



## Study of thermal and optical properties of dibenzoylmethane Eu(III) organic complexes

Ilze Malina<sup>\*</sup>, Nikolajs Juhnevics, and Valdis Kampars

Institute of Applied Chemistry, Riga Technical University, Paula Valdena Str. 3, Riga, LV-1048, Latvia

Received 28 April 2017, revised 14 July 2017, accepted 21 August 2017, available online 30 November 2017

© 2017 Authors. This is an Open Access article distributed under the terms and conditions of the Creative Commons Attribution-NonCommercial 4.0 International License (<http://creativecommons.org/licenses/by-nc/4.0/>).

**Abstract.** Two Europium(III) organic complexes (*ternary* complex  $\text{Eu}(\text{DBM})_3(\text{PHEN})$  and *tetrakis* complex  $[\text{Eu}(\text{DBM})_4]\text{N}(\text{Et})_4$ , where DBM is dibenzoylmethane and PHEN is 1,10-phenantroline) were synthesized and their structures proven with  $^1\text{H-NMR}$  spectroscopy, elemental analysis, FT-IR and mass spectroscopy. Their photophysical properties have been investigated in solution, solid-state and in poly-*N*-vinylcarbazole (PVK) films varying complex composition from 1 to 15 wt%. Both complexes exhibit intense UV light absorption and bright red-light emission with maximum wave length at 612 nm. It was shown that *tetrakis* complex in solution, solid-state and PVK films have enhanced photoluminescence properties compared to *ternary* complex due to four DBM molecules in  $\text{Eu}^{3+}$  coordination sphere, which leads to more effective excited energy transfer to  $\text{Eu}^{3+}$  ion. In THF solutions both complexes are characterized with low photoluminescence quantum yields (4% and 6%), in PVK films – moderate quantum yields (14–48%), but in solid state with high quantum yields (56% and 75%). Thermal properties for pure complexes and their PVK films were studied with thermogravimetric analysis. Both complexes exhibit high thermal degradation temperatures of 304 °C for *ternary* and 267 °C for *tetrakis* complex, but their PVK films show even higher degradation temperature (over 370 °C).

**Key words:** optical materials, europium, dibenzoylmethane ligands, luminescence, Poly-*N*-vinylcarbazole films.

### 1. INTRODUCTION

Unique optical properties such as narrow emission bands, high photoluminescence quantum yields, large Stokes shifts and long excited state lifetimes mark out  $\text{Eu}^{3+}$  organic complexes among other organic red-light emitting materials for technological application in solid-state lighting and flat panel displays [1]. Luminescence of complexes arises from efficient excited energy transfer from organic ligand molecules to central metal ion, resulting in bright emission of  $\text{Eu}^{3+}$ . Investigation of effective ligands for  $\text{Eu}^{3+}$  organic complexes mainly focuses on  $\beta$ -diketones due to their intense UV absorption (high extinction coefficient), relatively easy synthesis,

good solubility in commonly used solvents and good thermal stability. Dibenzoylmethane (DBM) is one of the most used ligand for  $\text{Eu}^{3+}$  organic complexes. Many scientific articles report DBM  $\text{Eu}^{3+}$  *ternary* complexes, where  $\text{Eu}^{3+}$  is coordinated with three DBM ligands and one secondary ligand, such as 1,10-phenantroline (PHEN) [2,3]. This complex and its poly-*N*-vinylcarbazole films have been fully examined as emitting layers in organic light emitting diodes (OLED) [4,5]. However, to our knowledge there are only 3 works devoted to investigate *tetrakis*  $\text{Eu}^{3+}$  complexes with DBM ligands with general structure  $[\text{Eu}(\text{DBM})_4]^-$  ( $\text{Eu}^{3+}$  complex is anionic and charge neutralization is required by quaternary ammonium ion counteraction) [6–8].  $\text{Eu}^{3+}$  *tetrakis* complexes usually exhibit higher luminescence efficiency and chemical stability as well as better solubility in solvents than

<sup>\*</sup> Corresponding author, [malina.ilze1@gmail.com](mailto:malina.ilze1@gmail.com)

*ternary* complexes. There are no data in the literature dealing with comparison of *ternary* and *tetrakis* complexes bearing the same  $\beta$ -diketone ligands, therefore in this work DBM is synthesized, and two  $\text{Eu}^{3+}$  complexes – *ternary* complex  $\text{Eu}(\text{DBM})_3(\text{PHEN})$  and *tetrakis* complex  $[\text{Eu}(\text{DBM})_4]\text{N}(\text{Et})_4$  are characterized and their thermal and optical properties are reported. However, pure organic complexes display low thermal- and photo-stability as well as poor mechanical properties and film formability, which limits their practical use. Therefore, another objective of this work is the investigation of optical and thermal properties of poly-*N*-vinylcarbazole (PVK) films containing different concentration of the  $\text{Eu}^{3+}$  complexes.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials and methods

$\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (99.99%) was purchased from Acros Organics, 1,10-phenantroline (99%), ammonium tetrabutylbromide (98%), acetophenone (>96%), ethylbenzoate (>99%) – from Alfa Aesar and poly-*N*-vinylcarbazole (PVK) from ABCR (GmbH&Co).

