



TRIPOD TYPE 2,2'-BIPYRIDINE LIGAND FOR THE LANTHANIDE CATIONS: THE SYNTHESIS AND THE PHOTOPHYSICAL STUDIES ON COORDINATION TO TRANSITION METAL CATIONS

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TRIPOD TYPE 2,2'-BIPYRIDINE LIGAND FOR LANTHANIDE CATIONS: SYNTHESIS AND PHOTOPHYSICAL STUDIES ON COORDINATION TO TRANSITION METAL CATIONS

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Abstract

New tripod-type 2,2'-bipyridine ligand consisting of a central polyaminocarboxylic moiety for the coordination to lanthanide cations and three appended 5-phenyl-2,2'-bipyridine fragments for the coordination to various transition metal cations have been prepared. A europium complex of this ligand was prepared, and its photophysical properties and a luminescent response towards transition metal salts (particularly, CdI₂, Cd(OAc)₂, Zn(ClO₄)₂, Cu(OAc)₂, HgCl₂) have been studied. Europium cation luminescence quenching in the presence of transition metal salts in solution was observed in all cases. In addition, it was observed that the fluorescent response of the europium complex was quite individual depending on the type of the metal salt. The obtained data were compared with the earlier published data for some lanthanide complexes bearing additional sites for the chelation of transition metal cations.

Key words: Europium complex, luminescence, 2,2'-bipyridine, polyaminocarboxylic acid, ditopic ligand.

Introduction

Today lanthanide (III) cation complexes are of great interest due to their wide applications¹. In particular, luminescent in the visible spectrum lanthanide complexes are severely used as electroluminescent materials for OLEDs² and phosphorescent labels for bioimaging.³ A common ligand for the luminescent complexes consists of a chromophore part (antenna) for absorbing light in

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order to transfer energy to the lanthanide cation, which is strongly bound by the chelating part of a hard character for the saturation of all the coordination bonds. In some cases, the antenna participates in the coordination of the lanthanide cation, while in other cases the antenna is separated by a spacer unit. In addition, for the cases where the antenna is a ligand fragment (for instance, functionalized 2,2'-bipyridine) the further coordination of other metal cations at this site is possible. In that case, this second chelation can be used as an additional tool for tuning the photophysical properties of the complex. In a number of cases, a luminescent response was reported upon adding some metal cations to the solution of such lanthanide complexes.^{4,5} The importance of these dual cation complexes was proven by their use in cellular imaging,⁶ bimodal imaging,⁷ as well as for MRI agents.⁸

In this paper, we are pleased to report a convenient method for the preparation of a dual-mode ligand comprising a lanthanide cations binding site, *i.e.* polyaminocarboxylic unit, and the substituted aryl-2,2'-bipyridines for the coordination to other transition metal cations. This ligand was used to study the energy transfer between aryl-bipyridine chromophores and Eu^{3+} cation, as well as the influence of the bipyridine coordination to different metal cations on the photophysical properties of the resulting complexes.

Experimental section

General procedures

All common reagents and solvents were used from commercial suppliers without further purification. Melting points were determined with a Boetius apparatus. ^1H NMR spectra were acquired on a Bruker Avance II spectrometer (400 MHz), 298 K, digital resolution ± 0.01 ppm, using TMS as internal reference. Mass-spectra were recorded on MicrOTOF-Q II (Bruker Daltonics), electrospray as a method of ionization. Microanalyses (C, H, N) were performed using a PerkinElmer 2400 elemental analyzer. Absorption spectra were recorded on a Shimadzu UV-2401PC spectrometer. Luminescence spectra were recorded on a Varian Cary Eclipse fluorimeter. Starting compounds: 5'-methoxycarbonyl-5-phenyl-2,2'-bipyridine **2**⁹ and 5'-hydroxyphenyl-5-phenyl-2,2'-bipyridine **3**⁵ were synthesized according to the previously described method.

5'-Phenyl-2,2'-bipyridine-5-carbaldehyde (1). Hydroxymethylbipyridine **3** (1.31 g, 5 mmol) was dissolved in 1,2-dichloroethane (70 mL). Activated MnO_2 (17.4 g, 50 mmol) was added to the obtained solution and the resulting mixture was stirred under reflux for 10 h. Then, the resulting suspension was filtered off, and the mother liquid was evaporated under reduced pressure

to afford the corresponding aldehyde **1** which was used for the next step without additional purification. Yield 77% (1 g). M.p. 164-166 °C. $^1\text{H NMR}$ (DMSO- d_6 , δ , ppm): 7.39-7.57 (m, 3H, Ph), 7.76 (m, 2H, Ph), 8.20 (dd, 1H, $^3J = 8.3$ Hz, $^4J = 2.0$ Hz, H-4'), 8.36 (dd, $^3J = 8.0$ Hz, $^4J = 1.9$ Hz, H-4), 8.58 (d, 1H, $^3J = 8.3$ Hz, H-3'), 8.64 (d, 1H, $^3J = 8.0$ Hz, H-3), 8.99 (d, $^4J = 2.0$ Hz, H-6'), 9.15 (d, $^4J = 1.9$ Hz, H-6), 10.18 (s, 1H, COH). **ESI-MS**, m/z : found 261.10 $[\text{M}+\text{H}]^+$, required 261.10.

