Luminescence of Europium Complexes with Triazole-Containing Ligands

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Abstract In the present work, eleven new complexes of europium and terbium with substituted azoles ligands were obtained as candidates for sensor materials for phosphin oxide. As a result, a new material with high sensitivity of up to 9%/μL was obtained.

Keywords luminescence, europium, sensor, triazole, triphenylphosphine oxide

Introduction

The unique luminescent properties of lanthanide coordination compounds (CCs) make them ideal materials for sensor applications.^[1–3] Indeed, unlike any other class of compounds, in particular organic dyes, they demonstrate high Stokes shift values and narrow emission bands, which allow easy to separate the excitation beam and emitted light easily. The constant position of the bands, the unique lanthanide property, allows exact tuning of the detectors. Europium complexes are often used due to the combination of high photoluminescence quantum yields (PLQYs).^[4–6] Among these materials, aromatic carboxylates^[7–12] and β-diketonates^[13–16] play an important role due to high PLQYs values and high chemical stability. Very little attention is paid to complexes with NH-acid anions as anionic ligands. At the same time, the use of europium CCs in bioimaging often involves obtaining conjugates based on them, for example, containing biologically active fragments such as peptides.^[17–19] Conjugation is often carried out by the reaction of azide-alkyne Huisgen cycloaddition,^[20–23] during which a triazole-containing compound is formed. However, the role of triazole in lanthanide luminescence is also poorly understood.

Thus, the purpose of this work was to study the luminescent properties of a number of europium compounds with pyrazole and triazole-containing ligands (Figure 1). The corresponding core is marked in red. The substituent variation was selected to adjust the luminescent properties, in particular luminescence intensity. Ligand H₂L⁷ was added to the set of ligands to investigate the luminescence dependence on the presence of pyrazole, not only triazole. HL² was additionally used to compare the role of triazole with tetrazole. Two CCs of terbium, as well as a CC with a tetrazole-containing ligand, are also included in the study.

Owing to listed unequaled properties, lanthanide CCs are very promising materials with a number of applications including sensor materials. Among the sensor materials, sensors for phosphine oxides are important since a number of chemical warfare agents such as sarin and soman correspond to this class of compounds.^[24] The search of sensors for the materials is preferable to avoid working with them directly. As a substitute for the selected phosphine oxides, another phosphine oxide, namely triphenylphosphine oxide (TPPO), was used in the present work.^[25] The objective of the work was to obtain complexes with very good sensory properties. In particular, they should have sufficient luminescence intensity to ensure the

Figure 1 Selected ligands.

possibility of its quenching by TPPO. On the other hand, the luminescence should not be very intense, so that the quenching effect would be significant.

Experimental

Materials and methods

Sodium ascorbate and methyl propiolate were purchased from abcr; *t*-BuOH, THF, DCM, EtOAc, CuSO₄·5H₂O, HCl and KOH were obtained from IREA 2000; EuCl₃·6H₂O, TbCl₃·6H₂O, and 1,10-phenanthroline (Phen) were achieved from Sigma Aldrich. Precursors were used without additional purification.

IR spectra were registered on a Thermo Scientific Nicolet iS5 FTIR spectrometer with iD1 Transmission and iD7 ATR (diamond) accessories. ¹H NMR and ¹³C NMR spectra were acquired on Bruker Avance 400 (400 and 101 MHz, respectively), Bruker DRX-500 (500 and 126 MHz, respectively), Bruker AM-300 (300 and 75 MHz, respectively), and Bruker Avance IIIHD 500 (500 and 126 MHz, respectively) spectrometers at 298 K (unless other temperature is indicated). For ¹H NMR and ¹³C NMR, TMS was used as internal standard. Mass spectra were recorded on a Finnigan MAT INCOS-50 (direct injection, EI, 70 eV) mass spectrometer. High-resolution mass spectra were recorded on a Bruker MicroOTOFII mass spectrometer with electrospray ionization. Elemental analysis

was performed on a PerkinElmer Series II 2400 CHNS/O analyzer. Melting points were determined by the capillary method on Stuart SMP20 and Electrothermal IA9000 apparatuses. Monitoring of reaction progress and assessment of the purity of synthesized compounds were done by TLC on Merck TLC Silica gel 60G F254 plates. Carl Roth Silica gel 60, 0.04–0.063 mm, was used for column chromatography. Thermal analysis with mass-detection of the evolved gases was performed on a Netzsch STA449 F1 + QMS403 Aelos thermal analyzer. Luminescence and excitation spectra were measured with the Fluorolog 3 spectrofluorometer over excitation with a xenon lamp.

