

## PHOTOLUMINESCENT PROPERTIES OF NOVEL TRIS, TERNARY AND TETRAKIS EU(III) ORGANIC COMPLEXES WITH 2-ACETYL-1,3-INDANDIONE LIGANDS

Ilze Malina, Valdis Kampars

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

### Abstract

Three structurally different, highly luminescent  $\text{Eu}^{3+}$  complexes – tris complex  $\text{Eu}(\text{2AID})_3(\text{H}_2\text{O})$ , ternary complex  $\text{Eu}(\text{2AID})_3(\text{PHEN})$  and tetrakis complex  $[\text{Eu}(\text{2AID})_4]\text{N}(\text{Et})_4$ , where 2AID stands for 2-acetyl-1,3-indandione and PHEN for 1,10-phenanthroline, were obtained and characterized with element analysis,  $^1\text{H-NMR}$ , FT-IR and mass spectroscopy. Thermal properties were investigated with thermogravimetric analysis and it was shown, that independently from their structure all three complexes exhibit high thermal stability over 280 °C. Photophysical properties were investigated in THF solutions, solid-state and poly-N-vinylcarbazole (PVK) films with complex mass of 8%. Complexes exhibit identical UV/Vis absorption and excitation spectra from 250-400 nm in THF, but in solid-state excitation window is shifted to near UV and even visible light region (300-500 nm). In solutions all three complexes exhibit weak emission at 613 nm with low absolute quantum yields (2-3%), but in solid state emission is enhanced and highest quantum yield – 34% was obtained for tetrakis complex. PVK films showed low PLQY.

**Key words:**  $\text{Eu}^{3+}$  organic complex,  $\beta$ -diketone ligands, 2-acetyl-1,3-indandione, red light emission, luminescent PVK films

### INTRODUCTION

Organic complexes containing lanthanide element  $\text{Eu}^{3+}$  ions are promising candidates for red-light luminescent materials due to unique optical properties such as line-like emission bands, long emission lifetimes and high luminescence quantum yields (Binnemans, 2009). Luminescence from complexes arises from efficient excited energy transfer from organic ligand molecules to central metal ion, which results in intense emission of  $\text{Eu}^{3+}$ . Emission intensity of complexes is affected by many factors including efficiency of ligand to  $\text{Eu}^{3+}$  energy transfer, ligand ability to absorb excitation energy, as well as structure of whole complex. Mainly investigated are *tris* complexes, where  $\text{Eu}^{3+}$  is coordinated with 3 ligand and 2 solvent molecules, *ternary* complexes, where  $\text{Eu}^{3+}$  is coordinated with 3 ligand and 1 or 2 secondary ligand molecules (N- or O-donor containing compounds) and *tetrakis* complexes, where  $\text{Eu}^{3+}$  is coordinated with 4 ligand molecules and 1 counteraction molecule (alkali metal cations or quaternary ammonium ions). Many scientific manuscripts compare the luminescence efficiency between *tris* and *ternary* complexes, concluding, that *ternary* complexes have higher quantum yields than *tris* complexes due to absence of solvents molecules in  $\text{Eu}^{3+}$  ion coordination sphere (Bala, 2014, Wang 2014, Jingya, 2012). It is known, that solvent molecules lead to increase of non-radiative rates for  $\text{Eu}^{3+}$  ion in complex (Teotonio, 2006). When these undesirable solvent molecules are replaced by secondary ligands, which intensively absorbs UV light and helps to transfer it to  $\text{Eu}^{3+}$  ion, complex luminescence efficiency increase. It is possible to replace the solvent molecules in coordination sphere using fourth diketone ligand, obtaining *tetrakis* complexes. In our knowledge there is no report in literature about systematic comparison of *tris*, *ternary* and *tetrakis* complexes.

$\beta$ -Diketones have been the most investigated ligands for  $\text{Eu}^{3+}$  complexes, due to strong absorption in the wide spectral range (UV, Vis), ability to form stable adducts with lanthanide ions, good solubility in most used solvents as well as high chemical stability.  $\beta$ -Diketones with at least one carbonyl in cycle could magnify complex luminescence properties due to restriction of thermal vibration by rigid ligand, which leads to reduction of nonradiative deactivation of whole complex. From rigid ligands, indone (Jingya, 2012, Li, 2013) and 1,3-indandione derivatives (Teotonio, 2006, Teotonio, 2009) have been employed as antenna ligands for  $\text{Eu}^{3+}$  complexes. Therefore, to supplement literature data about

rigid ligand utilization in  $\text{Eu}^{3+}$  organic complex chemistry we present the investigation of 3  $\text{Eu}^{3+}$  complexes (*tris* complex  $\text{Eu}(\text{2AID})_3(\text{H}_2\text{O})_2$ , *ternary* complex  $\text{Eu}(\text{2AID})_3(\text{PHEN})$  and *tetrakis* complex  $[\text{Eu}(\text{2AID})_4]\text{N}(\text{Et})_4$ , where 2AID is 2-acetyl-1,3-indandione and PHEN is 1,10-phenantroline), their chemical characterization, thermal, UV-VIS absorption and emission properties. The relationship between complex structure and luminescence properties will be discussed. Additionally, poly-N-vinylcarbazole films containing these complexes will be investigated.