(E)-N¹-((5'-phenyl-2,2'-bipyridin-5-yl)methylene)-N²,N²-bis(2-((E)-(5'-phenyl-2,2'-bipyridin-5-yl)methyleneamino)ethyl)ethane-1,2-diamine (4). Aldehyde **1** (1 g, 3.85 mmol) was dissolved in ethanol (150 mL). Tris(2-aminoethyl)amine (202 μL , 1.35 mmol) was added into this and the resulting mixture was refluxed for 2 h. The resulting mixture was allowed to cool to room temperature for 7 h. The obtained precipitate was filtered off, washed with ethanol and dried to afford the product. This product was used for the next step without additional purification. Yield 78% (870 mg). M.p. 178-180 °C. $^1\text{H NMR}$ (CDCl_3 , δ , ppm): 3.03 (m, 6H, $\text{CH}=\text{NCH}_2\text{CH}_2$), 3.80 (m, 6H, $\text{CH}=\text{NCH}_2\text{CH}_2$), 7.34-7.52 (m, 9H, Ph), 7.60 (m, 6H, Ph), 7.93 (dd, 3H, $^3J = 8.3$ Hz, $^4J = 2.3$ Hz, H-4'), 8.08 (dd, 3H, $^3J = 8.3$ Hz, $^4J = 1.8$ Hz, H-4), 8.30 (s, 3H, $\text{CH}=\text{NCH}_2\text{CH}_2$), 8.42 (m, 6H, H-3,3'), 8.57 (d, 3H, $^4J = 2.3$ Hz, H-6'), 8.87 (d, 3H, $^4J = 1.8$ Hz, H-6).

N¹-((5'-phenyl-2,2'-bipyridin-5-yl)methyl)-N²,N²-bis(2-((5'-phenyl-2,2'-bipyridin-5-yl)methylamino)ethyl)ethane-1,2-diamine (5). Compound **4** (870 mg, 1 mmol) was suspended in ethanol (80 mL), NaBH_4 (3 g, excess) was added into this and the resulting mixture was refluxed for 2 h. Solvent was removed under the reduced pressure, and water (50 mL) was added to the obtained residue. The resulting mixture was heated to reflux and then cooled to room temperature. The product was extracted with DCM (3 x 40 mL) and the combined extracts were dried with anhydrous sodium sulfate, filtered and evaporated to dryness under the reduced pressure. The resulting product was purified by recrystallization from a small amount of ethanol. Yield 85% (750 mg). M.p. 116-118 °C. $^1\text{H NMR}$ (CDCl_3 , δ , ppm): 2.63 (m, 6H, $\text{NHCH}_2\text{CH}_2\text{N}$), 2.72 (m, 6H, $\text{NHCH}_2\text{CH}_2\text{N}$), 3.85 (s, 6H, $\text{CH}_2\text{NHCH}_2\text{CH}_2$), 7.32-7.49 (m, 9H, Ph), 7.58 (m, 6H, Ph), 7.74 (dd, 3H, $^3J = 8.3$ Hz, $^4J = 2.0$ Hz, H-4'), 7.92 (dd, 3H, $^3J = 8.3$ Hz, $^4J = 2.5$ Hz, H-4), 8.34 (d, 3H, $^3J = 8.3$ Hz, H-3'), 8.39 (d, 3H, $^3J = 8.3$ Hz, H-3), 8.60 (d, 3H, $^4J = 2.0$ Hz, H-6'), 8.85 (d, 3H, $^4J = 2.5$ Hz, H-6). Found, %: C 77.61, H 6.30, N 16.03. $\text{C}_{57}\text{H}_{54}\text{N}_{10}$. Calculated, %: C 77.88, H 6.19, N 15.93.

Triethyl 2,2',2''-(2,2',2''-nitrilotris(ethane-2,1-diyl)tris(((5'-phenyl-2,2'-bipyridin-5-yl)methyl)azanediyl))triacetate (7). Compound **5** (0.75 g, 0.85 mmol) was dissolved in dry DMF (15 mL), potassium carbonate (1.17 g, 8.5 mmol) and ethyl bromoacetate (131 μ L, 2.82 mmol) were added into this, and the resulting mixture was stirred at room temperature for 10 h. Then, water (30 mL) and DCM (30 mL) were added and the resulting mixture was stirred for 2 h at room temperature for phase separation. The product was extracted with DCM (3 x 40 mL), the combined extracts were dried with anhydrous sodium sulfate, filtered and evaporated under the reduced pressure. The residue was purified by column chromatography (ethylacetate as eluent) to afford the product. Yellow oil. Yield 72% (0.69 g). $^1\text{H NMR}$ (CDCl_3 , δ , ppm): 1.25 (t, 9H, $^3J = 7.1$ Hz, CH_2CH_3), 2.62 (m, 6H, bipy- $\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}$), 2.75 (m, 6H, bipy- $\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}$), 3.34 (s, 6H, CH_2COOEt), 3.83 (m, 6H, bipy- CH_2N), 4.14 (q, 6H, $^3J = 7.1$ Hz, CH_2CH_3), 7.32-7.55 (m, 9H, Ph), 7.61 (m, 6H, Ph), 7.81 (dd, 3H, $^3J = 8.0$ Hz, $^4J = 2.0$ Hz, H-4'), 7.94 (dd, 3H, $^3J = 8.4$ Hz, $^4J = 2.4$ Hz, H-4), 8.37 (d, 3H, $^3J = 8.0$ Hz, H-3'), 8.41 (d, 3H, $^3J = 8.4$ Hz, H-3), 8.59 (d, 3H, $^4J = 2.0$ Hz, H-6'), 8.86 (d, 3H, $^4J = 2.4$ Hz, H-6).

