

LUMINESCENT THIN FILMS BASED ON N-(DIPHENYLPHOSPHORYL)BENZAMIDE Eu^{III} AND Tb^{III} COMPLEXES FOR LIGHT EMITTING DIODE TECHNOLOGY

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Abstract. A series of lanthanide coordination compounds LnL_3 , LnL_3Phen , and LnL_3Dipy with aryl-functionalised carbacylamidophosphate (CAPH) ligand N-(diphenylphosphoryl)benzamide ($\text{HL} = \text{PhC}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{Ph}_2$) were synthesized for luminescent thin films producing. The bulky organic ligands provide a hydrophobic shell around Ln^{III} ion leading to highly luminescent terbium and europium complexes with long-lived emission. The thin films of the complexes were obtained by spin coating and, for the first time, by vacuum evaporation. The films exhibit an intensive monochromatic photoemission with decay times equal to 0.78-1.34 ms.

Keywords: lanthanide complex, photoluminescence, carbacylamidophosphate, chelate ligand, thin film.

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Introduction

Lanthanide photoluminescent complexes attract a growing interest due to their potential role as spectroscopic probes [1,2], materials for LED technology [3,4], medical diagnostics [5] and lasing systems [6]. For light-conversion systems based on Ln^{III} ions, the main requirements are high ligand absorption coefficients, efficient ligand-to-metal energy transfer and minimal non-radiative deactivation of the excited state of metal-ion. To satisfy these criteria, two strategies can be used. The first strategy presents the encapsulation of the Ln^{III} ion by a polydentate/macrocyclic ligand (e.g. cryptands [7], calixarenes [8,9], polyaminopolycarboxylic acids [10] and podands [11]), while the second strategy consists in the saturation of the metal coordination sphere by combining mono- and bidentate ligands containing bulky aromatic units. Both strategies aim to provide the stable complexes with rigid environments of metal ion and without coordinated solvent molecules.

In the present work, we have used the second approach, which excludes the multi-step synthesis of a macrocyclic ligand and it is commonly used in coordination chemistry of

β -diketones and their structural analogues. Heretofore, the main research concerned the lanthanide β -diketonate complexes, which are limited in terms of practical applications due to their poor photo and electro stability [12]. Recently, as an alternative to these complexes, lanthanide imidodiphosphinate complexes have been studied for LED producing [13,14]. In contrast to the lanthanide β -diketonates, where the binding site of each ligand is surrounded by two aryl units, the lanthanide imidodiphosphinates (Figure 1(a)) have four aryl units per ligand and can collect more light. Compared to the lanthanide β -diketonates, the longer emission lifetimes observed for lanthanide imidodiphosphinates resulted from the absence of C-H bonds in the binding site and from a better protection of the metal ion from the solvents [15-18]. For the last two decades, the luminescent properties of complexes with other types of β -diketones analogues such as carbacylamidophosphates (CAPH) (Figure 1(b)) and sulfonylamidophosphates (SAPH) (Figure 1(c)) have been extensively studied [19] and a rather long-lived bright emission was observed for *tetrakis*- and *tris*-complexes with general formulas

KatLnL₄ [20-22], LnL₃Phen, LnL₃Dipy, and LnL₃*i*-prOH [23-25].

Herein, we report the synthesis and study of new CAPH based LnL₃ complexes as well as the investigation of luminescent thin films of lanthanide *tris*-complexes based on N-(diphenylphosphoryl)benzamide (HL) obtained by vacuum evaporation and spin coating. The chosen ligand contains three aromatic units

and has a more asymmetric structure in comparison to dibenzoylmethane and tetraphenyl imidodiphosphinate that can lead to increasing of 4*f*-luminescence intensity in complexes due to the increase of anisotropy around the europium ion [26]. Additionally, bulky chelating ligands have been successfully used to improve the volatility of lanthanide *tris*-complexes [27].