## 1. EXPERIMENTAL SECTION

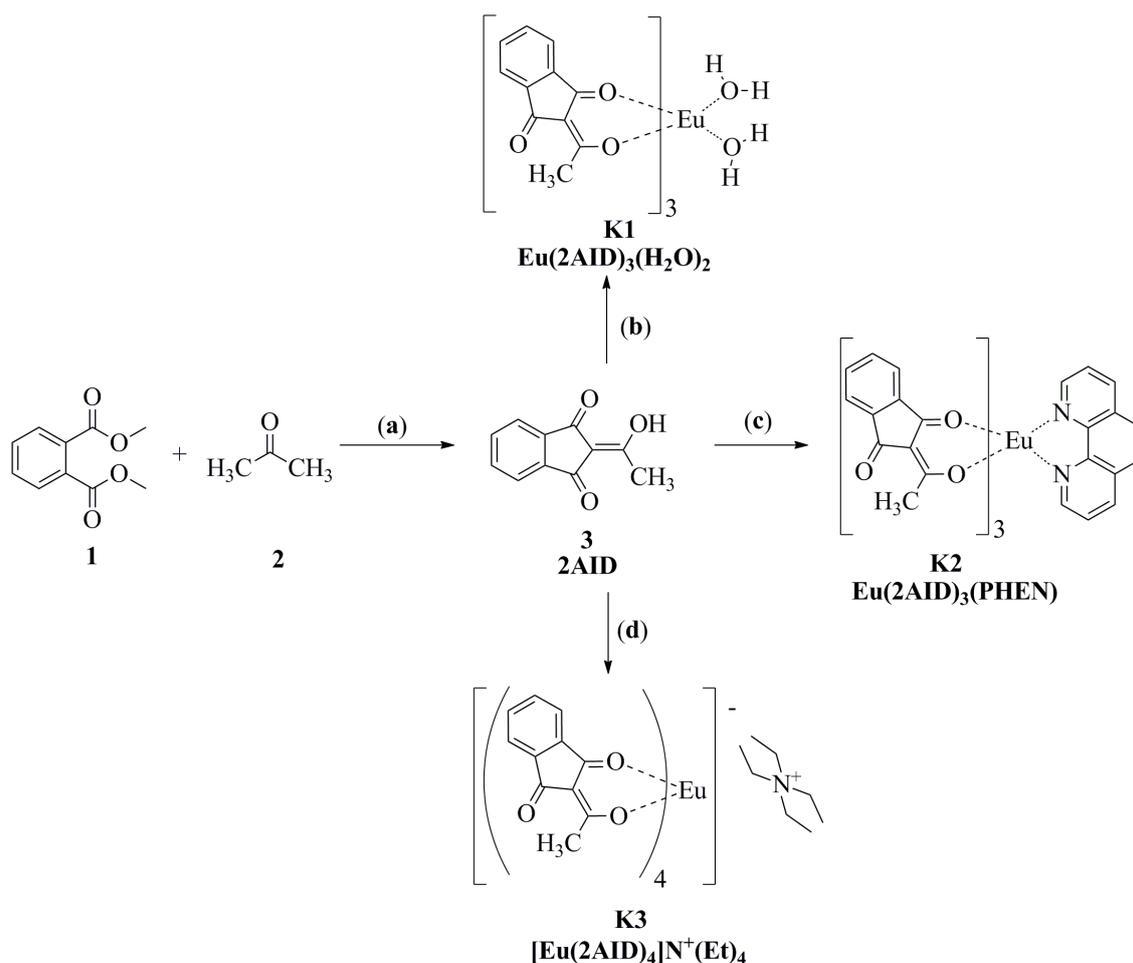
### 1.1. Materials and Methods

$\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (99,99%) was purchased from Acros Organics, 1,10-Phenantroline (99%) and ammonium tetraethylbromide (98%) from Alfa Aesar and poly-N-vinylcarbazole (PVK) from ABCR (GmbH&Co). CHN elemental analyses were acquired on Euro Vector EA 3000 analyzer.  $^1\text{H-NMR}$  spectra were recorded in  $(\text{CD}_3)_2\text{CO}$  solutions (~5-7 mg/ml) on a Bruker Avance 300 MHz spectrometer at 300 MHz for  $^1\text{H}$  nuclei. Chemical shifts were expressed in parts per million (ppm) relative to solvent signal. The FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 FTIR spectrometer using KBr pellets. Low resolution mass spectra were acquired on a Waters EMD 1000MS mass detector (ESI mode, voltage 30 V). Thermal properties of solid complexes were determined on a Perkin Elmer STA 6000 instrument. Solid complexes were heated from 30-880 °C with heating rate 10 °C/min in nitrogen atmosphere. The UV-Vis absorption spectra (solutions and films) were acquired on Perkin-Elmer 35 UV/Vis spectrometer using 1 cm path length cuvettes. Emission and excitation spectra were measured on QuantaMaster 40 steady state spectrofluorometer (Photon Technology International, Inc.) using 1 cm path length cuvettes for solution sample. Absolute photoluminescence quantum yields were determined at room temperature using 6 inch integrating sphere by LabSphere coupled to the spectrofluorometer. The values reported are the average of three independent measurements for each sample. Laurell WS-400B-NPP/LITE spin coater was used for obtain thin films.

### 1.2. Synthesis

The synthesis of  $\text{Eu}^{3+}$  *tris* (**K1**), *ternary* (**K2**) and *tetrakis* (**K3**) complexes as well as ligand – 2-acetyl-1,3-indandione (2AID) are shown in Scheme 1. 2-Acetyl-1,3-indandione was obtained according to literature (Teotonio, 2006).

**K1:** To a solution of 2AID (0,30 g, 1.60mmol, 3 eq) in 15 ml distilled water, 10% NaOH solution was added until pH~7-8. Then resulting solution was heated at 60 °C until all is dissolved. Afterwards, 5 ml distilled water solution containing  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.19 g, 0.53 mmol, 1 eq) was added dropwise. Resulting mixture was stirred at room temperature for 2 h and then formed precipitate was filtered and washed with distilled water and ethanol. Crude product was crystallized from MeCN and MeOH mixture (10:1). Yield: 52%,  $^1\text{H-NMR}$  (300 MHz,  $(\text{CD}_3)_2\text{CO}$ , ppm): 8.40 (3H, br s, Indandione-H), 7.62 (3H, br s, Indandione-H), 7.01 (3H, br s, Indandione-H), 6.25 (3H, br s, Indandione-H), 1.30 (9H, s,  $\text{CH}_3$ ). Anal.Calc. For  $\text{EuC}_{33}\text{H}_{23}\text{O}_{10}$ : C, 54.17; H, 3.15; found C, 54.67; H, 3.05; FT-IR (KBr,  $\text{cm}^{-1}$ ): 3023, 2971 ( $\nu_{\text{Csp}2\text{H}}$ ); 2945 ( $\nu_{\text{Csp}3\text{H}}$ ); 1738, 1673 ( $\nu_{\text{C=O}}$ ); 1617, 1580, 1518, 1455 ( $\nu_{\text{C=C}}$ ); ESI(+)-MS: ( $m/z$ ) 525.2 [ $^{151}\text{Eu}(\text{2AID})_2+\text{H}$ ] $^+$ ; 527.2 [ $^{153}\text{Eu}(\text{2AID})_2+\text{H}$ ] $^+$ ; 713.4 [ $^{151}\text{Eu}(\text{2AID})_3+\text{H}$ ] $^+$ ; 715.3 [ $^{153}\text{Eu}(\text{2AID})_3+\text{H}$ ] $^+$ .