Synthesis

Methyl 1-[3-(ethoxycarbonyl)-1H-pyrazol-5-yl]-1H-1,2,3-triazole-4-carboxylate (HL¹). Ethyl 5-azido-1H-pyrazole-3-carboxylate (obtained as in Ref. [26]) (1.7 mmol) and methyl propiolate (1.7 mmol) were dissolved in *t*-BuOH (4 mL). A solution of sodium ascorbate (34 mg, 0.17 mmol, 10 mol%) in H₂O (2 mL) was added with vigorous stirring to the reagent solution. The flask was evacuated and filled with argon. A solution of CuSO₄·5H₂O (21 mg, 0.085 mmol, 5 mol%) in H₂O (2 mL) was then added to the reaction mixture. The reaction mixture was stirred at 25 °C for 12 h, and the mixture was poured into ice water. The formed precipitate was filtered off and washed with a small amount of H₂O, then dried in a vacuum desiccator over P₂O₅. The filtrate was extracted with EtOAc. Then, the organic phase was separated and dried over anhydrous Na₂SO₄. The dried organic phase was evaporated under reduced pressure on the rotary evaporator to afford a solid. Both solids were combined. Yield 390 mg (86%), beige solid, m.p. 190–191 °C. IR (KBr) ν_{max} : 3196 (NH), 1719 (C=O), 1684 (C=O) cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 14.59 (1H, s, NH), 9.28 (1H, s, H-5 triazole), 7.29 (1H, s, H-4 pyrazole), 4.35 (2H, q, *J* = 6.9 Hz, OCH₂CH₃), 3.86 (3H, s, OCH₃), 1.33 (3H, t, *J* = 6.9 Hz, OCH₂CH₃). ¹³C NMR (101 MHz, DMSO-*d*₆) δ : 160.4, 158.2, 145.4, 139.2, 135.4, 127.4, 100.6, 61.5, 52.1, 14.1. HRMS (ESI): calcd for C₁₀H₁₂N₅O₄ [M+H]⁺ 266.0884, found 266.0886. Calcd for C₁₀H₁₁N₅O₄: C 45.29, H 4.18, N 26.41. Found: C 45.31, H 4.08, N 26.43.

5-[4-(Hydroxymethyl)-1H-1,2,3-triazol-1-yl]-1H-pyrazole-3-carboxylic acid (H₂L⁵). Ethyl 5-[4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl]-1H-pyrazole-3-carboxylate (obtained as in Ref. [26]) (0.0019 mol) was dissolved in aqueous KOH (330 mg, 0.0059 mol; 25 mL of solution). The formed solution was stirred at 60 °C for 12 h. Then, the solution was passed through a thin layer of silica gel and acidified by 2 M aqueous HCl to pH 1. The formed precipitate was filtered off and dried in a vacuum desiccator over P₂O₅. The filtrate was extracted with EtOAc, then the organic phase was separated and dried over anhydrous Na₂SO₄. The dried organic phase was evaporated under reduced pressure on the rotary evaporator to afford a solid. Both solids were combined. Yield 318 mg (80%), orange solid, m.p. 264–265 °C. IR (KBr) ν_{max} : 3213 (OH), 2971–2350 (COOH), 1699 (C=O) cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 14.27 (1H, s, NH), 13.81 (1H, br. s, COOH), 8.45 (1H, s, H-5 triazole), 7.11 (1H, s, H-4 pyrazole), 5.29 (1H, br. s, CH₂OH), 4.58 (2H, s, CH₂OH). ¹³C NMR (101 MHz, DMSO-*d*₆) δ : 160.0, 148.7, 146.2, 136.6, 120.9, 99.4, 54.8. HRMS (ESI): calcd for C₇H₈N₅O₃ [M+H]⁺ 210.0622, found 210.0614.