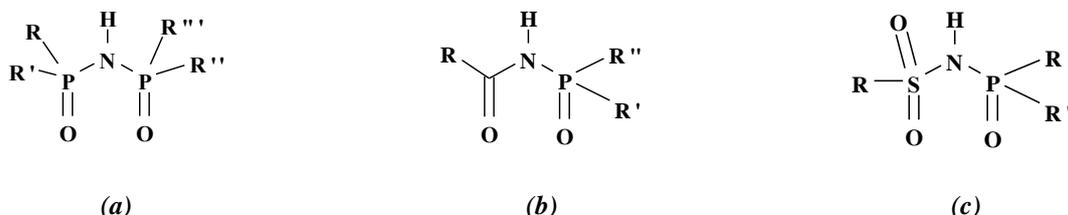


Figure 1. General formulas of imidodiphosphinates (a), carbacylamidophosphates (b) and sulfonylamidophosphates (c).

Experimental

Synthesis

All reagents and solvents were used of commercial grade without further purification.

N-(diphenylphosphoryl)benzamide (HL) was synthesized according to the procedure described previously [28]. NaL was obtained by replacement reaction between NaOMe and HL in methanol with a yield equal to 95%. The identification of the ligand and NaL was performed by measuring melting points, IR and NMR spectra, which were in agreement with literature data [23].

The synthesis of LnL₃Dipy and LnL₃Phen complexes was reported by us earlier [23]. The complexes LnL₃ (Ln= Eu, Tb, Lu) were synthesized according to the procedure described in [15,29]. The water solution of Ln(NO₃)₃.nH₂O was added dropwise to a solution of NaL (3 mmol) in H₂O/MeOH mixture (5:1, v/v). The solid that immediately precipitated was filtered off, washed with distilled water several times and dried in a desiccator over concentrated sulphuric acid. For further purification, the dry product was dissolved in CH₂Cl₂ resulting in a slightly opalescent solution, which then was filtered out and completely dried under vacuum. The yield was equal to ~80%.

$C_{57}H_{45}N_3O_6P_3Eu$ (M= 1113.17). Anal. calc.: Eu, 13.7; C, 61.44; H, 4.07; N, 3.77%. Found: Eu, 13.6; C, 60.97; H, 4.31; N, 3.69%. FT-IR (KBr, cm⁻¹): 3057 [w, ν(CH)], 1591 [w, ν(CC)], 1507 [vs, ν(C=O)], 1438 [s, ν(CC)], 1383 [vs, ν(Amide2)], 1178 m, 1128 [vs, ν(P=O)],

1083 w, 1066 w, 910 [w, ν(PN)], 727 s, 696 s, 548 s.

$C_{57}H_{45}N_3O_6P_3Tb$ (M= 1119.18). Anal. calc.: Tb, 14.2; C, 61.11; H, 4.05; N, 3.75%. Found: Tb, 14.2; C, 60.92; H, 4.12; N, 3.58%. FT-IR (KBr, cm⁻¹): 3056 [w, ν(CH)], 1591 [w, ν(CC)], 1508 [vs, ν(C=O)], 1437 [s, ν(CC)], 1386 [vs, ν(Amide2)], 1179 m, 1130 [vs, ν(P=O)], 1084 w, 1063 w, 9010 [w, ν(PN)], 727 s, 693 s, 548 s.

$C_{57}H_{45}N_3O_6P_3Lu$ (M= 1135.19). Anal. calc.: Lu, 15.4; C, 60.25; H, 3.99; N, 3.70%. Found: Lu, 14.9; C, 59.98; H, 4.09; N, 3.55%. FT-IR (KBr, cm⁻¹): 3058 [w, ν(CH)], 1591 [w, ν(CC)], 1510 [vs, ν(C=O)], 1438 [s, ν(CC)], 1387 [vs, ν(Amide2)], 1180 m, 1129 [vs, ν(P=O)], 1085 w sh, 1066 w, 912 [w, ν(PN)], 728 s, 694 s, 550 s. ¹H NMR (CDCl₃): δ 7.19 (m, 18 H), 7.33 (m, 9 H), 7.79 (m, 12 H), 7.99 (d, 6H).

The obtained *tris*-complexes are soluble in dimethyl sulfoxide, acetone, CH₂Cl₂, methanol, benzene, less soluble in 2-propanol and insoluble in water. The PXRD of the compounds LnL₃ reveal their amorphous nature. Melting point of the obtained *tris*-complexes was observed in the temperature range 110–140°C.