**Scheme 1.** Synthesis of complexes **K1**, **K2** and **K3**; (a) – 1) NaOCH<sub>3</sub>, toluene, 80 °C; 2) 10% HCl; (b) - 10% NaOH/H<sub>2</sub>O, EuCl<sub>3</sub>·6H<sub>2</sub>O; (c) - 10% NaOH/H<sub>2</sub>O, 1,10-Phenanthroline, EuCl<sub>3</sub>·6H<sub>2</sub>O ; (d) - 10% NaOH/H<sub>2</sub>O/EtOH, N(Et)<sub>4</sub>Br, EuCl<sub>3</sub>·6H<sub>2</sub>O.

**K2:** To a solution of 2AID (0,30 g, 1.60 mmol, 3 eq) and 1,10-phenanthroline (0,10 g, 0.53 mmol, 1 eq) in 15 ml ethanol and water mixture (1:2) 10% NaOH solution was added until pH~7-8. Then, 5 ml distilled water solution containing EuCl<sub>3</sub>·6H<sub>2</sub>O (0.19 g, 0.53 mmol, 1 eq) was added dropwise. Resulting mixture was stirred at room 60 °C for 2 h and then formed precipitate was filtered and washed with distilled water and ethanol. Crude product was crystallized from MeCN and MeOH mixture (10:1). Yield: 55%. <sup>1</sup>H-NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, ppm): 10.16 (2H, d, PHEN-H), 9.39 (2H, br s, PHEN-H), 8.40 (2H, br s, PHEN-H), 7.16 (2H, br s, PHEN-H), 7.44 (3H, t, Indandione-H), 7.20 (3H, d, Indandione -H), 6.88 (3H, t, Indandione-H), 6.18 (3H, t, Indandione-H), 0.37 (9H, s, CH<sub>3</sub>). Anal.Calcd. For EuC<sub>45</sub>H<sub>29</sub>N<sub>2</sub>O<sub>9</sub>: C, 60.47; H, 3.25; N, 3.14; found C, 59.97; H, 3.04; N, 3.22; FT-IR (KBr, cm<sup>-1</sup>): 3072, 3016, (ν<sub>Csp2H</sub>); 2971, 2947, 2922 (ν<sub>Csp3H</sub>); 1739, 1688 (ν<sub>C=O</sub>); 1619, 1583, 1517, 1464 (ν<sub>C=C</sub>); 1423 (ν<sub>C=N</sub>); ESI(+)-MS: (m/z) 181.1 [PHEN+H]<sup>+</sup>; 713.4 [<sup>151</sup>Eu(2AID)<sub>3</sub>+H]<sup>+</sup>; 715.3 [<sup>153</sup>Eu(2AID)<sub>3</sub>+H]<sup>+</sup>; 525.2 [<sup>151</sup>Eu(2AID)<sub>2</sub>+H]<sup>+</sup>; 527.2 [<sup>153</sup>Eu(2AID)<sub>2</sub>+H]<sup>+</sup>.

**K3:** To a solution of 2AID (0,30 g, 1.60 mmol, 3 eq) and ammonium tetraethylbromide (0,13 g, 0.60 mmol, 1.5 eq) in 20 ml ethanol and water mixture (1:2) 10% NaOH solution was added until pH~7-8. Then, 5 ml distilled water solution containing EuCl<sub>3</sub>·6H<sub>2</sub>O (0.19 g, 0.53 mmol, 1 eq) was added dropwise. Resulting mixture was stirred at room 60 °C for 2 h and then formed precipitate was filtered and washed with distilled water and ethanol. Crude product was crystallized from MeCN and MeOH mixture (10:1). Yield: 49%. <sup>1</sup>H-NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, ppm): 7.43 (4H, br s, Indandione-H), 7.09-6.35 (12H, br m, Indandione -H), 4.55 (8H, br s, (CH<sub>3</sub>-CH<sub>2</sub>)<sub>4</sub>N<sup>+</sup>), 1.89 (12H, s, (CH<sub>3</sub>-CH<sub>2</sub>)<sub>4</sub>N<sup>+</sup>),

1.28 (12H, s, CH<sub>3</sub>). Anal.Calcd. For EuC<sub>52</sub>H<sub>48</sub>NO<sub>12</sub>: C, 60.58; H, 4.66; N, 1.36; found C, 60.14; H, 4.41; N, 1.31; FT-IR (KBr, cm<sup>-1</sup>): 3060, 3019 (ν<sub>Csp2H</sub>); 2965, 2927, 2852 (ν<sub>Csp3H</sub>); 1733, 1679 (ν<sub>C=O</sub>); 1626, 1590, 1525 (ν<sub>C=C</sub>); ESI(+)-MS: (m/z) 130.2 [N(Et)<sub>4</sub>]<sup>+</sup>; ESI(-)-MS: (m/z) 899.5 [<sup>151</sup>Eu(2AID)<sub>4</sub>]<sup>-</sup>; 901.6 [<sup>153</sup>Eu(2AID)<sub>4</sub>]<sup>-</sup>.

### 1.3. Fabrication of PVK films

PVK (20 mg) and required amount of complexes **K1-K2** (1.6 mg) 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.