5-(4-Phenyl-1H-1,2,3-triazol-1-yl)-1H-pyrazole-3-carboxylic acid (H₂L⁶). Ethyl 5-(4-phenyl-1H-1,2,3-triazol-1-yl)-1H-pyrazole-3-carboxylate (obtained as in Ref. [26]) (0.0019 mol) was dissolved in aqueous KOH (330 mg, 0.0059 mol; 25 mL of solution). The formed solution was stirred at 60 °C for 12 h. Then, the solution was passed through a thin layer of silica gel and acidified by 2 M aqueous HCl to pH 1. The formed precipitate

was filtered off and dried in a vacuum desiccator over P₂O₅. The filtrate was extracted with EtOAc, and the organic phase was separated and dried over anhydrous Na₂SO₄. The dried organic phase was evaporated under reduced pressure on the rotary evaporator to afford a solid. Both solids were combined. Yield 344 mg (71%), colourless solid, m.p. 269–270 °C. IR (KBr) ν_{max} : 3141 (NH), 2985 (OH), 1689 (C=O) cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 14.38 (1H, s, NH), 13.88 (1H, br. s, COOH), 9.18 (1H, s, H-5 triazole), 7.98 (2H, d, *J* = 7.3 Hz, H Ph), 7.48 (2H, t, *J* = 7.5 Hz, H Ph), 7.37 (1H, t, *J* = 7.3, H Ph), 7.19 (1H, s, H-4 pyrazole). ¹³C NMR (101 MHz, DMSO-*d*₆) δ : 159.8, 146.9, 146.2, 136.5, 130.0, 129.0, 128.4, 125.5, 119.5, 99.6. HRMS (ESI): calcd for C₁₂H₁₀N₅O₂ [M+H]⁺ 256.0829, found 256.0834.

1-(3-Carboxy-1H-pyrazol-5-yl)-1H-1,2,3-triazole-4-carboxylic acid (H₃L³). Methyl 1-[3-(ethoxycarbonyl)-1H-pyrazol-5-yl]-1H-1,2,3-triazole-4-carboxylate (obtained as in Ref. [26]) (0.0019 mol) was dissolved in aqueous KOH (330 mg, 0.0059 mol; 25 mL of solution). The formed solution was stirred at 60 °C for 12 h. Then, the solution was passed through a thin layer of silica gel and acidified by 2 M aqueous HCl to pH 1. The formed precipitate was filtered off and dried in a vacuum desiccator over P₂O₅. The filtrate was extracted with EtOAc. Then, the organic phase was separated and dried over anhydrous Na₂SO₄. The dried organic phase was evaporated under reduced pressure on the rotary evaporator to afford a solid. Both solids were combined. Yield 340 mg (80%), colourless solid, m.p. 190–191 °C. IR (KBr) ν_{max} : 3142 (NH), 3088–2526 (COOH), 1694 (C=O) cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 14.38 (1H, s, NH), 13.59 (2H, br. s, COOH), 9.13 (1H, s, H-5 triazole), 7.20 (1H, s, H-4 pyrazole). ¹³C NMR (101 MHz, DMSO-*d*₆) δ : 161.4, 159.7, 145.5, 140.3, 136.6, 127.1, 100.4. HRMS (ESI): calcd for C₇H₆N₅O₄ [M+H]⁺ 224.0414, found 224.0414.