Characterization

IR measurements were performed on a Perkin–Elmer Spectrum BX spectrometer on samples in the form of KBr pellets with resolution of 2 cm⁻¹ and accumulations of 8 scans, which were combined to average out random absorption artefacts in the spectral range 4000–400 cm⁻¹.

¹H NMR spectra in DMSO-*d*₆ solutions were recorded on an AVANCE 400 Bruker NMR spectrometer at room temperature.

The thermal stability of the complexes was determined in air up to 400°C with a heating rate of 10°C·min⁻¹ using simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) analyser Shimadzu DTG-60H. The crystalline powder of α -Al₂O₃ was used as standard for comparison.

The evaporation experiments under vacuum were carried out in the following conditions: sample weight – 10–20 mg, heating time – 30 min, pressure – 0.001–1 Pa, and temperature – 115–240°C. The obtained thin films were studied by IR and luminescence spectroscopy.

Emission and excitation spectra of the complexes and their thin films were recorded using the Fluorolog FL 3-22 spectrofluorimeter at 298 K. The energy of the lowest triplet state of the coordinated CAPH ligands was determined based on the phosphorescence spectrum of LuL₃ complex solution in acetonitrile at 77 K. The *f*-luminescence lifetime measurements were carried out at room temperature using the FL-1040 Horiba Jobin Yvon phosphorimeter accessory for the Fluorolog 3-22 instrument (pulsed Xe–Hg arc lamp, 3 μ s bandwidth).

Quantum yield (Q) measurements for the solid europium complex were carried out according to the method developed by Brill, A. *et al.* [30,31] and described in details elsewhere [32]. The Y₂O₃:Eu 3% (Q_{st} = 85%, λ_{exc} = 254 nm) and (Y,Gd)BO₃:Eu (Q_{st} = 77%, λ_{exc} = 254 nm) [33] were used as emission standards. A cross-reference experiment was performed to estimate the accuracy of measurements, which was found to be 15%.

Results and discussion

Thermogravimetric analysis

The TG curves for europium and terbium complexes are similar to each other. According to the TG curves (Figures 2 and 3), the compounds EuL₃ and TbL₃ are stable up to 180 and 185°C, respectively. The absence of any weight losses up to the mentioned temperature suggests the absence of any solvents in the composition of the complexes. The DTA curves exhibit endothermic maximum at ~80 °C. Considering the absence of any weight losses at this temperature, the observed endothermic process can be assigned to a phase transition. Being heated above 180°C, the complexes decompose abruptly with a weight loss of about 28%. Upon further heating, a smooth decomposition of the complexes was observed and the mass of the sample did not reach a constant value at the boundary value of the

experimental temperature. According to the IR spectra and the calculated metal content of residues of the complexes after their heating up to 400°C, the thermal decomposition of the complexes is an endothermic removal of PhCN due to the destruction of organic ligands.

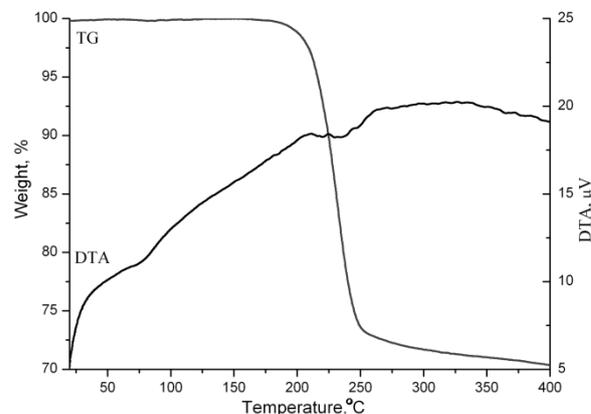


Figure 2. Thermogravimetric (TG) and differential thermal analysis (DTA) of EuL₃.