## 2. RESULTS AND DISCUSSION

### 2.1. Characterization of complexes

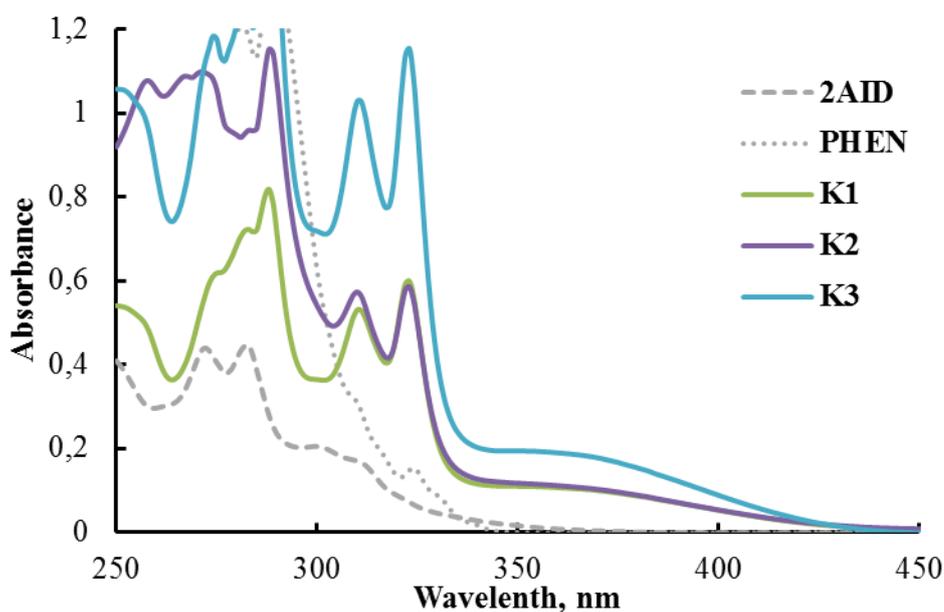
Structures of synthesized Eu<sup>3+</sup> complexes were proven with elemental analysis, <sup>1</sup>H-NMR, FT-IR and mass spectroscopy. All methods were in agreement, that in complex **K1** Eu<sup>3+</sup>:2AID molar ratio is 1:3, for example, mass spectra of **K1** shows peaks with m/z: 713.4 and 715.3 corresponding to mass of [<sup>151</sup>Eu(2AID)<sub>3</sub>+H]<sup>+</sup> and [<sup>153</sup>Eu(2AID)<sub>3</sub>+H]<sup>+</sup>. Furthermore, in <sup>1</sup>H-NMR spectra of this complex chemical shifts of 2AID proton signals are shifted to higher fields and are broader due to presence of paramagnetic metal ion, for example, -CH<sub>3</sub> group signal which usually are observed near 2 ppm in **K1** are observed at 1.30 ppm. For *ternary* complex **K2** mass spectra shows peaks with m/z: 181.1; 713.4 and 715.3, which corresponds on following ions: [PHEN+H]<sup>+</sup>; [<sup>151</sup>Eu(2AID)<sub>3</sub>+H]<sup>+</sup>; [<sup>153</sup>Eu(2AID)<sub>3</sub>+H]<sup>+</sup> and establishes, that Eu<sup>3+</sup> is coordinated with three 2AID molecules. <sup>1</sup>H-NMR spectra of **K2** demonstrates the ratio of proton signals of PHEN and 2AID ligands is 8:21, confirming, that PHEN:2AID is 1:3. At last for *tetrakis* complex **K3** mass spectra contains positive peak with m/z 130.1 ([N(Et)<sub>4</sub>]<sup>+</sup>) and two negative peaks with m/z being 899 and 901 ([<sup>151</sup>Eu(2AID)<sub>4</sub>]<sup>-</sup>; [<sup>153</sup>Eu(2AID)<sub>4</sub>]<sup>-</sup>), confirming that Eu<sup>3+</sup> ion is complexed with four 2AID molecules. Furthermore, in <sup>1</sup>H-NMR spectra of **K3** ratio of proton signals of N<sup>+</sup>(Et)<sub>4</sub> and 2AID are 20:28, establishing, that Eu<sup>3+</sup> is coordinated with four DBM and one N<sup>+</sup>(Et)<sub>4</sub> molecule.

### 2.2. Absorption properties

The absorption properties of newly synthesized complexes and their ligands were investigated in THF solutions (c~1.5·10<sup>-5</sup>M). Obtained data is collected in Table 1 and spectra shown in Fig.1. 2AID exhibit composite absorption spectra from 260 to 400 nm with multiple maximums at 273 and 283 nm, which can be assigned to π→π\* transitions of benzene ring, and at 301 and 312 nm, which can be assigned to n→π\* transitions. Secondary ligand PHEN also exhibits very intense UV light absorption in the 250-320 nm range with maximum at 290 nm. Furthermore, both ligands show high molar absorbance coefficient ε values. Intense absorption in UV region as well as high ε value affirms that 2AID could act as efficient antenna ligand for Eu<sup>3+</sup> complexes. Absorption spectra of complexes **K1-K3** shows similar profile to the free ligand - 2AID, but with higher intensity to all maximums. Moreover, molar absorbance coefficient ε for complexes shows higher values (36433-58303 M<sup>-1</sup>·cm<sup>-1</sup>) than for free ligand 2AID. A new absorption band in the range from 340-400 nm arises in the spectra due to complexation with metal ion. All three complexes are with different structure, but as it can be seen from their absorption spectra they exhibit similar profile. **K1** and **K3** owing only 2AID ligands have exactly the same UV-Vis band position and the only difference is in the intensity of the band maximums – **K3** with four 2AID ligands absorbs UV light much intensively than **K1**. Complex **K2** exhibits new absorption band at 289 nm due to presence of secondary ligand – PHEN.