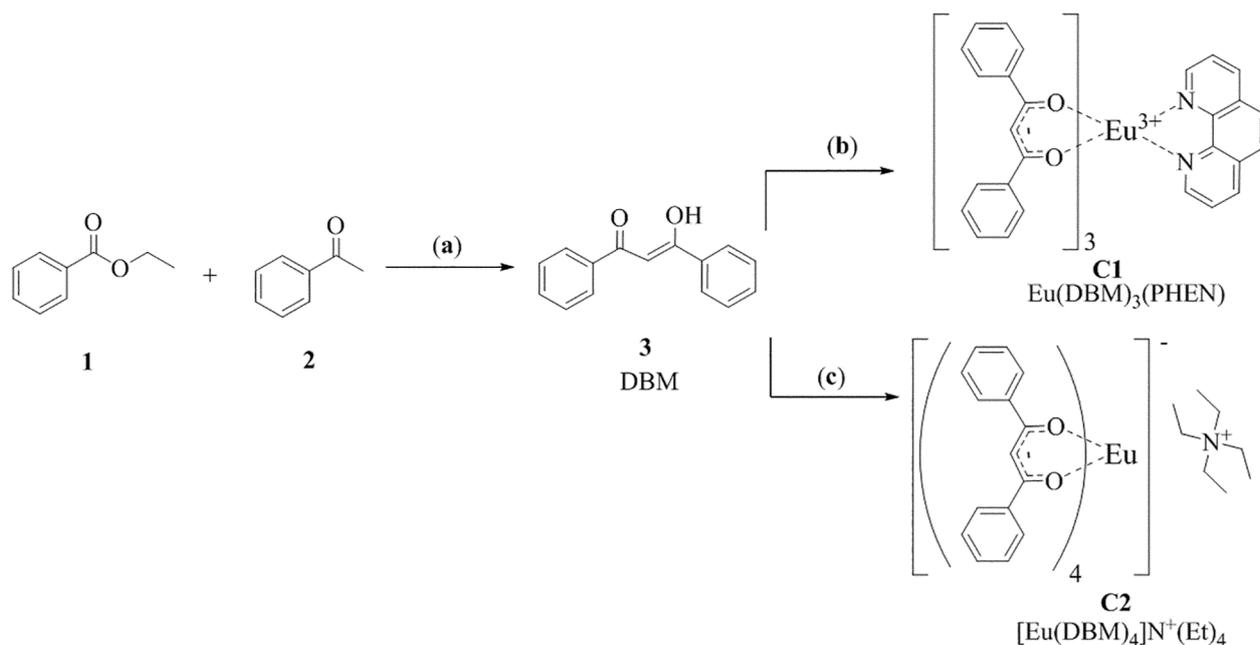
$^1\text{H-NMR}$  spectra were recorded in  $\text{CDCl}_3$  and  $(\text{CD}_3)_2\text{CO}$  solutions (~5–7 mg/ml) on a Bruker Avance 300 MHz spectrometer. CHN elemental analyses were performed on Euro Vector EA 3000 analyser. The FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 FTIR spectrometer using KBr pellets. Low resolution

mass spectra were determined on a Waters EMD 1000MS mass detector (ESI mode, voltage 30 V). Thermal properties of solid complexes and PVK films were determined on a Perkin Elmer STA 6000 instrument. Solid complexes were heated from 30–900 °C with heating rate 10 °C/min, but PVK films from 30–700 °C with heating rate 3 °C/min in nitrogen atmosphere. The UV-Vis absorption spectra (solutions and films) were determined on Perkin-Elmer 35 UV/Vis spectrometer. Emission and excitation spectra were measured on QuantaMaster 40 steady state spectrofluorometer (Photon Technology International, Inc.). Absolute photoluminescence quantum yields were determined using 6 inch integrating sphere by LabSphere coupled to the spectrofluorometer. The values reported are the average of three independent measurements for each sample. PVK thin films were obtained with Laurell WS-400B-NPP/LITE spin coater.

### 2.2. Synthesis

The synthesis of DBM (**3**) and its *ternary*  $\text{Eu}(\text{DBM})_3(\text{PHEN})$  **C1** and *tetrakis* complexes  $[\text{Eu}(\text{DBM})_4]\text{N}(\text{Et})_4$  **C2** are shown in Fig. 1. DBM was synthesized as in reference [9].

**C1**: To a solution of DBM (**3**) (0.0963 g, 0.429 mmol, 3 eq.) and 1,10-phenantroline (0.0258 g, 0.143 mmol, 1 eq.) in 15 ml ethanol 10% NaOH solution was added until pH~7–8. Then, 2 ml distilled water solution



**Fig. 1.** Synthesis of complexes **C1** and **C2**; (a) – 1) NaH, THF, 65 °C; 2) 10% HCl; (b) – 10% NaOH/H<sub>2</sub>O/EtOH, 1,10-Phenantroline,  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ ; (c) – 10% NaOH/H<sub>2</sub>O/EtOH,  $\text{N}(\text{Et})_4\text{Br}$ ,  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ .

containing  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.0525 g, 0.143 mmol, 1 eq.) was added dropwise and resulting solution was refluxed and stirred for 2 hours. Formed precipitate was separated by suction filtration, washed with ethanol (10 ml) and distilled water (10 ml) and dried in vacuum at 50 °C for 24 hours. Light yellow powder, yield 75%;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ , ppm): 10.98 (2H, d, PHEN-H), 10.59 (2H, br s, PHEN-H), 9.95 (2H, br s, PHEN-H), 8.95 (2H, br s, PHEN-H), 6.82–6.75 (18H, m, Ar-H), 5.95–5.93 (12H, m, Ar-H), 2.88 (3H, s, C=CH). Anal. Calcd. For  $\text{EuC}_{57}\text{H}_{41}\text{N}_2\text{O}_6$ : C, 68.33; H, 4.12; N, 2.80; found C, 67.67; H, 4.41; N, 2.75; FT-IR (KBr,  $\text{cm}^{-1}$ ): 3059, 3026, 2925 ( $\nu_{\text{Csp}2\text{H}}$ ); 1595 ( $\nu_{\text{C=O}}$ ); 1550, 1528, 1478 ( $\nu_{\text{C=C}}$ ); 1411 ( $\nu_{\text{C=N}}$ ); ESI(+)-MS: ( $m/z$ ) 181.1  $[\text{PHEN+H}]^+$ ; 821.4  $^{151}\text{Eu}(\text{DBM})_3+\text{H}^+$ ; 823.3  $^{153}\text{Eu}(\text{DBM})_3+\text{H}^+$ .