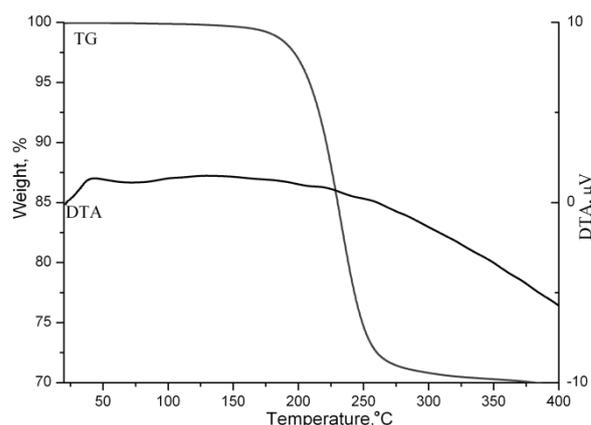


Figure 3. Thermogravimetric (TG) and differential thermal analysis (DTA) of TbL₃.

IR spectroscopy

The IR spectra of synthesized coordination compounds LnL₃ look similar to each other and reveal the CAPH-ligands coordination to lanthanide ions in deprotonated form in bidentate chelating manner (Figure 4). The ν (NH) and ν (CH) absorption bands in the IR spectra of obtained compounds overlap, however the deprotonation of N-(diphenylphosphoryl) benzamide in NaL and lanthanide complexes was suggested, due to a significant decrease of band intensity in the region of 3100–3200 cm⁻¹ in their IR spectra compared with that in the HL spectrum. This result is also in agreement with the ¹H NMR spectra of NaL and LuL₃ compounds, where no signal of amide hydrogen was observed. The bidentate chelating

coordination manner of the ligands is confirmed by low frequency shifts of $\nu(\text{P}=\text{O})$ and $\nu(\text{C}=\text{O})$ absorption bands in the IR spectra of the complexes compared with the free HL spectrum ($\Delta\nu_{\text{HL}}(\text{P}=\text{O})\sim 70\text{ cm}^{-1}$, $\Delta\nu_{\text{HL}}(\text{C}=\text{O})\sim 160\text{ cm}^{-1}$). Such shifts are typical for the CAPH based lanthanides coordination compounds and caused by PO and CO bonds order decrease due to the presence of π -conjugation in the chelate fragment [34-36].

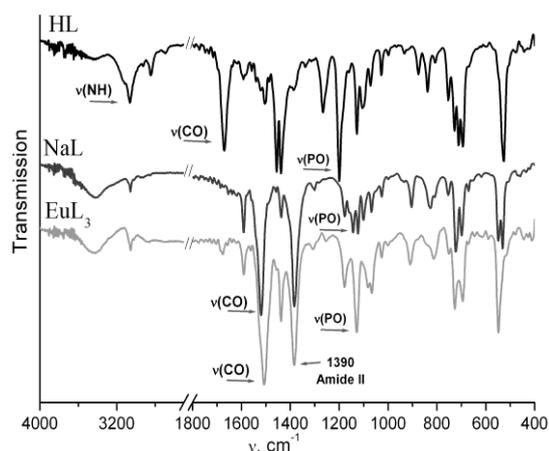


Figure 4. IR spectra of HL, NaL and EuL_3 .

Photoluminescence studies

The solid-state excitation and emission spectra of Eu^{III} and Tb^{III} *tris*-complexes are shown in Figures 5 and 6. The excitation spectra were recorded by monitoring the emission intensity of the $^5\text{D}_0\rightarrow^7\text{F}_2$ and $^5\text{D}_4\rightarrow^7\text{F}_5$ transitions, respectively. The excitation spectra are dominated by the broad band in the range of 250–330 nm arising from the absorption transitions to the ligand singlet states, thus confirming the efficient sensitization of lanthanide-centered emission by organic ligands.

The energy of the lowest ligand triplet state (E_{T}) for the complexes under study was determined as 26110 cm^{-1} on the basis of zero-phonon line maximum position in the phosphorescence spectrum of LuL_3 complex. The E_{T} is high enough to exclude back energy transfer from metal to ligand in case of europium and terbium complexes.