**Table 1.** Optical properties of ligands and Eu<sup>3+</sup> complexes in THF solutions and solid-state

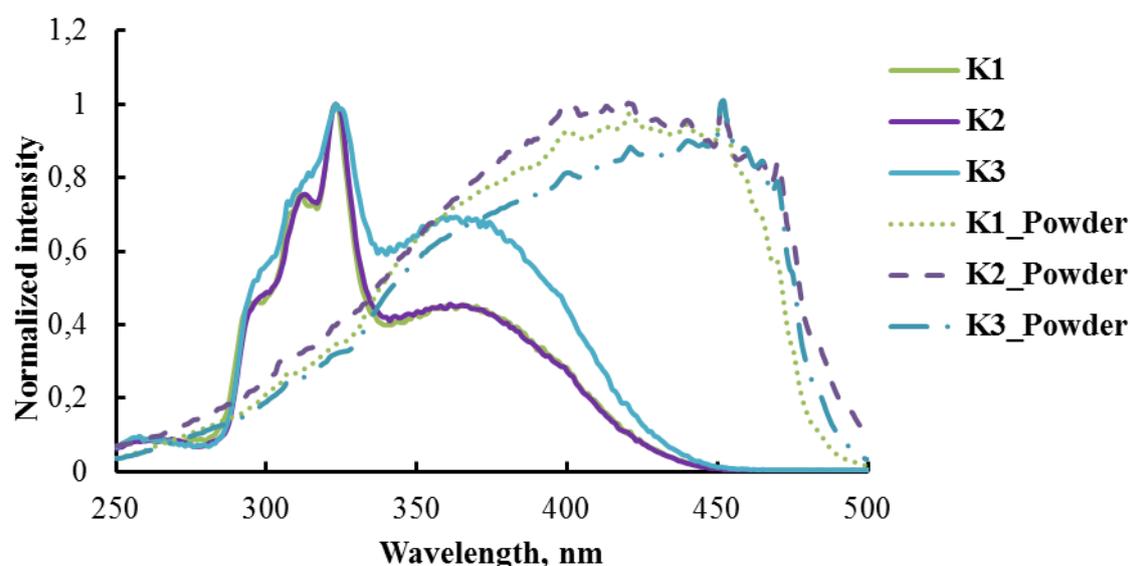
Compound	$\lambda_{\text{abs}}$ , nm ( $\epsilon, \text{M}^{-1} \cdot \text{cm}^{-1}$ )	THF solution			Solid-state		
		$\lambda_{\text{exc}}$ , nm	$\lambda_{\text{em}}$ , nm	PLQY	$\lambda_{\text{exc}}$ , nm	$\lambda_{\text{em}}$ , nm	PLQY
2AID	272 (29307), 283 (29706)	-	-	-	-	-	-
PHEN	290 (50881)	-	-	-	-	-	-
<b>K1</b>	308 (36433), 323 (39053)	322	613	0.02	450	614	0.29
<b>K2</b>	311 (37573), 323 (39053)	322	612	0.02	450	616	0.08
<b>K3</b>	311 (51919), 321 (58303)	322	613	0.03	450	614	0.34



**Fig. 1.** UV/Vis absorption spectra of ligands 2AID and PHEN and complexes **K1-K3** in THF solutions ( $c \sim 1.5 \cdot 10^{-5} \text{M}$ )

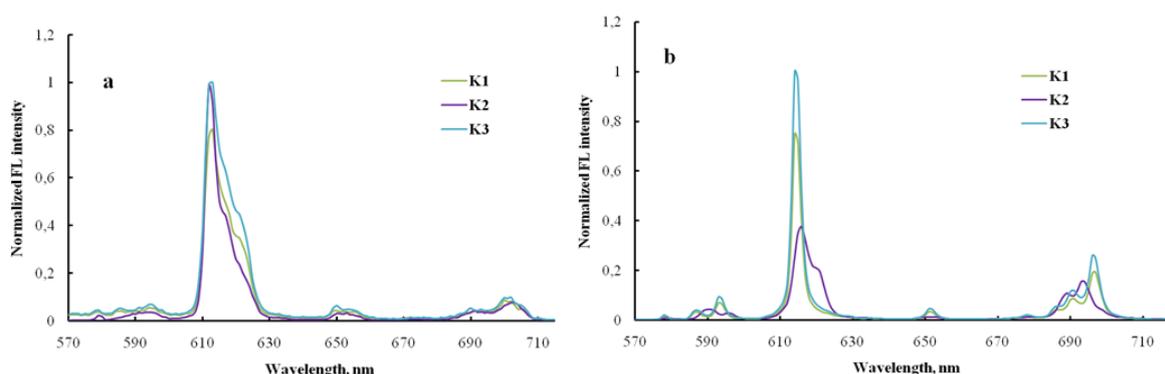
### 2.3. Photoluminescence properties in solid-state and THF solutions

Photoluminescence properties of newly synthesized complexes **K1-K3** were investigated in THF solutions ( $c \sim 1.5 \cdot 10^{-5} \text{M}$ ) and in solid-state. Excitation spectra in solutions and solid-state are shown in Fig.2. In comparison with absorption spectra of complexes **K1-K3** in THF solutions, the excitation spectra monitored at 612 nm also shows intense bands at 311 and 323 nm and intense band with maximum at 363 nm, which can be assigned to newly formed conjugation system of  $\beta$ -diketonate Eu<sup>3+</sup> complex. Also no Eu<sup>3+</sup> ion excitation bands are observed in the spectra (at 296, 362, 381, 394, 415, 466 and 527 nm) indicating, that an efficient energy transfer occurs between ligands and metal ion. As absorption and excitation spectra of **K1-K3** in THF overlaps it can be concluded, that emission arise from energy absorbed by ligands. Excitation spectra in solid-state shows outstanding shift to the visible region of the spectrum. The excitation bands are wide (300-500 nm) with maximum at 450 nm. Such large excitation bands red shift compared to the ones in solutions are very worthy, because in many luminescent material applications, such as in biological labeling, UV light cannot be used as excitation source, due to potential damage to live organisms, therefore there is explicit demand for Eu<sup>3+</sup> organic complexes with visible light excitation wavelength.