**C2:** Solution of DBM (**3**) (0.1504 g, 0.671 mmol, 3 eq.) in 15 ml ethanol was stirred until complete dissolution. Then ammonium tetraethylbromide (0.0528 g, 0.252 mmol, 1.5 eq.) in 2 ml ethanol was added. 10% NaOH was added to the solution until pH~7–8. Afterwards, 2 ml distilled water solution containing  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.0617 g, 0.168 mmol, 1 eq.) was added dropwise and resulting solution was stirred for 2 hours in the room temperature. Formed precipitate was separated by suction filtration, washed with ethanol (10 ml) and distilled water (10 ml), then crystallized from acetonitrile and dried in vacuum at 50 °C for 24 hours. Light orange needles, yield 85%;  $^1\text{H-NMR}$  (300 MHz,  $(\text{CD}_3)_2\text{CO}$ , ppm): 7.78–7.75 (16H, br m, Ar-H), 7.22–7.14 (24H, br m, Ar-H), 4.00 (8H, br q,  $(\text{CH}_3-\text{CH}_2)_4\text{N}^+$ ), 2.85 (4H, s, C=CH), 1.65 (12H, br t,  $(\text{CH}_3-\text{CH}_2)_4\text{N}^+$ ). Anal. Calcd. For  $\text{EuC}_{68}\text{H}_{64}\text{NO}_8$ : C, 69.50; H, 5.49; N, 1.19; found C, 69.57; H, 5.67; N, 1.52; FT-IR (KBr,  $\text{cm}^{-1}$ ): 3056, 3026 ( $\nu_{\text{Csp}2\text{H}}$ ); 2988, 2926 ( $\nu_{\text{Csp}3\text{H}}$ ); 1600 ( $\nu_{\text{C=O}}$ ); 1557, 1513, 1478, 1417 ( $\nu_{\text{C=C}}$ ); 1307, 1278 ( $\nu_{\text{C=N}}$ ); ESI(+)-MS: ( $m/z$ ) 130.1  $[\text{N}(\text{Et})_4]^+$ ; ESI(-)-MS: ( $m/z$ ) 1043.8  $^{151}\text{Eu}(\text{DBM})_4^-$ ; 1045.0  $^{153}\text{Eu}(\text{DBM})_4^-$ .

### 2.3. Fabrication of PVK films

PVK and required amount of complexes **C1** or **C2** were dissolved in 1 ml THF and the resulting mixture was heated at 40 °C for 0.5 h. Afterwards polymer film was spin-coated on a glass substrate using following parameters: speed 800 rpm, acceleration 800 rpm/sec 1 min. Then obtained films were dried in 45 °C for 2 h.

## 3. RESULTS AND DISCUSSION

### 3.1. Molecular structure confirmation

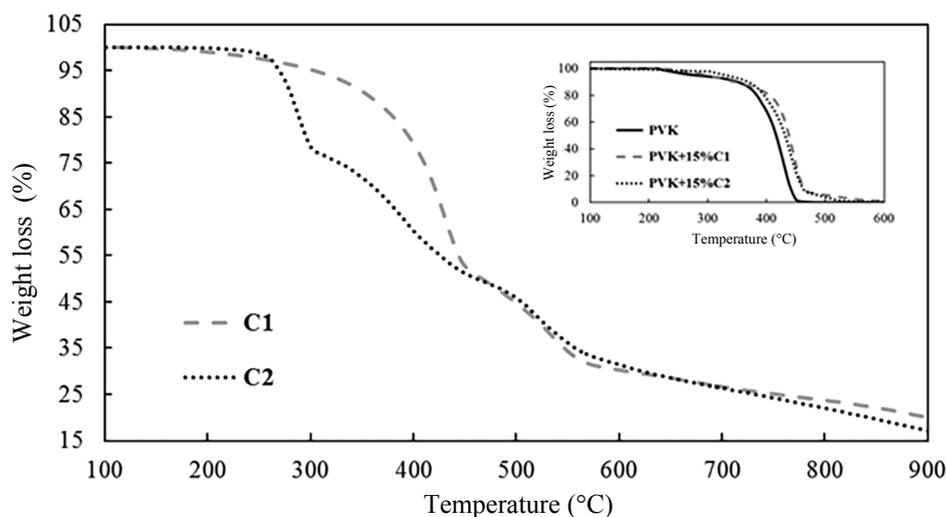
The elemental analysis,  $^1\text{H-NMR}$  spectroscopy and mass spectra data of complex **C1** ( $\text{Eu}(\text{DBM})_3(\text{PHEN})$ ) demonstrates that mole ratio of  $\text{Eu}^{3+}:\text{DBM}:\text{PHEN}$  is 1:3:1, but

for complex **C2** ( $[\text{Eu}(\text{DBM})_4]\text{N}(\text{Et})_4$ )  $\text{Eu}^{3+}:\text{DBM}:\text{N}(\text{Et})_4$  is 1:4:1. Mass spectra analysis of **C1** shows peaks with  $m/z$ : 181.1; 821.4 and 823.3 corresponding to  $[\text{PHEN+H}]^+$ ;  $^{151}\text{Eu}(\text{DBM})_3+\text{H}^+$ ;  $^{153}\text{Eu}(\text{DBM})_3+\text{H}^+$ , which confirms that  $\text{Eu}^{3+}$  is coordinated with three DBM molecules. In the  $^1\text{H-NMR}$  spectra of complex **C1** four signals at 10.98, 10.59, 9.95 and 8.95 ppm corresponding to eight protons from 1,10-phenanthroline molecule were observed. Furthermore, in the higher fields two multiplets (~6.80 and 5.94 ppm) and singlet (2.88 ppm) corresponding to 33 protons from three DBM molecules were observed, proving, that ratio of proton signals of PHEN and DBM molecules are 8:33, supplementing evidence, that **C1** is ternary complex with DBM:PHEN being 3:1. Furthermore, the  $^1\text{H-NMR}$  spectra of complex **C1** show some changes compared to ligands DBM (**3**) spectra, due to coordination to paramagnetic metal. All signals are broader and show shift to higher field, for example, methine group signal (C=CH) exhibited a shift from 6.88 ppm and showed signal at 2.88 ppm.