Being excited into the ligand singlet state at 277 nm, the europium and terbium complexes showed characteristic emission with narrow bands (Figures 5 and 6, respectively) corresponding to $^5\text{D}_0\rightarrow^7\text{F}_J$ ($J=0-4$) transitions of Eu^{III} and to $^5\text{D}_4\rightarrow^7\text{F}_J$ ($J=6-3$) transitions of Tb^{III} , respectively. The assumption regarding the low-symmetry of the coordination environment for europium can be confirmed by the presence of the $^5\text{D}_0\rightarrow^7\text{F}_0$ transition band in the emission spectrum,

as well as by the relatively high value of the $^5\text{D}_0\rightarrow^7\text{F}_2/^5\text{D}_0\rightarrow^7\text{F}_1$ transitions bands intensity ratio (red/orange ratio), which equals to 12.5 at 298 K. The determined value of red/orange ratio is higher compared to other CAPH based Eu^{III} complexes [20,23,25,37] and it is comparable with the ones for *tris*-(β -diketonate) europium complexes with an asymmetric coordination sphere which have red/orange ratios ranging from 6.6 to 27 [38].

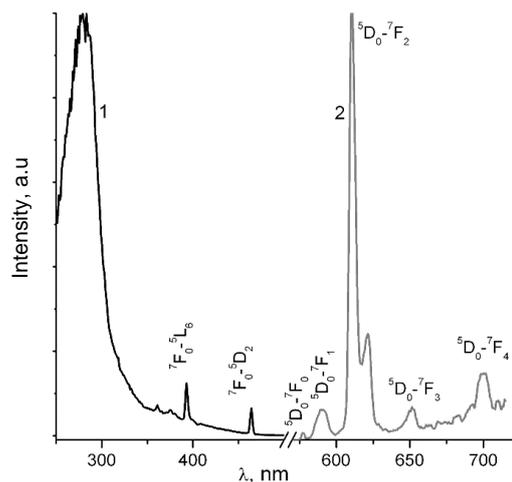


Figure 5. Excitation (1) and emission (2) spectra of EuL_3 recorded at room temperature.

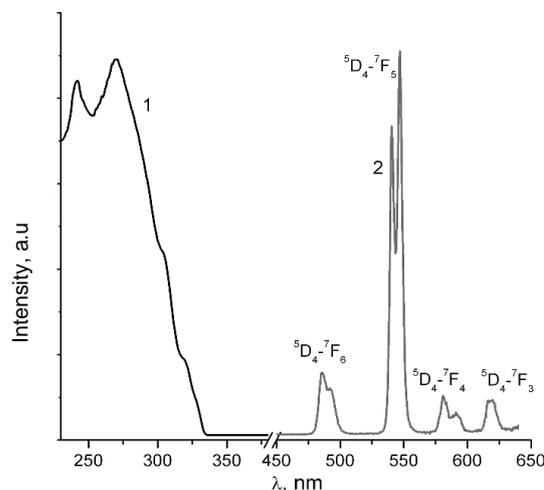


Figure 6. Excitation (1) and emission (2) spectra of TbL_3 recorded at room temperature.

Emission lifetimes of Eu^{III} and Tb^{III} complexes at room temperature were determined by monitoring the emission within the maximum of $^5\text{D}_0\rightarrow^7\text{F}_2$ and $^5\text{D}_4\rightarrow^7\text{F}_5$ transitions, respectively, and exciting into the ligand absorption band. The decay curves can be best fitted by a single-exponential function and yield lifetimes of 1.39 and 1.71 ms for europium and terbium complexes, respectively. The $^5\text{D}_0$ overall emission quantum yield for the solid europium complex was found to be 31%.

The low electro activity of Eu^{3+} complexes is often reported as one of the drawbacks associated with their unsatisfactory electroluminescence performance [4]. Due to this, one of the approaches for successful application of lanthanide complexes in LED technology is blending the complexes with a blue emitting electroluminescent polymer. It is suggested that the light emitted by the polymer can be absorbed by ligands and transferred to the metal ion. Thus, only visible light absorbing complexes can be used in this approach. To shift the absorption of the EuL_3 complex to lower energies, we used a Michler's ketone (MK) co-ligand, which is known for its n, π^* triplet state with a large quantum yield, as well as a small singlet-triplet energy gap [39]. Previously, this co-ligand was successfully used to obtain the visible light excited europium emission from ternary Eu^{III} β -diketonates [40]. It has been shown that MK allows increasing the efficiency of energy transfer from the polymer to the complex in LEDs due to a good overlap between the emission spectra of the electroluminescent polymer and MK absorbance [41,42]. Lanthanide complexes with visible light excited emission may also be of interest for luminescent label production in time-resolved fluorescence microscopy, since visible light is less harmful for biological tissues.