**Fig. 2.** Excitation spectra ( $\lambda_{\text{mon}}=612$  nm) of complexes in THF solutions and in solid-state

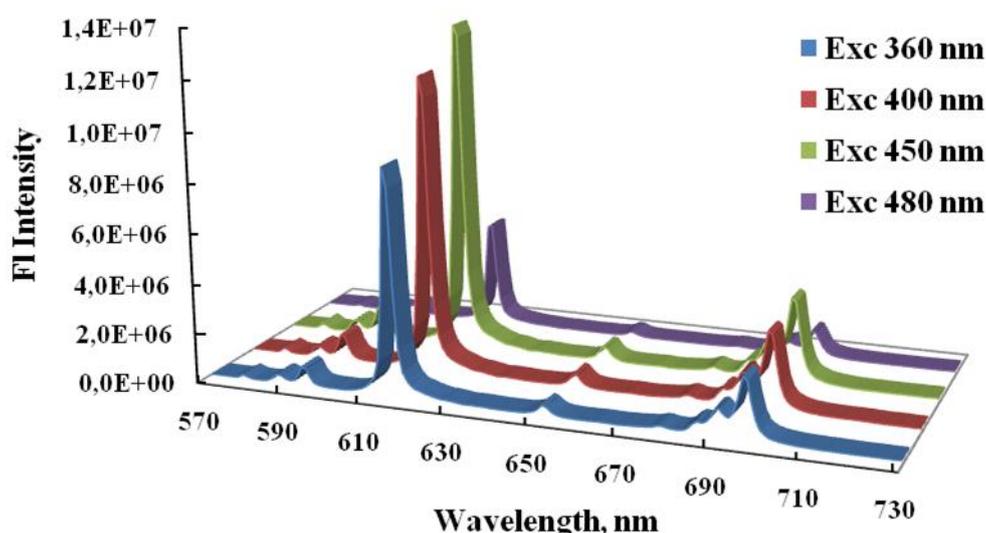
Emission spectra in THF and solid-state are depicted in Fig.3 and all spectra contains characteristic narrow emission bands at 579, 594, 613, 650 and 702 nm corresponding to the transitions  $^5D_0 \rightarrow ^7F_J$  ( $J=0-4$ ) of  $\text{Eu}^{3+}$  ion. Between all emission lines one at 613 nm is the most intense and is influenced by coordination environment of  $\text{Eu}^{3+}$  ion. As it can be seen, intensity of transition  $^5D_0 \rightarrow ^7F_2$  (613 nm) changes depending on complex structure. As it was expected, in solutions intensity decreases in following order:  $\mathbf{K3} > \mathbf{K2} > \mathbf{K1}$ . The lowest intensity for **K1** can be explained with presence of water molecules in  $\text{Eu}^{3+}$  ion coordination sphere. These solvent molecules usually promote non-radiative deactivation process of  $\text{Eu}^{3+}$  ion. Similar conclusions were made for other  $\beta$ -diketone  $\text{Eu}^{3+}$  complexes (Li 2013, Teotonio, 2006, Wang 2012).



**Fig. 3.** Emission spectra ( $\lambda_{\text{exc}}=322$  nm) in THF solutions (a) and in solid-state ( $\lambda_{\text{exc}}=450$  nm) (b)

Replacement of water molecules with one PHEN or 2AID molecule leads to increase of complex luminescence intensity, due to effective shielding of  $\text{Eu}^{3+}$  ion from surrounding environment as well as decreased non-radiative deactivation of  $\text{Eu}^{3+}$  ion due to absence of OH oscillators in coordination sphere of this metal ion. Furthermore, in solutions dominant emission bands at 613 nm shows broadening, due to complexes sensitivity to local environment. In THF the complexes are exposed to collisions with solvents molecules as well as electrostatic interactions, which lead to emission lines

broadening (Malba, 2015). Absolute photoluminescence quantum yields PLQY (Table 1) are below 4% for all complexes, indicating, that emission in solutions for these complexes is non-effective process. However, from data depicted in Fig.3 (b) it can be seen, that in solid-state *tris* **K1** and *tetrakis* **K3** complexes exhibit quite different shape of emission lines (much narrower) with enhanced intensity than in solutions, due to different orientations of complex molecules in different states and also absence of solvents molecules. *Ternary* complex **K2** did not show difference in the shape of emission spectra in solution and solid-state. Similar emission spectrum shape dependence on complex structure was reported for other *ternary* and *tetrakis*  $\text{Eu}^{3+}$ - $\beta$ -diketone complexes (Lunstroot, 2010). Moreover, in solid-state the emission line at 696 nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_4$ ) shows enhanced intensity and comparing intensity ratio between  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  lines for complex **K3** in solution ( $I(^5\text{D}_0 \rightarrow ^7\text{F}_2)/I(^5\text{D}_0 \rightarrow ^7\text{F}_4)=10,09$ ) and in solid-state ( $I(^5\text{D}_0 \rightarrow ^7\text{F}_2)/I(^5\text{D}_0 \rightarrow ^7\text{F}_4)=3,85$ ) it can be concluded, that in solid-state emission at 696 nm is enhanced more than three times. PLQY in solid-state are higher than in solution with moderate values (8-34%), for example, complex **K1** quantum yield in solid-state is 14,5 times higher than in solution.



**Fig. 4.** Influence of excitation wavelength on emission spectra intensity of complex **K3** in solid-state.

As it can be seen from Fig.2 2AID  $\text{Eu}^{3+}$  complexes in solid-state exhibit wide excitation window (300-500 nm), therefore experiments about different  $\lambda_{\text{exc}}$  impact on emission spectrum intensity was carried out. Four different  $\lambda_{\text{exc}}$  (360, 400, 450 and 480 nm) were used and acquired spectra for complex **K3** are depicted in Fig.4. As it was expected the highest intensity for emission line at 614 nm was acquired using 450 nm as excitation wavelength, indicating, that these complexes in solid-state shows enhanced emission with visible light as excitation source. When complex is excited with 360 nm, a large degree of absorbed energy is lost in non-radiative processes than to excited state energy transfer between ligands and metal ion, therefore emission intensity decreases. However, when excited with 450 nm, the larger degree of absorbed energy is used for ligand to fluorescence than lost in other processes. Similar dependence of excitation wavelength impact on emission line intensity was reported for *ternary*  $\text{Eu}^{3+}$  complex with 1-thiophenyl-3-(4-(4-pentylcyclohexyl)phenyl)propan-1,3-dione and PHEN ligands (Knyazev, 2016). Complexes **K1** and **K3** also showed the highest emission spectra intensity, when excited with 450 nm.