5,5'-(4,4'-[(1,5-Dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)bis(methylene)]bis(1H-1,2,3-triazole-4,1-diyl))bis(1H-pyrazole-3-carboxylic acid) hydrochloride dihydrate (18-HCl·2H₂O) (H₄L⁴). Diethyl 5,5'-(4,4'-[(1,5-dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)bis(methylene)]bis(1H-1,2,3-triazole-4,1-diyl))bis(1H-pyrazole-3-carboxylate) (obtained as in Ref. [26]) (1.543 g, 0.0025 mol) was dissolved in aqueous KOH (0.56 g, 0.01 mol; 25 mL of solution). The formed solution was stirred at 70 °C for 24 h. Then, the solution was passed through a thin layer of silica gel and acidified by 2 M aqueous HCl to pH 2–3. The formed beige precipitate was filtered off, washed with a small amount of cold H₂O, and dried in a vacuum desiccator over P₂O₅ to constant weight. Yield 933 mg (68%), light-grey solid, m.p. 267–268 °C. IR (KBr) ν : 3111 (OH), 1713 (C=O) cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 14.28 (2H, s, NH), 11.52 (2H, br. s, COOH), 8.80 (2H, s, H-5 triazole), 7.11 (2H, s, H-4 pyrazole), 4.24 (4H, s, 2NCH₂), 3.62 (4H, d, *J* = 10.6 Hz, 2CH₂ bispidine), 2.96 (4H, d, *J* = 10.6 Hz, 2CH₂ bispidine), 0.87 (6H, s, 2CH₃). ¹³C NMR (126 MHz, DMSO-*d*₆) δ : 208.7, 159.8, 146.0, 139.4, 137.1, 123.7, 99.2, 62.2, 49.6, 45.6, 16.0. HRMS (ESI): calcd for C₂₃H₂₇N₁₂O₅ [M+H]⁺ 551.2222, found 551.2213. Calcd for C₂₃H₃₁ClN₁₂O₇: C 44.34, H 5.02, N 26.98. Found: C 44.40; H 5.50; N 26.90.

Diethyl 2,2'-(4,4'-[(1,5-dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)bis(methylene)]bis(1H-1,2,3-triazole-4,1-diyl))diacetate (H₂L⁷). 1,5-Dimethyl-3,7-di(prop-2-yn-1-yl)-3,7-diazabicyclo[3.3.1]nonan-9-one (obtained as in Ref. [26]) (732 mg, 3.0 mmol) and ethyl 2-azidoacetate (774 mg, 6.0 mmol) were dissolved in 7.5 mL of *tert*-butanol under argon. Solutions of sodium ascorbate (160 mg, 0.3 mmol) in 1.9 mL of water and CuSO₄·5H₂O in 1.9 mL of water were added sequentially. A reaction mixture was stirred at r.t. for 24 h. The

solution was evaporated to dryness and quenched with 50 mL of DCM and 10 mL water. The organic layer was separated and washed with several portions of 15 mL of water until discoloration of water layer. The organic layer was dried over sodium sulfate and evaporated to dryness. Yield 1.103 g (73%), sticky oil. ^1H NMR (400 MHz, DMSO- d_6) δ : 7.96 (2H, s, H-5 triazole), 5.35 (4H, s, CH_2CO_2), 4.16 (4H, t, $J = 7.2$ Hz, CH_2CH_3), 3.64 (4H, s, NCH $_2$), 2.98 (4H, d, $J = 10.6$ Hz, 2CH $_2$ bispidine), 2.32 (4H, d, $J = 10.6$ Hz, 2CH $_2$ bispidine), 1.19 (6H, d, $J = 7.2$ Hz, CH_2CH_3), 0.83 (6H, s, 2CH $_3$). ^{13}C NMR (101 MHz, DMSO- d_6) δ : 214.3, 167.2, 143.4, 125.1, 64.4, 61.4, 51.0, 50.3, 45.9, 20.0, 14.0. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{35}\text{N}_8\text{O}_5$ $[\text{M}+\text{H}]^+$ 503.2730, found 503.2735.