Sodium 2,2',2''-(2,2',2''-nitrilotris(ethane-2,1-diyl)tris(((5'-phenyl-2,2'-bipyridin-5-yl)methyl)azanediyl))triacetate (6). Compound **7** (0.69 g, 0.61 mmol) was suspended in ethanol (50 mL), sodium hydroxide (73 mg, 1.83 mmol) was added into this, and the resulting mixture was stirred at reflux for 7 h. Ethanol (30 mL) was removed under reduced pressure. The obtained precipitate was filtered off and air-dried to afford the product. Yield 505 mg (0.45 mmol, 74%). $^1\text{H NMR}$ (D_2O , δ , ppm): 2.47 (m, 12H, CH_2CH_2), 3.03 (m, 6H, CH_2COONa), 3.34 (m, 6H, bipy- CH_2N), 6.72-6.99 (m, 15H, Ph), 7.09 (dd, 3H, $^3J = 8.5$ Hz, $^4J = 2.0$ Hz, H-4'), 7.43 (m, 6H, H-3', 4), 7.61 (d, 3H, $^3J = 8.0$ Hz, H-3), 8.19 (m, 6H, H-6,6').

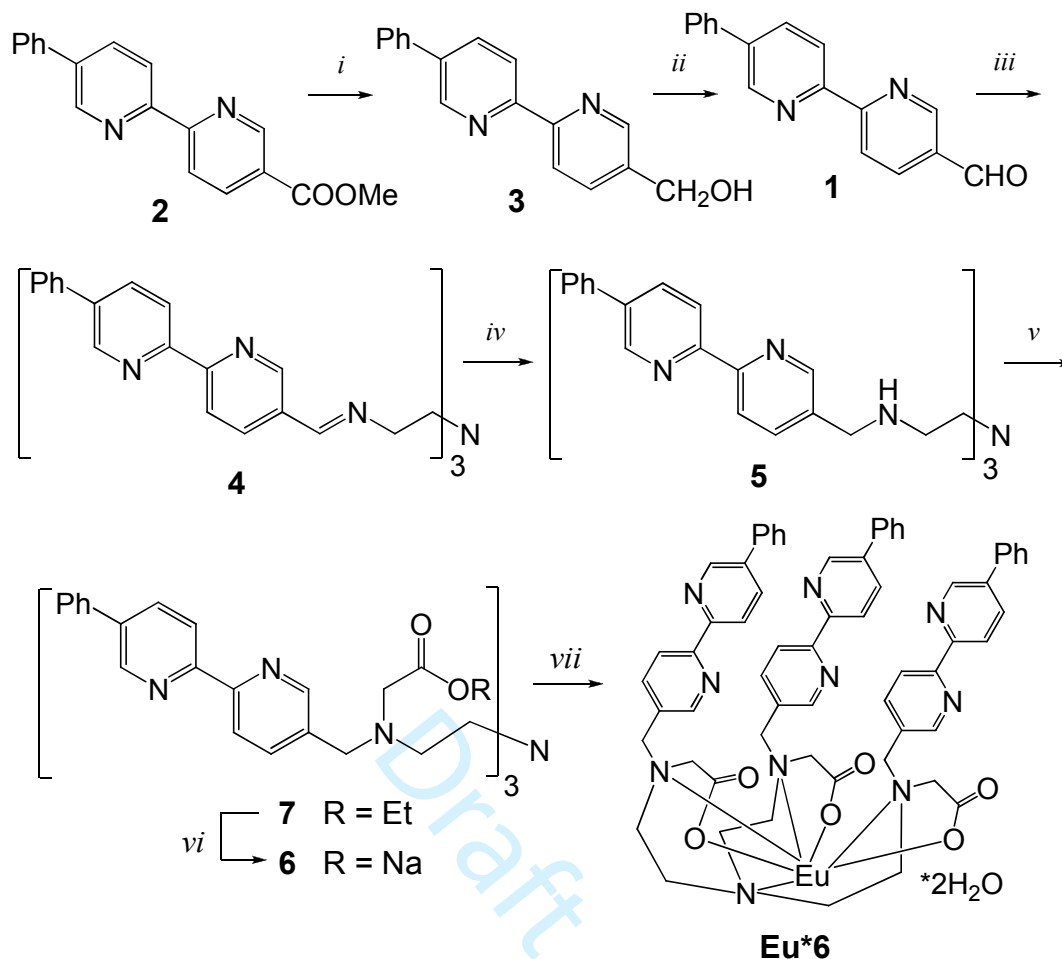
Eu*6. Salt **6** (0.3 g, 0.27 mmol) was dissolved in water (30 mL). $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (99 mg, 0.27 mmol) was added into this and the resulting mixture was stirred at room temperature for 2 h. The obtained precipitate was filtered off and dried under vacuum. The analytical sample was obtained by the recrystallization from a mixture mixture of DCM and methanol (1:1). Yield 322 mg (0.243 mmol, 90%). Found, %: C 58.21, H 4.56, N 10.60. $\text{C}_{63}\text{H}_{57}\text{N}_{10}\text{O}_6\text{Eu} \cdot 2\text{H}_2\text{O} \cdot \text{CH}_2\text{Cl}_2$. Calculated, %: C 58.10, H 4.80, N 10.59. **ESI-MS**, m/z : found 1199.48 $[\text{M}-\text{H}_2+\text{H}]^+$, required 1199.36.