For complex **C2** mass spectra analysis show mass peaks with  $m/z$ : 130.1; 1043.8 and 1045.0 corresponding to  $[\text{N}(\text{Et})_4]^+$ ;  $^{151}\text{Eu}(\text{DBM})_4^-$ ;  $^{153}\text{Eu}(\text{DBM})_4^-$ , which establishes, that complex is with tetrakis structure. Moreover,  $^1\text{H-NMR}$  spectra of **C2** shows two multiplets (~7.77 and 7.18 ppm) and one singlet (2.85 ppm) corresponding to 44 protons of four DBM molecules, but in higher fields quartet at 4 ppm and triplet at 1.65 ppm corresponding to 20 protons of  $\text{N}^+(\text{Et})_4$  molecule were observed, leading to conclusion, that  $\text{Eu}^{3+}$  is coordinated with four DBM and one  $\text{N}^+(\text{Et})_4$  molecule.

### 3.2. Thermal properties

To evaluate **C1** and **C2** thermal durability, thermogravimetric (TG) analysis were conducted in nitrogen atmosphere from 30–900 °C and TG curves are shown in Fig. 2. Both complexes **C1** and **C2** exhibit high thermal decomposition temperatures  $T_{5\%}$  ( $T_{5\%}$  is temperature of 5% weight loss) – 304 and 267 °C, respectively. TG curve of complex **C1** consist of two mass loss steps around 310–443, and 444–556 °C. First mass loss step (45%) corresponds to the loss of two DBM molecules, second stage (22%) – to one DBM molecule. Further thermal decomposition from 557 to 900 °C leads to loss of PHEN molecule and residual weight of 20%. Similar thermal degradation pattern was reported for other  $\text{Eu}^{3+}$  complexes with DBM derivatives and PHEN ligands [10]. Whereas TG curve of **C2** exhibits three thermal degradation stages: 268–295, 296–451, 452–590 °C, with mass losses of 19%, 30% and 19%, corresponding to loss of one DBM molecule, then one DBM and  $\text{N}^+(\text{Et})_4$  molecule, and lastly one DBM molecule, respectively. Further thermal decomposition from 591 to 900 °C



**Fig. 2.** Thermogravimetric curves of  $\text{Eu}^{3+}$  complexes **C1** and **C2**. Inset shows TG curves of pure PVK and PVK thin film containing 15% complex **C1** or **C2**.

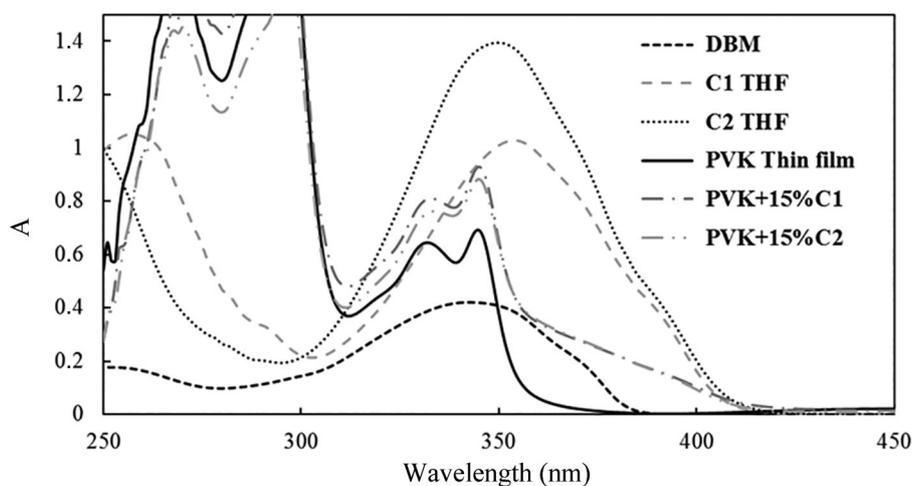
leads to loss of last DBM molecule and residual weight of 17%. Although  $T_{5\%}$  of complex **C2** is lower, compared to **C1**, it is still higher for 50 °C than other  $\text{Eu}^{3+}$  tetrakis complexes with  $\beta$ -diketone ligands and quaternary ammonium ions [11,12].

It is known, that thermal properties can be improved by incorporating complexes in polymer matrixes, therefore TG analysis of PVK films containing 15% **C1** or **C2** were also conducted. TG curves of pure PVK film and films containing complexes are depicted in inset of Fig. 2. Pure PVK film shows small mass loss till 300 °C, which can be assigned to entrapped solvent removal from polymer films. Degradation of polymer occurs in a narrow temperature interval (366–453 °C).

However, PVK films blended with complexes **C1** or **C2** show slight increase in thermal degradation temperature interval. For PVK+15% **C1** major degradation occurs at 392–467 °C, but for PVK+15% **C2** at 379–467 °C. The thermal degradation data indicate that incorporation of **C1** or **C2** in PVK leads to polymer films with high thermal decomposition endurance.

### 3.3. UV-Vis absorption properties

The UV-Vis absorption bands of pure DBM and complexes **C1** and **C2** were measured in THF solutions ( $c \sim 1.5 \cdot 10^{-5} \text{M}$ ), and are depicted in Fig. 3. Absorption spectra of DBM shows broad band with maximum at



**Fig. 3.** UV-Vis absorption spectra of DBM, **C1**, **C2** in THF solutions ( $\sim 1.5 \cdot 10^{-5} \text{M}$ ), pure PVK films and PVK thin films containing 15% of complexes **C1** and **C2**.