Potassium 2,2'-(4,4'-((1,5-dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)bis(methylene))bis(1*H*-1,2,3-triazole-4,1-diyl))diacetate (K_2L^7). H_2L^7 (706 mg, 1.4 mmol) was dissolved in 11 mL of THF and 3.23 mL of aqueous 0.87 M KOH solution was added. The reaction mixture was refluxed overnight and evaporated to dryness. Yield 730 mg (99%), white powder. ^1H NMR (400 MHz, DMSO- d_6) δ : 7.73 (2H, s, H-5 triazole), 4.57 (4H, s, CH_2CO_2), 3.58 (4H, s, NCH $_2$), 2.98 (4H, d, $J = 10.7$ Hz, 2CH $_2$ bispidine), 2.31 (4H, d, $J = 10.6$ Hz, 2CH $_2$ bispidine), 0.83 (6H, s, 2CH $_3$). ^{13}C NMR (101 MHz, water- d_2) δ : 220.5, 172.4, 142.0, 125.8, 63.7, 52.8, 49.6, 46.3, 18.1. Calcd for $\text{C}_{19}\text{H}_{24}\text{K}_2\text{N}_8\text{O}_5$: C 43.66, H 4.63, N 21.44. Found: C 43.48, H 4.72, N 21.34.

$\text{Eu}(\text{L}^1)_3(\text{H}_2\text{O})_4$ (I). The dry HL ligand (0.12 mmol) was dissolved in water solution of KOH or NaHCO_3 (0.12 mmol), stirred with a heated magnetic stirrer (15 min, 80 °C) and added to $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.04 mmol) dissolved in water. The resulting solution was filtered and dried in air for recrystallization. As a result, a poorly emitting materials **I** and **II** were obtained using KOH and NaHCO_3 , respectively.

$\text{Eu}(\text{L}^2)_3(\text{H}_2\text{O})_4$ (III). The dry HL^2 ligand (0.089 mmol) was dissolved in water solution of KOH (0.089 mmol), stirred using a heated magnetic stirrer (15 min, 80 °C) and added to $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved in water (0.03 mmol). The resulting solution was filtered and dried in air for recrystallization. As a result, luminescent complex **III** $\text{Eu}(\text{L}^2)_3(\text{H}_2\text{O})_4$ was obtained.

$\text{Eu}(\text{L}^3)_3(\text{H}_2\text{O})_4$ (IV). The dry ligand H_3L^3 (0.134 mmol) was dissolved in water solution of KOH (0.402 mmol), stirred using a heated magnetic stirrer (15 min, 80 °C), and added to $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, dissolved in water (0.134 mmol). The resulting solution was filtered and dried in air for recrystallization. After drying, it was centrifuged 2 times (5 min each). As a result, the luminescence complex **IV** $\text{Eu}(\text{L}^3)_3(\text{H}_2\text{O})_4$ was obtained.

$\text{Eu}_4(\text{L}^4)_3(\text{H}_2\text{O})_4$ (V). The dry ligand H_4L^4 (0.05 mmol) was dissolved in water solution of KOH (0.22 mmol), stirred using a heated magnetic stirrer (15 min, 80 °C), and added to $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, dissolved in water (0.073 mmol). The resulting solution was filtered and dried in air for recrystallization. After drying, it was centrifuged 2 times (5 min each). As a result, the luminescence complex **V** $\text{Eu}_4(\text{L}^4)_3(\text{H}_2\text{O})_4$ was obtained.

$\text{Eu}_2(\text{L}^5)_3(\text{H}_2\text{O})_4$ (VI). Dry ligand H_2L^5 (0.144 mmol) was dissolved in water solution of KOH (0.289 mmol), stirred using a heated magnetic stirrer (15 min, 80 °C), and added to $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, dissolved in water (0.096 mmol). The resulting solution was filtered and dried in air for recrystallization. As a result, luminescent complex **VI** $\text{Eu}_2(\text{L}^5)_3(\text{H}_2\text{O})_4$ was obtained.

$\text{Tb}_2(\text{L}^5)_3(\text{H}_2\text{O})_4$ (VII). Dry ligand H_2L^5 (0.144 mmol) was dissolved in water solution of KOH (0.289 mmol), stirred using a heated magnetic stirrer (15 min, 80 °C), and added to $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, dissolved in water (0.096 mmol). The resulting solution was filtered and dried in air for recrystallization. As a result, luminescent complex **VII** $\text{Tb}_2(\text{L}^5)_3(\text{H}_2\text{O})_4$ was obtained.