The excitation spectra of the EuL_3 complex solution (10^{-4} M) in toluene (Figure 7, curve 1) and the complex mixtures with MK (Figure 7, curves 2–4) were recorded by monitoring the emission within the maximum of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. The band with a maximum approximately at 290 nm in the excitation spectrum for the EuL_3 complex in toluene solution appeared from the absorption transitions to the N-(diphenylphosphoryl)benzamide singlet states. The addition of MK to the europium complex solution led to a decrease of the intensity of the mentioned band in the UV region and to the appearance of a new broad band in the region 375–450 nm (Figure 7, curves 2–4) caused by MK sensitization of Eu^{III} emission. The intensity of europium centered luminescence increased proportionally to MK concentration in the solution up to a ratio of 1:5 between the complex and MK. Further increasing of MK concentration did not affect the intensity of europium luminescence. The resulted mixture of the europium complex with MK was spin-coated on the glass, with the formation of a uniform transparent yellow film, which exhibited bright red Eu^{III} -centered photoluminescence under broadband excitation. The emission decay time

was determined by monitoring the emission within the maximum of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition and by excitation at 360 nm. The decay curve was fitted by a single-exponential function. The lifetime was found to be 0.78 ms. The broad band in the region of 300–450 nm in the excitation spectrum of the film (Figure 8, curve 1) was assigned to MK sensitization of Eu emission. The data confirm that the energy transfer from MK to Eu^{III} ion is efficient in solid state, as well. Europium emission sensitized by CAPH ligands was also observed for the obtained luminescent film; its intensity, however, was 1.5 folds lower compared to MK sensitized one.

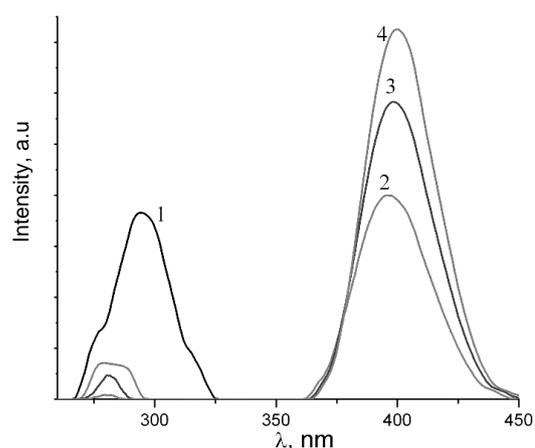


Figure 7. Excitation spectra of EuL_3 (1) and its mixtures with MK: EuL_3 :MK = 1:1 (2); 1:2 (3); 1:3 (4) in toluene solution.

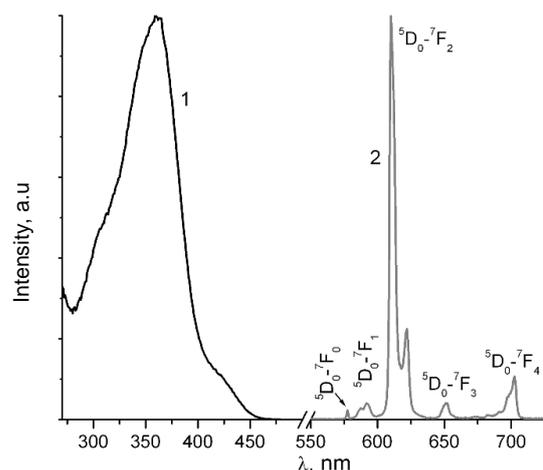


Figure 8. Excitation (1) and emission (2) spectra of the spin-coated film of the mixture EuL_3 :MK = 1:5.