343 nm, which is assigned to enolic  $\pi$ - $\pi^*$  transitions of the  $\beta$ -diketone moiety. Furthermore, DBM exhibit high molar absorbance coefficient  $\varepsilon$   $26287.5 \text{ M}^{-1}\cdot\text{cm}^{-1}$ . The absorption spectra of complexes **C1** and **C2** in THF solutions are similar to the one of free DBM molecule, confirming that coordination with  $\text{Eu}^{3+}$  ions do not affect ligands singlet excited states. Similar observations were reported for other  $\beta$ -diketones and their  $\text{Ln}^{3+}$  complexes [7,11]. The small red-shift (7–11 nm) of absorption band maximum for **C1** and **C2** compared to DBM can be explained with the more effective conjugation of  $\pi$ -electrons in  $\text{Eu}^{3+}$  complexes. Furthermore, absorption intensity is enhanced in the complexes **C1** and **C2** due to expanded  $\pi$ -conjugated system, which forms, when  $\text{Eu}^{3+}$  coordinates with DBM and PHEN molecules. The  $\varepsilon$  of **C1** and **C2** reaches 68553 and 92967  $\text{M}^{-1}\cdot\text{cm}^{-1}$ , which are 2.61 and 3.54 times higher than DBM molar absorptivity, suggesting, that these complexes exhibit strong ability to absorb light in the 320–380 nm region.

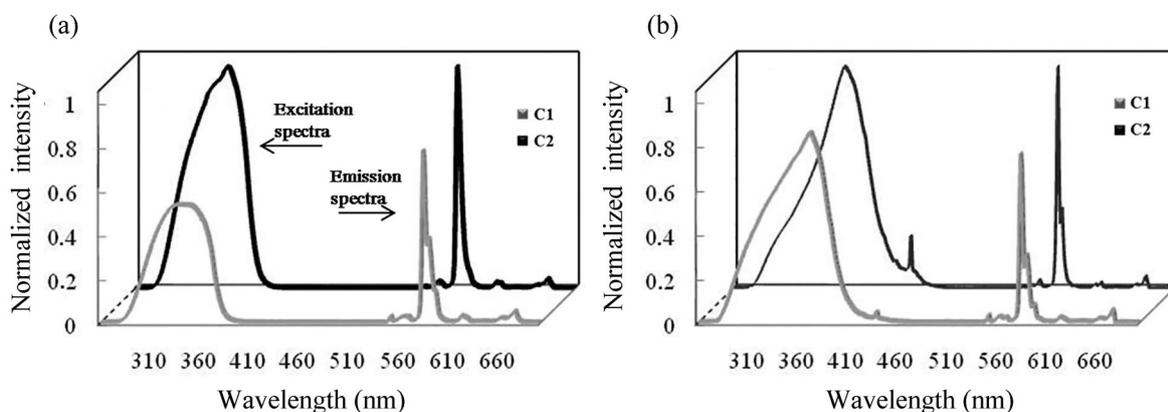
Figure 3 also shows absorption spectra of pure PVK and PVK thin films containing 15% of complexes **C1** or **C2**. Pure PVK film shows complicated band shape with absorption maxima at 271, 297, 332 and 346 nm, which can be assigned to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions. Absorption spectra of PVK films with **C1** and **C2** exhibit almost the same absorption profile as pure PVK film, only absorption intensity is increased at 332 and 346 nm due to overlap of PVK and complexes absorption spectra. Furthermore, new non-pronounced absorption band arises from 356 to 410 nm, which can be assigned to ligands absorption of complexes **C1** and **C2**.

### 3.4. Photoluminescence properties in solutions and solid state

Photoluminescence properties of  $\text{Eu}^{3+}$  complexes were investigated in THF solutions ( $\sim 1.5 \cdot 10^{-5} \text{ M}$ ) and in solid-

state. The excitation spectra of  $\text{Eu}^{3+}$  complexes monitoring  $\text{Eu}^{3+}$  transition at 612 nm are displayed in Fig. 4. The excitation spectra of **C1** and **C2** exhibit broad band between 300–425 nm in THF (Fig. 4(a)) and 300–480 nm in solid-state (Fig. 4(b)), which can be assigned to absorption of DBM ligands. As absorption spectra of DBM and excitation spectra of complexes overlap, one can conclude that in synthesized complexes energy transfer occurs from DBM ligands to  $\text{Eu}^{3+}$  ions. The maximums of excitation spectra for **C1** and **C2** in THF are at 373 and 384 nm, but in solid state a red shift to 402 and 403 nm occurs. This red shift of excitation wavelength maxima could be explained with the presence of strong  $\pi$ - $\pi$  interactions between ligands in the solid-state. The absorption bands of  $f$ - $f^*$  transitions of  $\text{Eu}^{3+}$  ion (at 296, 362, 381, 394, 415, 466 and 527 nm) are not present in the excitation spectra of THF solutions, however in solid-state spectra transition at 466 nm ( ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  transition) is clearly seen. This transition is usually observed for  $\text{Eu}^{3+}$  complexes in solid state [6,7].

Emission spectra of **C1** and **C2** in THF solutions as well as in solid-state shows characteristic  $\text{Eu}^{3+} {}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  ( $J=0-4$ ) transitions at 580, 593, 612, 651 and 703 nm. The highest intensity is observed for  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition at 612 nm, which is induced electric dipole transition and its intensity is dependent on coordination environment of  $\text{Eu}^{3+}$  ion. As it was expected *tetrakis*  $\text{Eu}^{3+}$  complex **C2** exhibits higher intensity for  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition than *ternary* complex **C1** in THF and in solid-state due to fact, that coordination sphere of  $\text{Eu}^{3+}$  in **C2** is filled with four DBM ligands, which efficiently transfer the excitation energy to central metal ion and also provides better shielding of metal ion from surrounding environment. Furthermore, it is known that in *ternary* complexes PHEN is coordinated weakly to  $\text{Eu}^{3+}$  ion, which could lead to dissociation of PHEN from some complex molecules and formation of *tris* complex  $\text{Eu}(\text{DBM})_3$ .