$\text{Eu}_2(\text{L}^6)_3(\text{H}_2\text{O})_4$ (VIII). Dry ligand H_2L^6 (0.118 mmol) was dissolved in water solution of KOH (0.236 mmol), stirred using a

heated magnetic stirrer (15 min, 80 °C), and added to $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, dissolved in water (0.079 mmol). The resulting solution was filtered and dried in air for recrystallization. As a result, luminescent complex **VIII** $\text{Eu}_2(\text{L}^6)_3(\text{H}_2\text{O})_4$ was obtained.

$\text{Tb}_2(\text{L}^6)_3(\text{H}_2\text{O})_4$ (IX). The dry H_2L^6 ligand (0.118 mmol) was dissolved in water solution KOH (0.236 mmol), stirred using a heated magnetic stirrer (15 min, 80 °C), and added to $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, dissolved in water (0.079 mmol). The resulting solution was filtered and dried in air for recrystallization. As a result, luminescent complex **IX** $\text{Tb}_2(\text{L}^6)_3(\text{H}_2\text{O})_4$ was obtained.

$\text{Eu}_2(\text{L}^7)_3(\text{H}_2\text{O})_4$ (X). Dry ligand K_2L^7 (0.287 mmol) was stirred using a heated magnetic stirrer (15 min, 80 °C), and added to $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, dissolved in ethanol (0.19 mmol). The resulting solution was evaporated and left in a closed state, filtered with a filter nozzle and a syringe and dried in air for recrystallization. As a result, luminescent complex **X** $\text{Eu}_2(\text{L}^7)_3(\text{H}_2\text{O})_4$ was obtained.

$\text{Eu}_2(\text{L}^7)_3(\text{Phen})$ (XI). Dry ligand K_2L^7 (0.19 mmol) was stirred using a heated magnetic stirrer (15 min, 80 °C), and added to an ethanol solution of a mixture of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ and Phen (0.127 mmol). The resulting solution was filtered using a filter nozzle and a syringe and dried in air for recrystallization. As a result, luminescent complex **XI** $\text{Eu}_2(\text{L}^7)_3(\text{Phen})$ was obtained.

Results and Discussion

In this work, europium complexes with triazole-containing anions of substituted pyrazoles were selected as the objects of research, and the main task was to establish the possibility of obtaining such compounds, as well as the presence of their luminescent properties. On the other hand, it was important to identify the effect of triazole fragments on luminescence quenching and the dependence of luminescence intensity on other functional groups in the ligand. Keeping this in mind, the practical goal was to establish the possibility of using luminescence of these compounds for phosphine oxide sensing an example of TPPO.

Synthesis and characterization

All the complexes were obtained by the exchange reaction between europium chlorides and potassium salts obtained by ligand deprotonation in the KOH solution, which was possible thanks to the sufficient acidity of the selected triazole derivatives. The composition of the compounds was established based on IR and NMR spectroscopy data, as well as on TGA data with mass-spectroscopic analysis of the evolved gases. In the ^1H NMR spectra of the obtained complexes, the same signals were observed in the spectra of corresponding ligands, while their shift and broadening, resulting from the proximity of the paramagnetic europium ion, witnesses the formation of the complex. In particular, the largest broadening and shift was observed for the signals nearest to the deprotonated NH-group, which is exemplified in Figure 1 on example of K_2L^7 and **X**. Such a feature is another evidence of the complex, and it is not just the formation of ligand-europium mixture.

NMR spectroscopy was particularly informative in the analysis of the mixed-ligand complex **XI**. Here, the anionic-to-neutral ligand ratio, which was found to be 3 : 1, was calculated based on the proton signals integration (Figure 2).

Both IR spectroscopy and TGA data witnessed the formation of hydrated complexes (Figure 3). This is indicated by the broad band at ca. 3000–3600 cm^{-1} in the IR spectra, as well as by the low-temperature weight loss, accompanied by the peak in the ionic current with $m/z = 18$, corresponding to water in the TGA data.