Vacuum evaporation is the most frequently used type of layering in the LED technology, but the possibility of vacuum evaporation of CAPH based coordination compounds has not been studied yet. Considering the rather wide temperature region of the liquid state of the obtained terbium *tris*-complex TbL_3

(m.p.= 138°C and decomposition temperature is 185°C), three different vacuum evaporation conditions were applied. Attempts to obtain films by evaporation at approximately 0.01 Pa and 115°C or at 1 Pa and 170°C have been ineffective. A green-emitting film of the complex was obtained under vacuum evaporation at 0.1 Pa and 170°C. According to the IR spectrum (Figure 9, curve 2), the obtained film contained the terbium complex with N-(diphenylphosphoryl)benzamide coordinated in bidentate chelating manner. The non-evaporated complex residue also exhibited green emission, however, its IR spectrum (Figure 9, curve 3) corresponded to terbium diphenylphosphinate ($(C_{12}H_{10}O_2P)_3Tb$) formed during TbL_3 decomposition, as it was shown in TG analyses. It should be noted that this very low degree of evaporation can be explained by the aggregation of *tris*-complex molecules similar to lanthanide *tris*-acetylacetonates [43] that later was shown to be a reason of their low evaporation degree compared to compounds $Ln(acac)_3Q$ with a saturated lanthanide coordination sphere [44].

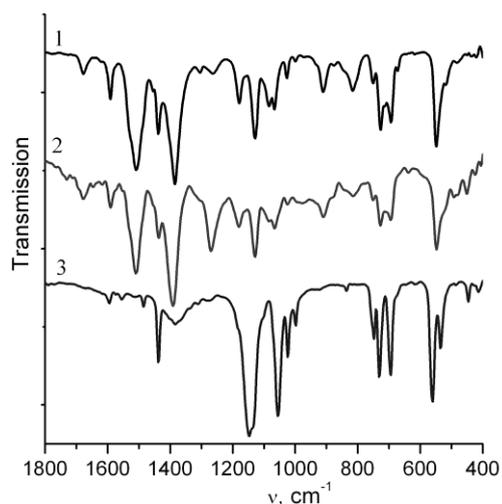


Figure 9. IR spectra of TbL_3 : the initial complex (1), sublimated film (2) and residue (3).

Considering the possible aggregation of complexes with unsaturated Ln^{III} coordination sphere, we expanded our study to vacuum evaporation of complexes LnL_3Dipy and LnL_3Phen [23]. Similar to TbL_3 , vacuum evaporation of EuL_3Dipy at 0.01 Pa and 115°C was ineffective. A red-luminescent film of EuL_3Dipy complex was obtained under vacuum evaporation at 0.1 Pa and 230°C. Vacuum evaporation of EuL_3Phen was successful at 0.01 Pa and 180°C. According to the IR spectrum (Figure 10, curve 2), the obtained film of EuL_3Phen compound contained europium complex with N-(diphenylphosphoryl)benzamide

coordinated in bidentate chelating manner. The IR spectrum of non-evaporated residue of EuL_3Phen compound (Figure 10, curve 3) reveals the initial complexes decomposition. The IR spectra recorded for the film and the residue of EuL_3Dipy complex are similar to those obtained for EuL_3Phen .

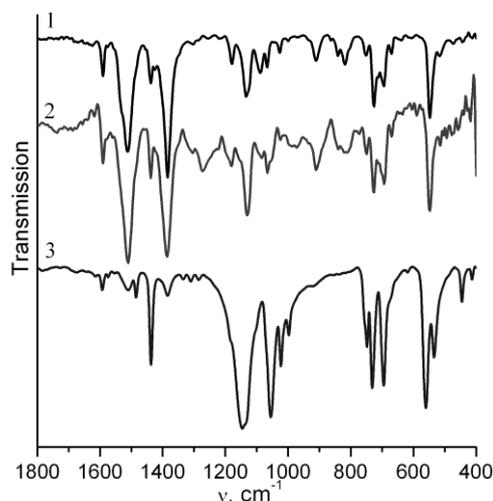


Figure 10. IR spectra of EuL_3Phen : the initial complex (1), sublimated film (2) and residue (3).