Results and Discussion

For the synthesis of target ligand a most straight-forward strategy has been selected, which involves the use of tris(2-aminoethyl)amine (Tren) as a platform for obtaining tripod-type Schiff base and its further functionalization. In the literature, few examples were reported for similar 2,2'-bipyridine-based ligands,¹⁰ however, no lanthanide complexes of such ligands are known so far. In addition, it should be noted that several "tripod"-based compounds with various central platforms were reported as chemosensors for various anions,¹¹ including warfare agents.^{10e} Some tripod-type compounds were also used as building blocks for the obtaining biologically active compounds,¹² as well as some catalysts.¹³

5'-Phenyl-2,2'-bipyridine was chosen as an antenna unit due to its successful utilization for the sensibilization of lanthanide luminescence.¹⁴ In addition, the presence of an additional aromatic substituent makes it possible to adjust the photophysical properties of the complexes by red-shifting the absorption maxima, and, thus, using the more accessible light sources for the photoexcitation.

The starting 5'-phenyl-2,2'-bipyridine-5-carbaldehyde **1** was prepared by the previously reported "1,2,4-triazine" methodology¹⁵ starting from methyl ester of 5'-phenyl-2,2'-bipyridine-5-carboxylic acid **2**⁹ (Scheme 1). Further reduction of **2** with sodium borohydride in a mixture of ethanol and chloroform afforded the alcohol **3** according to the previously reported procedure⁵. Aldehyde **1** was obtained by the reaction of alcohol **2** with activated MnO₂ in 1,2-dichloroethane under reflux. It is worthy to mention that the use of SeO₂ as an oxidant for such transformation also resulted the desired aldehyde **1** in lower yields along with the significant amount of the 2,2'-bipyridine carboxylic acid as a side-product. The condensation reaction of the aldehyde **1** with tris(2-aminoethyl)amine in ethanol led to the Schiff base **4** in 78% yield. The secondary amine **5** was obtained in 85% yield by reducing the compound **4** with an excess of sodium borohydride in ethanol. Finally, in order to increase the affinity between a given ligand and lanthanide cations, the acetic acid residues were introduced as hard chelating units. Thus, the trisodium salt of the target ligand **6** was isolated after the alkylation of the amine **5** with ethyl bromoacetate and followed by alkaline hydrolysis of the ester **7**. The interaction of the trisodium salt **6** with europium (III) chloride at room temperature in water afforded the **Eu*6** complex, which can be easily isolated by precipitation and subsequent filtration from the resulted water solution after a very short time standing at room temperature.



Scheme 1. A synthetic route to the target europium complex.

Reagents and conditions: *i*) NaBH_4 , ethanol-chloroform (8:1), reflux, 6 h, then NaBH_4 , ethanol, 4 h; *ii*) MnO_2 , 1,2-dichloroethane, reflux, 10 h; *iii*) tris(2-aminoethyl)amine, ethanol, reflux, 2 h, then room temperature, 7 h; *iv*) NaBH_4 , ethanol, 2 h, reflux; *v*) ethyl bromoacetate, K_2CO_3 , DMF, room temperature, 10 h; *vi*) NaOH , ethanol, reflux, 7 h; *vii*) $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, water, room temperature, 2 h.

The molecular composition of the **Eu*6** complex was confirmed on the basis of elemental analysis and mass spectrometry (electrospray). For instance in the ESI mass spectrum of the complex, the peaks of double- and triple-charged ions were observed, while the single charged molecular ion was missing. This fact could probably be explained by the large number of free pyridine rings (six) in the complex. In particular, for the double-charged ion $[\text{M}+2\text{H}]^{2+}$, series of signals with m/z ratio of 601.25, 601.75, 602.24, 602.74, 603.24 were observed,

and for the triple-charged $[M+3H]^{3+}$ ion signals with m/z ratio of 401.17, 401.51, 401.84 were observed. These multi-charged ions were further converted into the single charged ones *via* the deconvolution procedure to result in the molecular ion peaks with the m/z ratio of 1199.48, 1200.49, 1201.48, 1202.48 and 1203.48. The calculated molecular ion peak composition for the $[M-2H+H]^+$ ion fully correlates with the experimentally obtained isotopic distribution (see Figs. S12 and S13, Supplementary information). A relatively high error in the determination of the molecular weights could be attributed to the insufficient qualitative calibration of the instrument in the 400-600 Da mass range.