This allows concluding the obtaining of the above-

Figure 2 ^1H NMR spectra K_2L^7 , **X**, and **XI** in D_2O . Solvent signal is marked with a star. Phen proton signals are framed.

Figure 3 (a) IR spectrum and (b) TGA curve, as well as ionic currents with $m/z=18$ (water, red) and 44 (CO_2 , blue) of **X**.

mentioned complexes, as well as to determine their composition. However, very important information on the peculiarities of their formation was obtained using luminescence spectroscopy.

Luminescent properties

We immediately noticed that the triazole in the ligand actually leads to the quenching of the luminescence of all the obtained complexes—both of europium and terbium. The luminescence of these compounds was either low-intensity or absent. When discussing the results, we will compare the luminescence intensity of the new compounds among each other. However, in comparison with the high-intensity emitters based on other terbium and europium coordination compounds, the luminescence intensity of all these compounds is low.

Figure 4 (a) Excitation and (b) luminescence spectra of **III**.

In the spectrum of **III**, europium ionic luminescence is not observed, and its spectrum is represented by only ligand luminescence (Figure 4).

Apparently, in this case, the luminescence of europium was absent due to the fact that the triplet level of the ligand is lower in energy than in the excited state of europium. Thus, energy transfer to europium is not observed. This is evidenced by the fact that **III** does not only lack the luminescence of europium but also demonstrate rather high intensity of the ligand luminescence.

Next, we compared the luminescence of europium complexes **I**, **II**, and **IV** with the HL^1 (**I** and **II**) and H_3L^3 ligands (**IV**, see Experimental). It is important that the HL^1 ligand is an ester of H_3L^3 acid. As a result, the complex **IV** with the anion of H_3L^3 acid has a noticeable luminescence of europium, whereas the complex with the HL^1 anion either does not emit at all, or emits extremely weakly, depending on the synthesis technique, during which the deprotonation of the ligand is carried out (compounds **I** and **II**). When a weaker base NaHCO_3 was used for deprotonation, only the NH group is deprotonated, and the obtained complex **II** demonstrates no luminescence. When the

Figure 5 (a) Excitation and (b) luminescence spectra of I, II, and IV.

stronger potassium hydroxide is used, hydrolysis of ester groups takes place with partial formation of H_3L^3 acid, resulting in the appearance of faint luminescence of I.

It signifies that the anion of the H_3L^3 ligand sensitizes the luminescence of europium, unlike the anion of the HL^1 ligand. Thus, complex I, where the HL^1 ligand was deprotonated with KOH, is most likely to be a mixture of II and IV, *i.e.*, europium complexes with (L^1) ligand and with (L^3) $^{3-}$, which was partially formed during the synthesis of I.

Excitation spectra of I, II, and IV are in line with the conclusion made based on emission data. Therefore, the excitation spectrum of I is dominated by a wide through-ligand band centered at ca. 300 nm, while the excitation through Eu ion itself, including its most intense band at 390 nm, corresponding to the ${}^7F_0 \rightarrow {}^5L_6$, is less intense (Figure 5). Excitation spectrum of IV, in contrary, is dominated by through Eu excitation bands, while almost no band can be detected in the excitation spectrum of II due to almost no emission.

The H_4L^4 ligand is a dimer of the H_3L^3 ligand, and the luminescence of europium complexes V with this ligand is comparable in intensity with the one of IV. This is not surprising, and allows concluding that the bridging group, which was used

Figure 6 a) Excitation and b) luminescence spectra of I and V.

to form a dimer, does not affect the luminescent properties. Thus, the formation of a dimer using such a group does not harm luminescence and can also be further used for the formation of conjugates. Excitation spectrum of V is dominated by a wide through-ligand band with less intense through Eu excitation bands and resembles the one of I except for the appearance of an additional through-ligand excitation band at ca. 370 nm, resulted from an additional absorption due to the dimerization (Figure 6).

As for the synthesis of compounds VI and VII with the H_2L^5 ligand, it is important to note that this ligand differs from H_3L^3 in the absence of a second carboxy-group, instead of which there is an OH-group, which is known for its ability to quench europium luminescence. As a result, we observe low luminescence intensity of both the europium complex and the terbium complex.