The emission spectra of EuL_3Dipy , and EuL_3Phen complexes, and their films were measured at 298 K upon excitation into the ligand singlet state (Figures 11 and 12). The identical emission spectra obtained for solid complexes and films reveal the similar coordination environment of europium ions in the studied materials.

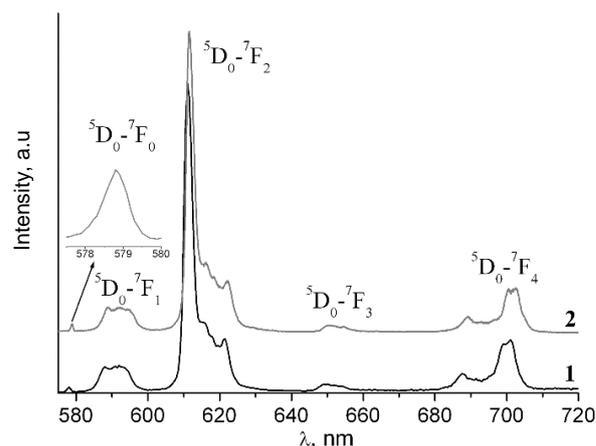


Figure 11. Luminescent spectra of EuL_3Dipy : solid sample (1) and film (2) recorded at 298 K.

Luminescence decay time for the films of EuL_3Dipy and EuL_3Phen complexes, measured at 300 K by excitation at 310 and 300 nm, respectively, can be fitted by a three exponential function giving values τ_1 , τ_2 , and τ_3 (Table 1). The longest component τ_3 corresponds to about 70% of

the total emission, while the shortest components have a few percent of participation in the total emission. In each case, the τ_3 value is in agreement with the luminescence decay time of EuL_3Dipy and EuL_3Phen initial complexes, while τ_1 and τ_2 can be assigned to other luminescent europium centers formed during the decomposition of complexes.

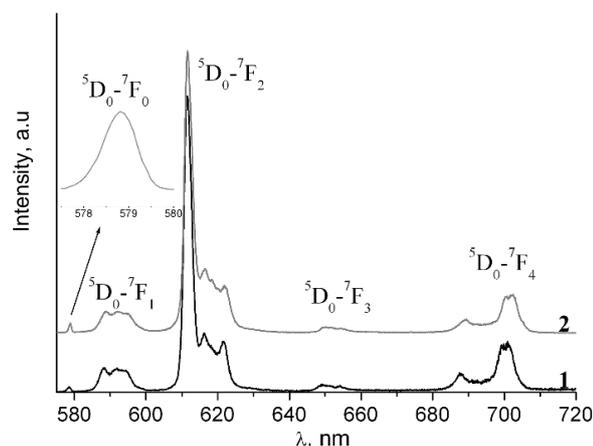


Figure 12. Luminescent spectra of EuL_3Phen : solid sample (1) and film (2) recorded at 298 K.

Table 1

Luminescence decay time for the films of EuL_3Dipy and EuL_3Phen complexes.

Compound	λ_{exc} , nm	$\tau_1/\tau_2/\tau_3$, μs (at 300 K)
EuL_3Dipy	310	106 / 638 / 1342
EuL_3Phen	300	173 / 659 / 1277

Conclusions

In this study we have demonstrated that the assembly of three aryl containing CAPH ligands around lanthanide ions leads to the formation of thermally stable complexes LnL_3 with bright luminescence. The Eu^{III} and Tb^{III} luminescence in the complexes is efficiently sensitized by N-(diphenylphosphoryl)benzamide and characterized by decay times equal to 1.39 and 1.71 ms, respectively. It was shown that the photoluminescence intensity of the obtained EuL_3 complex in toluene solution can be enhanced by adding the Michler's ketone co-ligand. Spin coating of EuL_3 and MK mixture solution results in the formation of red emitting uniform transparent films with Eu^{III} emission excited by blue light. The possibility of vacuum evaporation of CAPH based lanthanide coordination compounds with the formation of thin luminescent films was demonstrated for the first time. The obtained films were multicomponent, with the initial complexes prevailing in their composition. Thus, simple synthesis of the complexes, their intense emission and rather high

thermal stability, as well as the possibility of luminescent thin films formation make them promising emitting materials for LED technology.

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