Based on the photophysical properties studies of new **Eu*6** complex a moderate luminescence of the europium cation (1.8% quantum yield, measured relative to $[Ru(bpy)_3]Cl_2$, $\Phi = 2.8\%$ in water¹⁶) was observed. The luminescence lifetime of the europium cation (0.60 ms) was somewhat higher compare to a water-soluble Eu^{3+} complex bearing a similar chromophore, *i.e.* 5-phenyl-2,2'-bipyridine, and an appended DTTA residue, which was separated from the 2,2'-bipyridine moiety by the methylene group in the C5' position⁵ (0.37 ms). However, the observed lifetime of **Eu*6** complex was lower compare to the complexes possessing 5-aryl-2,2'-bipyridine ligands, which are involved in the coordination to Eu^{3+} cation to result in the full saturation of the first coordination sphere of this cation (the reported lifetime values for these complexes were up to 1.5 ms¹⁴). In addition, the **Eu*6** complex exhibited a significant residual fluorescence with a quantum yield value of 18.3% (with respect to quinine sulfate in 0.1N H_2SO_4 ($\Phi = 54.6\%$)¹⁷). It should be noted that, in earlier report only a weak fluorescence was observed for the “naked” 5-phenyl-2,2'-bipyridine chromophore (in acetonitrile solution the quantum yield value was 3.2%) due to the possible role of $n-\pi^*$ transitions, and the enhancement of the fluorescence was observed upon the addition of zinc perchlorate.⁹ Obviously, in our case the chelation of the europium cation causes the redistribution of the electron density in the 2,2'-bipyridine chromophore.

The luminescence response of the **Eu*6** complex towards metal cations was studied by adding a 5-fold excess of a number of metal salts to the solution of **Eu*6** in DCM. Despite of the type of the metal cation, the addition leads to a bathochromic shift of the absorption maxima, which corresponds to the literature data and thus confirms the presence of free fragments of 2,2'-bipyridine in the molecule of **Eu*6** complex. The values of the bathochromic shifts were in the range of 18-26 nm (see Table 1), and the maximum bathochromic shift was observed for zinc perchlorate.

As for the change in luminescence properties of the **Eu*6** complex, in all cases the addition of metal cation salts caused the bathochromic shift of the emission maxima, and again the maximum bathochromic shift was observed in case of zinc perchlorate (the bathochromic shift value up to 36 nm, Table 1). In all cases, both the Eu cation luminescence quenching and the decrease in the Eu cation luminescence lifetime were observed. The addition of cadmium iodide had the smallest effect both on the Eu cation luminescence quantum yield and the Eu cation luminescence lifetime (from 0.61 to 0.42 ms). A slightly more significant decrease in the lifetime of Eu cation luminescence was observed with the addition of mercuric chloride (up to 0.22 ms), which also correlates with the literature data (for example, a similar phenomenon was described in the case of Tb^{3+} complex of ligand **I** (Fig. 2)¹⁸). A significant decrease in the lifetime occurred when zinc perchlorate or cadmium acetate was added, and a complete Eu cation luminescence quenching was observed in the presence of copper acetate. It should be noted that, the luminescence quenching of lanthanide complexes in the presence of copper salts is very common (in particular, it was reported for europium complexes based on ligands **II**¹⁹ and **III**²⁰ (Fig. 2)). In addition, a similar luminescent response of the lanthanide complexes in the presence of zinc cations was reported in the literature (for example, for the Eu^{3+} complex **IV** (Fig. 2)²¹), although in some cases the lanthanide cations luminescence enhancement was observed (in particular, in case of complex **V** (Fig. 2)²²) or no change of the lanthanide cations luminescence was observed (in case of complex **VI**⁵ (Fig. 2)).