**Fig. 4.** Excitation ( $\lambda_{\text{mon}}=612 \text{ nm}$ ) and emission ( $\lambda_{\text{em}}=354 \text{ nm}$ ) spectra of complexes **C1** and **C2** in THF solutions (a) and in solid-state (b).

Formation of some *tris* complexes could also decrease luminescence intensity for **C1** complex. Furthermore, emission band at 612 nm for complex **C1** in both solution and solid-state is split and has secondary maximums at 618 and 622 nm. However, for complex **C2** in solution the emission band is broadened with one maximum at 612 nm. Similar observation was reported for other *tetrakis*  $\text{Eu}^{3+}$  complex with DBM ligands and trioctylmethylphosphonium as counteraction [7] and was explained by interactions between  $[\text{Eu}(\text{DBM})_4]^-$  and counteraction ions in solution.

The absolute photoluminescence quantum yields were 4% for *ternary* **C1** complex and 6% for *tetrakis* **C2** complex in  $1.5 \cdot 10^{-5} \text{M}$  THF solutions. Furthermore, in a solid-state photoluminescence quantum yield reached 56% for **C1** and 75% for **C2**. Such luminescence quantum yield enhancement in solid-state compared to solutions can be explained with deactivation of ligand molecules in solvent medium by collisions. For  $\text{Eu}^{3+}$  complexes with  $\beta$ -diketone ligands it is common to have higher luminescence quantum yields in solid-state rather than in solutions [7,10,12,14]. In conclusion, comparison of emission properties of *ternary* and *tetrakis*  $\text{Eu}^{3+}$  complexes shows that *tetrakis* complex  $[\text{Eu}(\text{DBM})_4]\text{N}(\text{Et})_4$  has enhanced emission properties in solid-state and has considerable potential for light emitting materials.

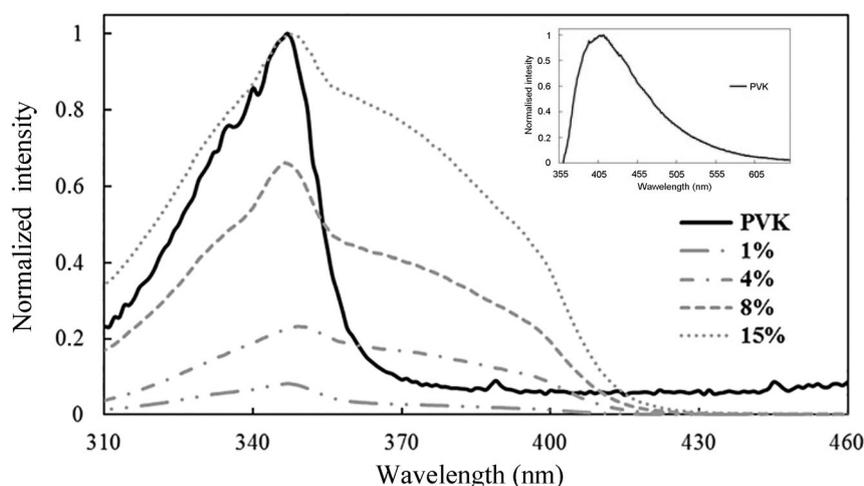
### 3.5. Photoluminescence properties in PVK thin films

In this work PVK was used as polymer matrix for  $\text{Eu}^{3+}$  complexes due to its excellent hole-transporting properties. Furthermore, only few polymers have been established as good hosts for organic lanthanide complexes

and PVK is one of them due to good match between triplet energy level of the polymer host and complex and also suitable overlap between emission spectra of polymer and absorption spectra of  $\text{Eu}^{3+}$  complex. PVK thin films doped with 1, 4, 8 and 15 wt% of complex **C1** or **C2** were prepared by spin-coating method from THF. Excitation spectra of polymer films with complex **C1** and pure PVK thin film are shown in Fig. 5, inset shows emission spectra of pure PVK film. Excitation spectra of doped polymer films overlaps with pure PVK emission spectra, indicating possibility of absorbed excitation energy transfer from polymer host to  $\text{Eu}^{3+}$  complex. Such energy transfer would give an advantage for thin PVK films, because polymer host would provide additional excitation energy for complex, which would lead to enhancement for film emission intensity.

The excitation spectra of PVK films shows broad bands in region from 300 to 410 nm with maximum at 348 nm, which corresponds to absorption of PVK matrix. However excitation bands have shoulder at 370 nm, which corresponds to absorption of **C1**.

The emission spectra of polymer films (depicted in Fig. 6) exhibit the same emission bands as those for complexes in THF solutions or solid-state. PVK films with 1% **C1** or **C2** also shows a weak polymer emission band from 360 till 560 nm indicating, that energy transfer from PVK to complexes is incomplete. This is due to great distance between polymer chain and complex in these films. However, for PVK films with higher complex concentration, the energy is completely transferred and no emission band of PVK is observed in spectra. Similar observations were reported for PVK films with *tetrakis* and *ternary*  $\text{Eu}(\text{III})$  complexes with 2-thenoyltrifluoroacetato ligands [15,16].



**Fig. 5.** Excitation spectra of pure PVK ( $\lambda_{\text{mon}} = 435 \text{ nm}$ ) and PVK thin films ( $\lambda_{\text{mon}} = 612 \text{ nm}$ ) containing 1, 4, 8 and 15 wt% complex **C1**. Inset shows emission spectra of pure PVK film.

