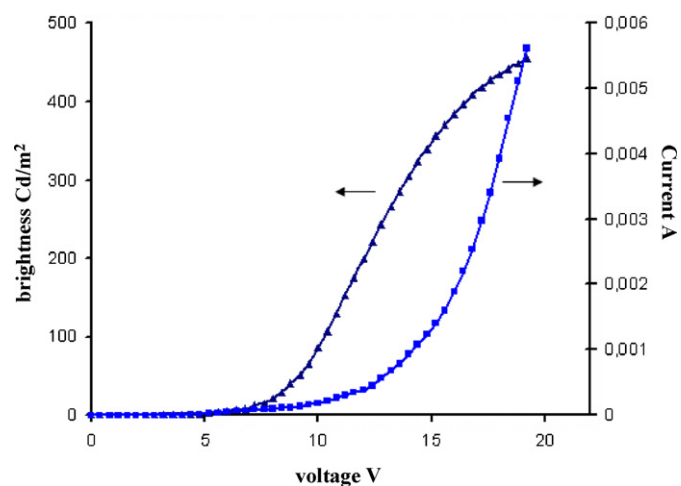


Fig. 7. Current density–voltage–luminescence characteristics of OLED devices 2.

at as low as 7.2 V for both cells. The maximum brightness of the double-layer EL cell 1 is about 197 cd/m<sup>2</sup> at a driving voltage of 19.2 V and cell 2 is about 455 at same voltage. The higher efficiency of the cell 2 may be associated with better film-forming properties of complex 2 due to the longer aliphatic spacer.

#### 4. Conclusions

In this article we described optophysical properties of europium(III) complex with an electron-transporting pyridyltriazole moiety including excitation and emission spectra, lifetime and quantum yield are described. The factors determining the high intensity of the luminescence are studied among them the optimal value of the triplet level of the ligand, symmetry of the nearest environment of europium ion, good shielding ability of triazole ligands. Two new double-layer OLED cells were fabricated. It is shown that the using of coordination compounds of europium with pyridyltriazole derivatives allows creating efficient OLED cells without electron-transport layers.

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