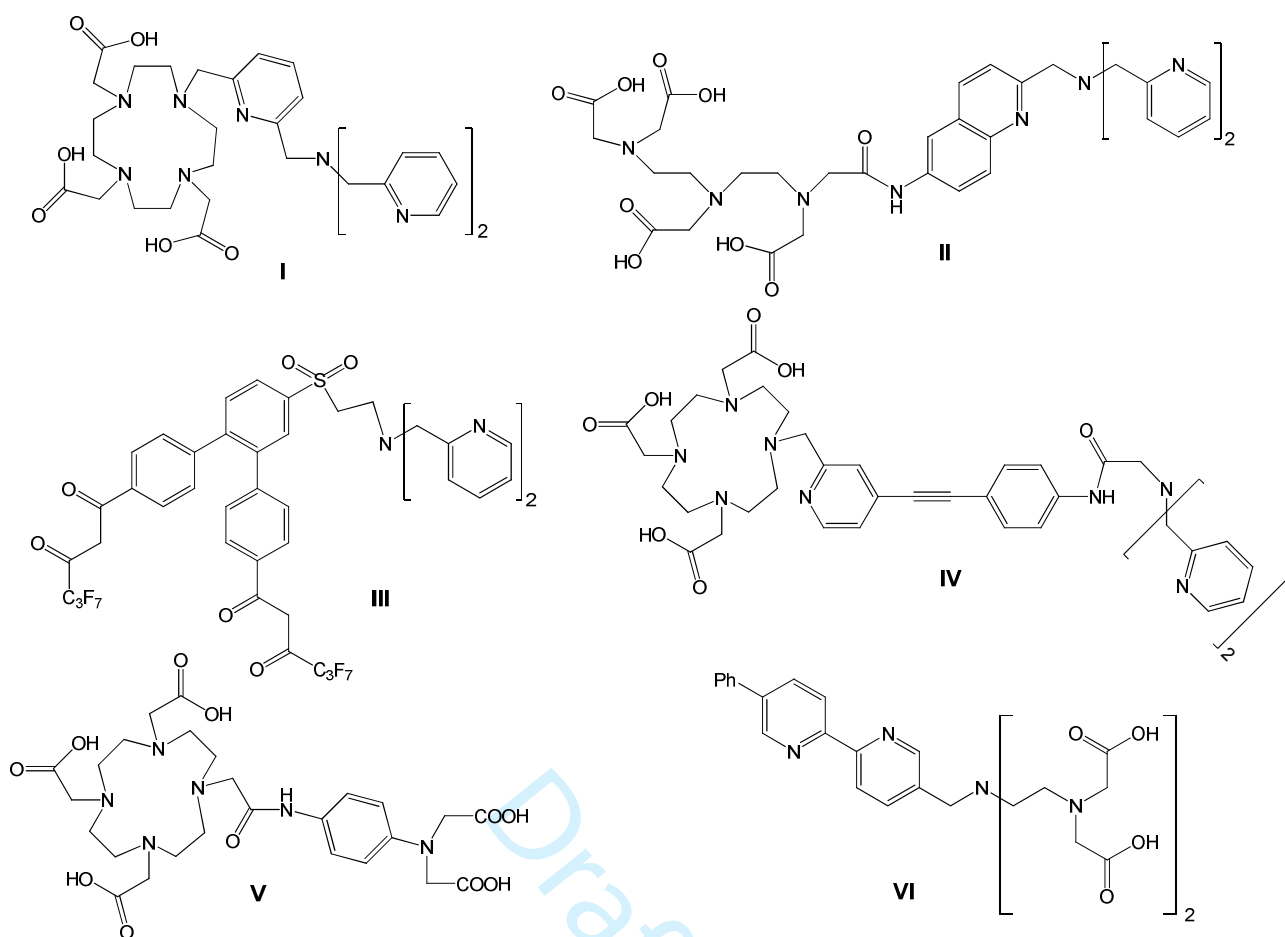


Fig. 2. The structures of previously published ditopic ligands for lanthanide cations

As for the fluorescent response, it strongly depends on the nature of the transition metal salt. Thus, the addition of zinc perchlorate caused a significant increase in the fluorescence intensity with a bathochromic shift of the emission maxima from 374 to 410 nm, which correlates well with the previously published results for this chromophore,⁹ as well as with data reported for the europium complex with ligand **IV**.²¹ A similar pattern was observed upon the addition of mercuric chloride. With respect to cadmium salts, a small bathochromic shift of the emission maximum with virtually no change in the emission intensity was observed when cadmium acetate was added, while the addition of cadmium iodide caused a fluorescence quenching. Finally, the addition of copper acetate caused the most significant fluorescence quenching, which was correlated well to the literature data⁹.

The photophysical data for the complex **Eu*6** itself, and after the addition of a 5-fold excess of the corresponding metal salts are collected in Table 1.

Table 1

	Eu*6	CdI ₂	Zn(ClO ₄) ₂	Cu(OAc) ₂	Cd(OAc) ₂	HgCl ₂
λ_{\max} , nm ^a	264, 308	333	334	331	325	326
λ_{em} , nm ^b	374	424	410	385	382	387
τ , ms ^c	0.60	0.42	0.03	-	0.01	0.22

^aabsorption maxima in DCM for complex **Eu*6** and after addition of 5-fold excess of salt at room temperature; ^bfluorescence maxima in DCM for complex **Eu*6** and after addition of 5-fold excess of salt at room temperature; ^ceuropium cation luminescence lifetime in DCM for complex **Eu*6** and after addition of 5-fold excess of salt at room temperature

The difference in spectroscopic behavior of Eu complex in the presence of different metal cations is most probably connected with the influence of the nature of the metal cations on the energy levels corresponding to the T₁ and S₁ states of 5-phenyl-2,2'-bipyridine ligand/fluorophore before and after the transition metal coordination event. These changes of the energy levels of the 5-phenyl-2,2'-bipyridine are, most probably, affect the efficiency of the energy transfer from the ligand to the ⁵D₀ energy level of the chelated Eu³⁺ cation. Additionally, we used various metal salts, containing, at first, metal cations of different geometric sizes (namely Cd²⁺, Zn²⁺, Hg²⁺ and Cu²⁺), and, at second, various anions as counter ions. That means the coordination between these salts and 2,2'-bipyridine-based Eu complex could change the geometry and/or the stoichiometry of the resulting Eu complex significantly, which also could affect the efficiency of the ligand to Eu³⁺ cation energy transfer.

The absorption spectra of the complex **Eu*6** is shown in Fig. 1 and the luminescence spectra of **Eu*6** with no time delay is shown in Fig. 2, and the Eu³⁺ cation luminescence spectra of complex **Eu*6** is shown in Fig. 3. The absorption and emission spectra of the complex **Eu*6** before and after the addition of an excess of the corresponding metal salts are presented in the Supplementary information.