#### 2.4. Thermal properties

Thermogravimetric (TG) analyses of synthesized complexes **K1-K3** were carried out to investigate their thermal stability as well as water content. TG analyses were acquired at nitrogen atmosphere in temperature range from 35 to 880 °C and TG curves are shown in Fig.5. For all  $\text{Eu}^{3+}$  complexes with 2AID ligands **K1-K3**  $T_{5\%}$  ( $T_{5\%}$  is temperature of 5% weight loss) are 316, 300 and 326 °C, respectively. Hydrated complex **K1** shows mass loss of 2,5% at temperature range 40-140 °C, which corresponds water molecule loss (theoretical 2,5%). After this loss of water molecules, complex with structure  $\text{Eu}(\text{2AID})_3$  is formed and it shows only one gently sloping mass loss stage from 327 to 880 °C corresponding to loss of only one 2AID molecule. Probably in this temperature range complex undergoes a series of complicated decomposition reactions, which leads to residual of  $\text{Eu}_2\text{O}_3$  with mass of 67,6%. Whereas no weight loss was observed for complexes **K2** and **K3** in temperature range from 40-140 °C, indicating on the absence of solvent molecules in the complexes structure. Complex **K3** exhibit two mass loss stages around 310-408 and 409-880 °C. First weight loss step (13,6%) corresponds to the loss of  $\text{N}^+(\text{Et})_4$  molecule, but second stage (39,3%) – to two 2AID molecules. **K3** also shows large residual weight of 46,9%, which could be mass of  $\text{Eu}_2\text{O}_3$ . Ternary complex **K2** exhibits the lowest  $T_{5\%}$  and similar to **K3** shows two major mass loss stages (283-454 and 455-880 °C). In the first stage (20,1%) PHEN molecule is lost (theoretical – 20,2%), and in the second stage 2AID molecules are lost. As it can seen from obtained results presence of PHEN molecule in the  $\text{Eu}^{3+}$  complexes with 2AID ligands lower their thermal stability. However newly synthesized complexes are thermally stable enough to be used as emitting layers in OLED.

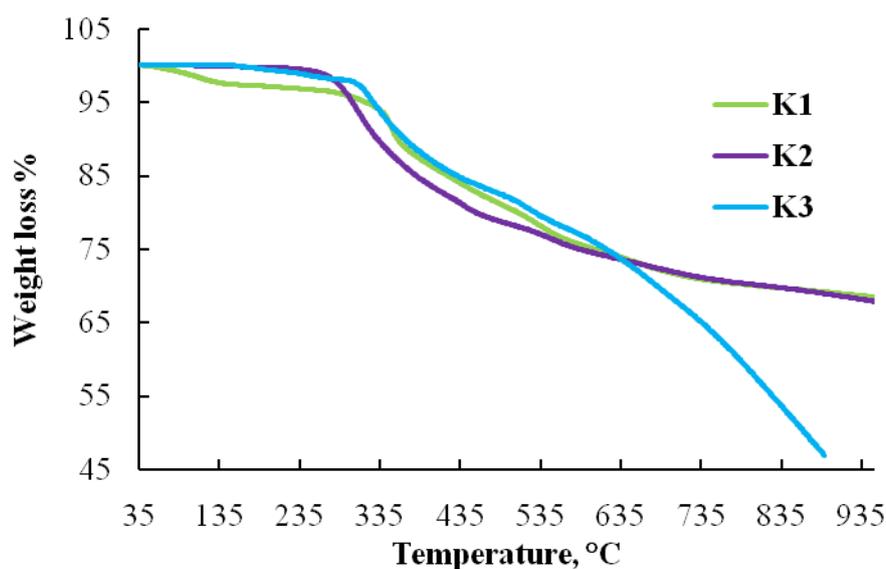
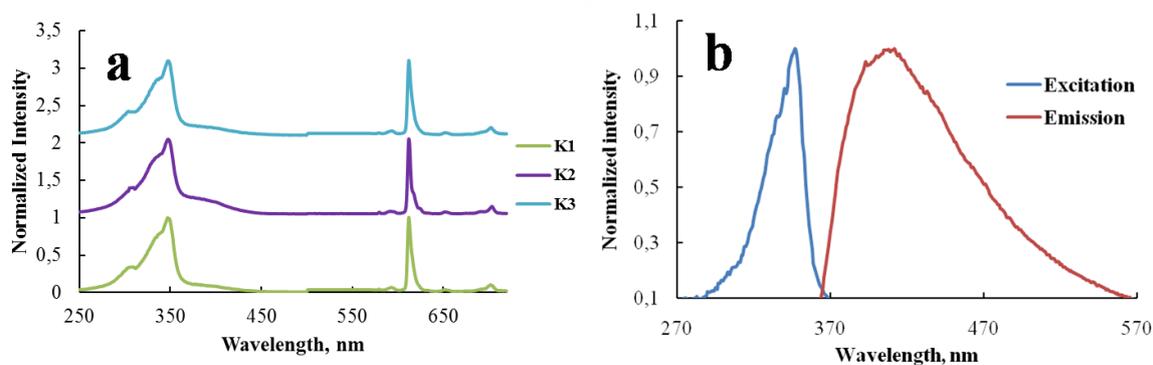


Fig. 5. Thermogravimetric curves of complexes **K1-K3**.

#### 2.5. Optical properties of poly-vinylcarbazole films doped with $\text{Eu}^{3+}$ complexes

$\text{Eu}^{3+}$  organic complexes usually display poor film formability, therefore for practical application, for example in emitting layers of OLED, doped polymer films is used (Ma 1998, Yu 2000). Doping organic complex in polymer matrix also improve its thermal and photo-stability as well as mechanical properties. For  $\text{Eu}^{3+}$  complexes with  $\beta$ -diketone ligands usually poly methyl methacrylate (PMMA) or poly-N-vinylcarbazole (PVK) are being used. In this work PVK was used as polymer matrix for complexes **K1-K3** due to good overlap between emission spectra of polymer and absorption spectra of  $\text{Eu}^{3+}$  complex. PVK thin films doped with 8 wt% of complex **K1-K3** were prepared by spin-coating method from THF. Excitation and emission spectra of polymer films are shown in Fig. 6 (a). Excitation spectra of PVK films show the same profile as pure PVK film (Fig. 6 (b)), except a

shoulder from 360-420 arises due to doped  $\text{Eu}^{3+}$  complex. Due to this new band there is wider overlap between polymer emission spectra (Fig. 6. (b) 370-570 nm) and excitation spectra of doped polymer films, therefore one can expect energy transfer between polymer matrix and  $\text{Eu}^{3+}$  complexes. Such energy transfer would be great advantage for thin PVK films containing  $\text{Eu}^{3+}$  organic complexes with 2AID ligands, because polymer host would provide additional excitation energy for complex, which would lead to increased emission intensity of film.