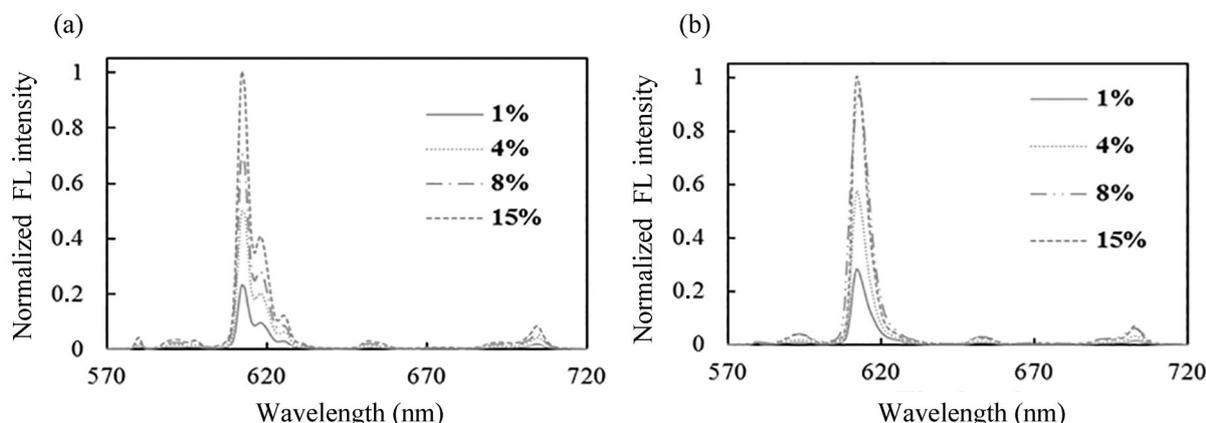


Fig. 6. Emission spectra of PVK films doped with 1, 4, 8 and 15 wt% of C1 (a) and of C2 (b).

Intensity of emission band at 612 nm and absolute photoluminescence quantum yields increases with increasing complex concentration in PVK matrix. The quantum yields for series of *ternary* complex C1 PVK films (1, 4, 8, 15 wt%) increase in following order 14%, 21%, 26% and 30%, respectively, but for *tetrakis* complex C2 films (1, 4, 8, 15 wt%) – 17%, 30%, 46% and 48%. For *tetrakis* complex C2 increasing complex mass in the PVK from 8% to 15% has an insignificant effect on  $^5D_0 \rightarrow ^7F_2$  (612 nm) transition intensity and quantum yield. This can be explained with the fact that in film with high  $\text{Eu}^{3+}$  ion concentration an energy transfer between  $\text{Eu}^{3+}$  ions occurs as a non-radiative process. Therefore intensity of complex luminescence does not increase and sometimes even decreases in films with high complex concentration [13,17]. Registered quantum yield values for investigated PVK films are at the same level as the ones for the known films of  $\text{Eu}^{3+}$   $\beta$ -diketone complexes in other polymers [18]. It can be concluded, that *tetrakis* complex  $[\text{Eu}(\text{DBM})_4]\text{N}(\text{Et})_4$  exhibits more intense emission not only in solution and solid-state, but also in PVK films.

#### 4. CONCLUSIONS

In summary *ternary* and *tetrakis*  $\text{Eu}^{3+}$  complexes with general structures  $\text{Eu}(\text{DBM})_3(\text{PHEN})$  and  $[\text{Eu}(\text{DBM})_4]\text{N}(\text{Et})_4$  were prepared and their structures were confirmed by elemental analysis, FT-IR,  $^1\text{H-NMR}$  and mass spectroscopy. Investigation of photoluminescence properties of complexes in THF, solid-state and PVK films shows that emission spectra contains characteristic  $\text{Eu}^{3+}$  ion emission lines with the most intense transition at 612 nm. Excitation window for both complexes lies in the near-UV region (300–400 nm),

providing large Stokes shifts. Enhanced emission intensity and photoluminescence quantum yields were found for both complexes in solid-state (quantum yields 56% and 75%). PVK polymer films containing  $\text{Eu}^{3+}$  DBM complexes also showed moderate quantum yields (14–48%). The luminescence intensity and quantum yields increased with increasing complex concentration in PVK films and reached maximum at doping concentration of 15 wt%. *Tetrakis* complex  $[\text{Eu}(\text{DBM})_4]\text{N}(\text{Et})_4$  in solution, solid-state and PVK films have enhanced photoluminescence properties compared to *ternary* complex due to four DBM molecules in  $\text{Eu}^{3+}$  coordination sphere, which leads to more effective excited energy transfer to  $\text{Eu}^{3+}$  ion. The results of thermogravimetric analysis of complexes revealed that they exhibit high thermal degradation temperatures.

#### ACKNOWLEDGEMENTS

This work was supported by the doctoral studies grants of Riga Technical University (grant No. 34-14000DOK.MLĶF/16) and the National Research Program of Latvia “IMIS2”. The authors thank MCs Chem. Kristine Lazdovica for help with thermogravimetric analysis. The publication costs of this article were covered by the Estonian Academy of Sciences and the University of Tartu.

#### REFERENCES

1. Binnemans, K. Lanthanide-Based Luminescent Hybrid Materials. *Chem. Rev.*, 2009, **109**, 4283–4374.
2. Singh, A. K., Singh, S. K., Mishra, H., Prakash, R., and Rai, S. B. Structural, Thermal, and Fluorescence Properties of  $\text{Eu}(\text{DBM})_3\text{Phen}_x$  Complex Doped in PMMA. *J. Phys. Chem. B*, 2010, **114**, 13042–13051.