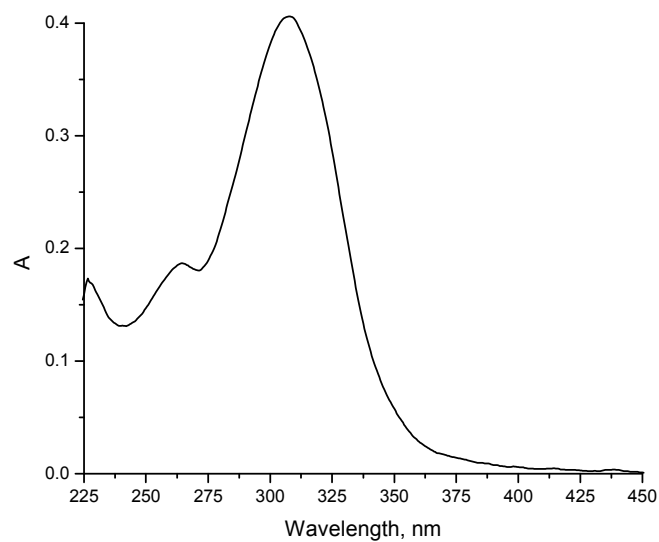


Fig. 1. Absorption spectra of complex **Eu*6** (10^{-5} M) in DCM at room temperature

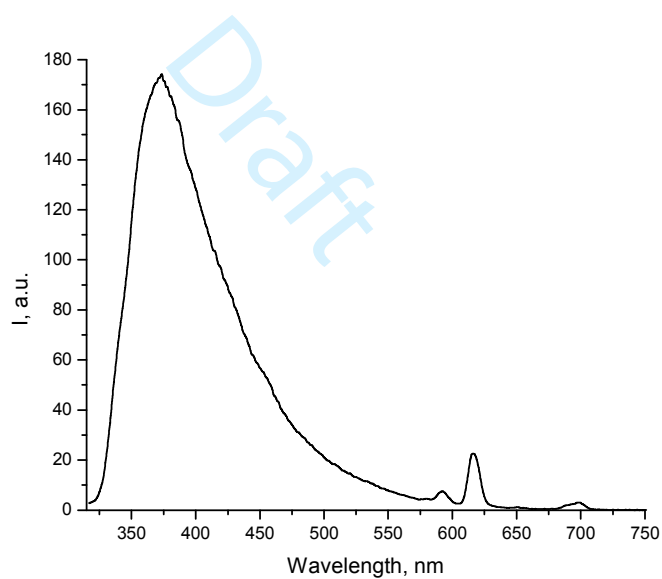


Fig. 2. Luminescence spectra of complex **Eu*6** (10^{-5} M) in DCM at room temperature with no time delay (excitation at 304 nm)

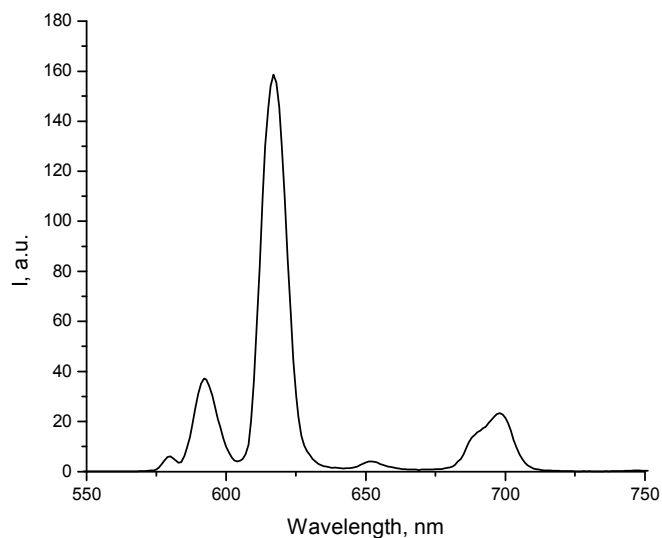


Fig. 3. Europium cation luminescence spectra of complex **Eu*6** (10^{-5} M) in DCM at room temperature (excitation at 304 nm)

Conclusions

In summary, in this paper, we have synthesized a new tripod-type 2,2'-bipyridine ligand consisting of three 5-phenyl-2,2'-bipyridine residues for the coordination to various transition metal cations and a central polyaminocarboxylic moiety for the coordination to lanthanide cations. The europium complex of this ligand was obtained, and its photophysical properties and a luminescent response towards metal salts (in particular, CdI_2 , $\text{Cd}(\text{OAc})_2$, $\text{Zn}(\text{ClO}_4)_2$, $\text{Cu}(\text{OAc})_2$, HgCl_2) were studied. In all the cases, the quenching of the Eu cation luminescence was observed, while the type and the degree of the fluorescent response of the 5-phenyl-2,2'-bipyridine moiety depended strongly on the nature of the metal salt. For example, the addition of zinc perchlorate caused a significant fluorescence enhancement with a bathochromic shift of the emission maximum of the resulted complex compare to the starting Eu complex. The obtained data are similar to the reported earlier ones for the lanthanide complexes bearing additional coordination sites for the coordination to transition metals cations.