It is important to show that the quenching of the luminescence of terbium VII with this ligand is not related to the lack of energy transfer from the ligand to the terbium ion, since the energy of the excited state of the terbium ion is higher than that of the europium ion (Figure 7). To this end, we examined

Figure 7 (a) Excitation and (b) luminescence spectra **VI** and **VII**.

the ligand H_2L^6 , which is also synthesized as a complex with europium and terbium. These two ligands differ in replacing the hydroxyl group with phenyl. In this case, the energy of the triplet ligand equation could only decrease, since we introduced an additional conjugated fragment. If terbium luminescence was not observed in the case of **VI** due to the low triplet level of the ligand, terbium luminescence should not be observed in the case of **VIII** either. However, luminescence **IX** was observed, which suggests that the quenching of the terbium ion with a low energy triplet level is not associated in the case of **VII**.

In the cases of **VIII** and **IX**, low-intensity, luminescence of europium and terbium was observed, which is associated with the introduction of another phenyl group, which increases absorption. It remains lower than in the case of H_2L^5 , but it is sufficient to observe the luminescence of europium and terbium ions (Figure 8).

Complex **X** contains an anion of $(L^7)^{2-}$, which differs from $(L^4)^{4-}$ in the absence of two pyrazole rings. As a result, K_2L^7 represents a potassium carboxylate with an anion of not an NH-acid. The formed compound **X** demonstrated detectable

Figure 8 Luminescence spectra of (a) **VIII** and (b) **IX**.

Figure 9 Luminescence spectra of **X** and **XI**.

europium-based luminescence, whose intensity can be expected to be further increased by the introduction of the Phen ligand, which is well-known for its possibility to sensitize europium luminescence. In Figure 9, the luminescence spectra of **X** and **XI** in ethanol solutions of the same concentration are given, representing the relative luminescence intensity of these complexes.

Sensory properties

Based on this data, we selected three complexes as potential TPPO sensor materials that have a detectable

europium luminescence of different intensity, *i.e.*, **VI**, **X**, and **XI**. To the ethanol solutions of TPPO was added dropwise (drop volume equaled to 5 μL), and the luminescence spectra were recorded.

The study revealed that luminescence of both **VI** and **X** was immediately quenched after the first drop of TPPO solution, meaning that these materials cannot be used for TPPO detection (Figure 10). At the same time, complex **XI** containing Phen ligand demonstrated gradual luminescence intensity decrease upon TPPO added volume.

Figure 10 Luminescence spectra of ethanol solutions of (a) **VII** and (b) **IX** upon added TPPO solution in ethanol.

The dependence of the **XI** luminescence intensity on added TPPO solution volume was studied, and the intensity at 612 nm was plotted (Figure 11). It revealed the decreasing dependence, which can be used for the determination of the TPPO presence and concentration. The sensitivity was characterized by a logarithmic derivative of luminescence intensity (I) on TPPO concentration (c) as:

$$Sr = (1/I) \times (dI/dc)$$

It increased upon the decrease of the added TPPO concentration and reached 9%/ μL , making it particularly sensitive to the small concentrations of TPPO.

Conclusions

It was demonstrated that the triazole group quenches luminescence of both europium and terbium. At the same time,

Figure 11 (a) Luminescence spectra of ethanol solution of **XI** upon added TPPO solution in ethanol (b), and (c) luminescence intensity at 612 nm depending on the added TPPO volume.

the addition of a sufficient number of conjugated fragments, which leads to high absorption of ligands, makes it possible to obtain europium complexes with noticeable luminescence. The formation of a dimer using a bispidine framework does not affect luminescent properties and can be used for the formation of luminescent conjugates.

Among the studied compounds, complex **XI** demonstrates enough luminescence, which can be easily quenched in the presence of TPPO at the same time. This allowed to successfully use it as sensors for phosphine oxides, in particular TPPO, with the sensitivity of up to 9%/ μL .

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Conflict of Interest

The authors declare no conflict of interest.

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