3. Liang, H., Xie, F., Liu, M., Jin, Z., Luo, F., and Zhang, Z. Luminescence studies of europium chelates with increasing benzene ring substituents ligand-doped polymer. *Spectrochim. Acta, Part A*, 2008, **71**, 588–591.
4. Ma, D.-G., Wang, D.-K., Hong, Z.-Y., Zhao, X.-J., Jing, X.-B., Song, F., et al. Bright red electroluminescent devices based on a soluble lanthanide complex Eu(DBM)<sub>3</sub>(phen). *Chin. J. Chem.*, 1998, **16**(1), 1–6.
5. Santos, G., Fonseca, F. J., and Andrade, A. M. The dependence of OLED external efficiency on the mass concentration of europium(III) dispersed in PVK. *ECS Trans.*, 2011, **39**(1), 475–480.
6. Mech, A., Karbowiak, M., Görrler-Walrand, C., and Van Deun, R. The luminescence properties of three tetrakis dibenzoylmethaneeuropium(III) complexes with different counter ions. *J. Alloys Compd.*, 2008, **451**, 215–219.
7. Malba, C. M., Enrichi, F., Facchina, M., Demitric, N., Plaisier, J. R., Natile, M. M., Selva, M., Riello, P., Perosa, A., and Benedetti, A. Phosphonium-based tetrakis dibenzoylmethane Eu(III) and Sm(III) complexes: synthesis, crystal structure and photoluminescence properties in a weakly coordinating phosphonium ionic liquid. *RSC Adv.*, 2015, **5**, 60898–60907.
8. Zhou, D., Huang, C., Yaong, G., Bai, J., and Li, T. Luminescent europium-dibenzoylmethane complexes and their Langmuir–Blodgett films, *J. Alloys Compd.*, 1996, **235**, 156–162.
9. Zawadiak, J. and Mrzyczek, M. Influence of substituent on UV absorption and keto–enol tautomerism equilibrium of dibenzoylmethane derivatives. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, 2012, **96**, 815–819.
10. Wang, D., Zheng, C., Fan, L., Zheng, J., and Wei, X. Preparation and fluorescent properties of europium(III) complexes with  $\beta$ -diketonate ligand and 1,10-phenanthroline. *Synth. Met.*, 2012, **162**, 2063–2068.
11. Biju, S., Xu, L.-J., Sun, C.-Z., and Chen, Z.-N. White OLEDs based on a novel Eu<sup>III</sup>-tetrakis- $\beta$ -diketonate doped into 4,4'-N,N'-dicarbazolebiphenyl as emitting material. *J. Mater. Chem. C*, 2015, **3**, 5775–5782.
12. Biju, S., Freire, R. O., Eom, Y. K., Scopelliti, R., Bunzli, J.-C.G., and Kim, H. K. A Eu<sup>III</sup> tetrakis ( $\beta$ -diketonate) dimeric complex: photophysical properties, structural elucidation by sparkle/AM1 calculations, and doping into PMMA films and nanowires. *Inorg. Chem.*, 2014, **53**, 8407–8417.
13. Li, W., Yan, P., Hou, G., Li, H., and Li, G. Efficient red emission from PMMA films doped with 5,6-DTFI europium(III) complexes: synthesis, structure and photophysical properties. *Dalton Trans.*, 2013, **42**, 11537–11547.
14. Ma, Q., Zheng, Y., Armaroli, N., Bolognesi, M., and Accorsi, G. Synthesis and photoluminescence properties of asymmetrical europium(III) complexes involving carbazole, phenanthroline and bathophenanthroline units. *Inorg. Chem. Acta*, 2009, **362**, 3181–3186.
15. Yu, G., Liu, Y., Wu, X., and Zhu, D. Soluble europium complexes for light-emitting diodes. *Chem. Mater.*, 2000, **12**, 2537–2541.
16. Deichmann, V. A. F., Novo, J. B. M., Cirpan, A., Karasz, F. E., and Akcelrud, L. Photo- and electroluminescent behaviour of Eu<sup>3+</sup> ions in blends with poly(vinyl-carbazole). *J. Braz. Chem. Soc.*, 2007, **18**(2), 330–336.
17. Raj, D. B. A., Francis, B., Reddy, M. L. P., Butorac, R. R., Lynch, V. M., and Cowley, A. H. Highly luminescent poly(methyl methacrylate)-incorporated europium complex supported by a carbazole-based fluorinated  $\beta$ -diketonate ligand and a 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene oxide co-ligand. *Inorg. Chem.*, 2010, **49**, 9055–9063.
18. Forster, P. L., Parra, D. F., Lugao, A. B., Kai, J., and Brito, H. F. Highly luminescent polycaprolactone films doped with diaquatris (thenoyltrifluoroacetate) europium(III) complex. *J. Lumin.*, 2015, **167**, 85–90.

## Dibensoüülmetaan-Eu(III) orgaaniliste komplekside termilised ja optilised omadused

Ilze Malina, Nikolajs Juhnevics ja Valdis Kampars

Sünteesiti kaks euroopium(III) orgaanilist kompleksi (kolmikkompleks Eu(DBM)<sub>3</sub>(PHEN) ja nelikkompleks [Eu(DBM)<sub>4</sub>]N(Et)<sub>4</sub>), kus DBM on dibensoüülmetaan ning PHEN on 1,10-fenantroliin. Nende struktuur tõestati, kasutades <sup>1</sup>H-NMR-spektroskoopiat, elementanalüüsi, FT-IR- ja mass-spektroskoopiat. Komplekside fotofüüsikalisi omadusi uuriti lahuses, tahkel kujul ja polü-*N*-vinüülkarbasool- (PVK) kiles, varieerides kompleksi kontsentratsiooni vahemikus 1 kuni 15 massiprotsenti. Mõlemad kompleksid on head UV neelajad ja kiirgavad eredalt punases spektri piirkonnas kiirgusriba keskpunktiga 612 nm. Näidati, et lahuses, tahkel kujul ja PVK-kiles on nelikkompleksil kolmikkompleksiga võrreldes võimendatud fotoluminesentsomadusi tänu neljale DBM-molekulile Eu<sup>3+</sup> koordinatsioonisfääris, mis põhjustavad efektiivsemat energia ülekannet Eu<sup>3+</sup> ioonile. THF-lahuses olid mõlemad kompleksid madala kvantefektiivsusega (4% ja 6%), PVK-kiles keskmise kvantefektiivsusega (14–48%) ning tahkel kujul kõrge kvantefektiivsusega (56% ja 75%). Mõlema kompleksi termilisi omadusi PVK-kiles uuriti termogravimeetria-meetoditega. Mõlemal kompleksil on kõrge termilise lagunemise temperatuur: kolmikkompleksil 304 °C ja nelikkompleksil 267 °C. PVK-kiles on vastav temperatuur aga mõlemal juhul üle 370 °C, seega veel kõrgem.