**Fig. 6.** (a)- Excitation (left) spectra ( $\lambda_{\text{mon}}=612$  nm) and emission (right) spectra ( $\lambda_{\text{exc}}=350$  nm) of doped PVK films with 8 wt% of complex **K1-K3**; (b) – Excitation spectra ( $\lambda_{\text{mon}}=455$  nm) and emission spectra ( $\lambda_{\text{exc}}=350$  nm) of pure PVK film

As it was expected emission spectra of all doped polymer films contains only  $\text{Eu}^{3+}$  characteristic emission bands and no PVK emission at 455 nm was observed, indicating on successful energy transfer between host and complex. The most intense emission with PLQY of 7% was observed for *ternary* complex **K2**, due to excellent solubility of this complex in solution of THF and PVK. Other two complexes **K1** and **K3** showed low solubility in solution of THF and PVK and it is possible, that in these films complex mass was below 8%, therefore obtained PLQY were low (2%).

## CONCLUSIONS

Synthesis and systematic investigation of optical and thermal properties of three  $\text{Eu}^{3+}$  complexes with 2-acetyl-1,3-indandione ligands with general formulas:  $\text{Eu}(\text{2AID})_3(\text{H}_2\text{O})$  (*tris*complex),  $\text{Eu}(\text{2AID})_3(\text{PHEN})$  (*ternary* complex) and  $[\text{Eu}(\text{2AID})_4]\text{N}(\text{Et})_4$  (*tetrakis* complex) were reported. The structures of complexes were characterized with elemental analysis, FT-IR,  $^1\text{H-NMR}$  and mass spectroscopy. In solutions all complexes exhibit strong near UV light absorption (250-400 nm), red-light emission with narrow emission bands at 579, 594, 613, 650 and 702 nm and low absolute photoluminescence quantum yields (2-3%). However, in solid-state, independently from structure all complexes shows strong blue light absorption with maximum at 450 nm and enhanced intensity red-light emission with photoluminescence quantum yields in the range from 8-34%. From all three complexes – *tetrakis* complex exhibit the highest thermal stability (326 °C), as well as enhanced photoluminescence properties and highest quantum yields in both solutions and solid-state, due four 2AID molecules in  $\text{Eu}^{3+}$  coordination sphere, which leads to more effective excited energy transfer to  $\text{Eu}^{3+}$  ion.

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## REFERENCES

- Bala, M., Kumar, S., Boora, P., Taxak, V.B., Khatkar, A., Khatkar, S.P 2014, 'Enhanced optoelectronics properties of europium(III) complexes with  $\beta$ -diketone and nitrogen heterocyclic ligands', *Journal of Materials Science: Materials in Electronics*, vol. 25, pp. 2850–2856.
- Binnemans, K 2009, 'Lanthanide-Based Luminescent Hybrid Materials', *Chemical Reviews*, vol. 109, pp. 4283-4374.
- Jingya, L., Hongfeng, L., Pengfei, Y., Peng, C., Guangfeng, H., Guangming, L 2012, 'Synthesis, Crystal Structure, and Luminescent Properties of 2-(2,2,2-Trifluoroethyl)-1-indone Lanthanide Complexes', *Inorganic Chemistry*, vol. 51, pp. 5050–5057.
- Knyazev, A.A., Krupin, A.S., Romanova, K.A., Galyametdinov, Y.G 2016, 'Luminescence and energy transfer in poly(N-vinylcarbazole) blends doped by a highly anisometric Eu(III) complex. *Journal of Coordination Chemistry*, vol. 69, pp. No. 9
- Li, W., Yan, P., Hou, G., Li, H., Li, G 2013. 'Efficient red emission from PMMA films doped with 5,6-DTFI europium(III) complexes: synthesis, structure and photophysical properties. *Dalton Transactions*, vol. 42, pp. 11537-11547.
- Lunstrook, K., Driesen, K., Nockemann, P., Viau, L., Mutin, P. H., Vioux, A., Binnemans, K, 2010, 'Ionic liquid as plasticizer for europium(III)-doped luminescent poly(methyl methacrylate) films', *Physical Chemistry Chemical Physics*, vol. 12, pp. 1879-1885.
- Ma, D.G., Wang, D.K., Hong, Z.Y., Zhao, X.J., Jing, X.B., Song F 1998, 'Bright red electroluminescent devices based on a soluble lanthanide complex  $\text{Eu}(\text{DBM})_3(\text{phen})$ ', *Chinese journal of chemistry*, vol. 16 No.1, pp. 1-6.
- Malba, C.M., Enrichi, F., Facchina, M., Demitri, N., Plaisier, J.R., Natile, M.M., Selva, M., Riello, P., Perosa, A., Benedetti, A 2015, 'Phosphonium-based tetrakis dibenzoylmethane Eu(III) and Sm(III) complexes: synthesis, crystal structure and photoluminescence properties in a weakly coordinating phosphonium ionic liquid', *RSC Advances*, vol. 5, pp. 60898-60907.
- Teotonio, E.E.S., Brito, H.F., Viertler, H., Faustino, W.M., Malta, O.L., Sa, G.F., Claudia, M., Felinto, F.C., Santos, R.H.A., Cremona, M 2006, 'Synthesis and luminescent properties of  $\text{Eu}^{3+}$ -complexes with 2-acyl-1,3-indandionates (ACIND) and TPPO ligands: The first X-ray structure of Eu-ACIND complex', *Polyhedron*, vol. 25, pp. 3488–3494.
- Teotonio, E.E.S., Brito, H.F., Cremona, M., Quirino, W.G., Legnani, C., Felinto, M.C.F.C 2009, 'Novel electroluminescent devices containing  $\text{Eu}^{3+}$ -(2-acyl-1,3-indandionate) complexes with TPPO ligand', *Optical Materials*, vol. 32, pp. 345–349.
- Wang, D., Zheng, C., Fan, L., Hu, Y., Zheng, J 2014, 'Photoluminescence behavior of europium (III) complexes containing 1-(4-tert-butylphenyl)-3-(2-naphthyl)-propane-1,3-dione ligand', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 117, pp. 245–249.
- Wang, D., Zheng, C., Fan, L., Zheng, J., Wei, X 2012, 'Preparation and fluorescent properties of europium(III) complexes with  $\beta$ -diketone ligand and 1,10-phenantroline. *Synthetic metals*, vol. 162, pp. 2063-2068.
- Yu, G., Liu, Y., Wu, X., Zhu D 2000, 'Soluble Europium Complexes for Light-Emitting Diodes', *Chemistry of Materials*, vol. 12, pp. 2537-2541.