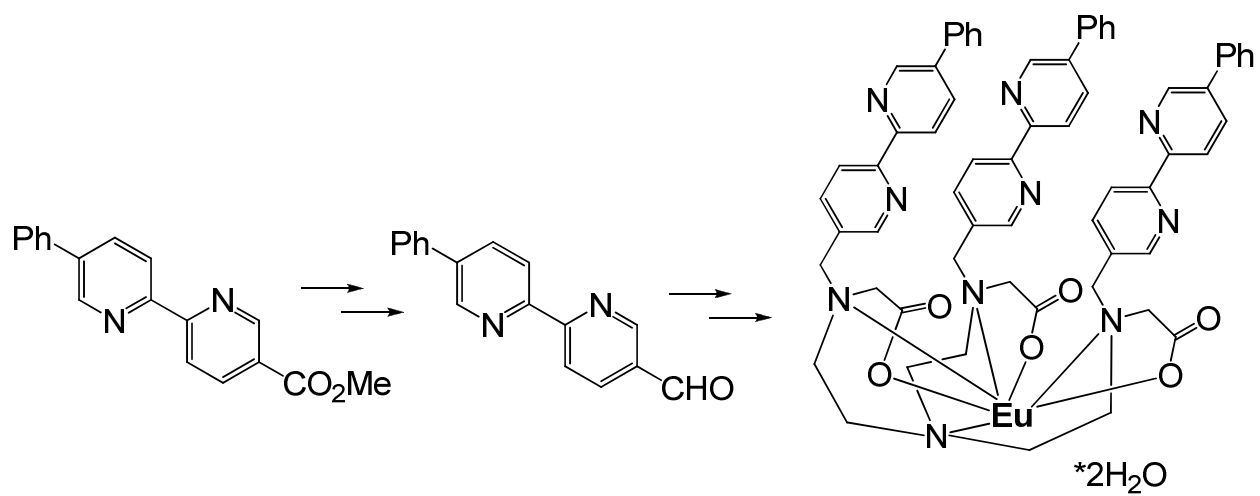
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References

1. (a) Armelao, L.; Quici, S.; Barigelletti, F.; Accorsi, G.; Bottaro, G.; Cavazzini, M.; Tondello, E. *Coord. Chem. Rev.* **2010**, *254*, 487; (b) Faulkner, S.; Pope, S. J. A.; Burton-Pye, B. P. *Applied Spectroscopy Reviews* **2005**, *40*, 1.
2. (a) Thejo Kalyania, N.; Dhoble, S. J. *Renewable and Sustainable Energy Reviews* **2012**, *16*, 2696; (b) de Bettencourt-Dias, A. *Dalton Trans.* **2007**, 2229.
3. (a) Hagan, A. K.; Zuchner, T. *Anal. Bioanal. Chem.* **2011**, *400*, 2847; (b) Hovinen, J.; Guy, P. M. *Bioconjugate Chem.* **2009**, *20*, 404.
4. (a) Ye, Z.; Wang, G.; Chen, J.; Fu, X.; Zhang, W.; Yuan, J. *Biosensors and Bioelectronics* **2010**, *26*, 1043; (b) Hanaoka, K.; Kikuchi, K.; Kojima, H.; Urano, Y.; Nagano, T. *Angew. Chem. Int. Ed.* **2003**, *42*, 2996.
5. Kopchuk, D. S.; Pavlyuk, D. E.; Kovalev, I. S.; Zyryanov, G. V.; Rusinov, V. L.; Chupakhin, O. N. *Can. J. Chem.*, **2016**, *94*, 599.
6. Baggaley, E.; Cao, D.-K.; Sykes, D.; Botchway, S. W.; Weinstein, J. A.; Ward, M. D. *Chem. Eur. J.* **2014**, *20*, 8898.
7. Dehaen, G.; Verwilt, P.; Eliseeva, S. V.; Laurent, S.; Vander Elst, L.; Muller, R. N.; De Borggraeve, W. M.; Binnemans, K.; Parac-Vogt, T. N. *Inorg. Chem.* **2011**, *50*, 10005.
8. Costa, J.; Ruloff, R.; Burai, L.; Helm, L.; Merbach, A. E. *J. Am. Chem. Soc.* **2005**, *127*, 5147.
9. Kozhevnikov, V. N.; Shabunina, O. V.; Kopchuk, D. S.; Ustinova, M. M.; König, B.; Kozhevnikov, D. N. *Tetrahedron* **2008**, *64*, 8963.
10. (a) Amendola, V.; Fabbrizzi, L.; Mangano, C.; Manotti Lanfredi, A.; Pallavicini, P.; Perottia, A.; Ugozzoli, F. *J. Chem. Soc., Dalton Trans.* **2000**, 1155; (b) Weibel, N.; Charbonnière, L. J.; Ziessel, R. F. *J. Org. Chem.* **2002**, *67*, 7876.
11. (a) Wei, L.-H.; He, Y.-B.; Wu, J.-L.; Qin, H.-J.; Xu, K.-X.; Meng L.-Z. *Chinese Journal of Chemistry*, **2005**, *23*, 608; (b) Sasaki, S.; Citterio, D.; Ozawa, S.; Suzuki, K. *J. Chem. Soc., Perkin*

- Trans.* **2**, **2001**, 2309; (c) Zyryanov, G. V.; Palacios, M. A.; Anzenbacher, Jr, P. *Angew. Chem. Int. Ed.* **2007**, *46*, 7849; (d) Bai, Y.; Zhang, B.-G.; Xu, J.; Duan, C.-Y.; Dang, D.-B.; Liu, D.-J.; Meng, Q.-J. *New J. Chem.* **2005**, *29*, 777; (e) Esipenko, N. A.; Koutnik, P.; Minami, T.; Mosca, L.; Lynch, V. M.; Zyryanov, G. V.; Anzenbacher, P. *Chemical Science* **2013**, *4*, 3617.
12. Makhubela, B. C. E.; Meyer, M.; Smith, G. S. *Journal of Organometallic Chemistry* **2014**, *773*, 229.
13. Makhubela, B. C. E.; Jardine, A. M.; Westman, G.; Smith, G. S. *Dalton Trans.* **2012**, *41*, 10715.
14. (a) Prokhorov, A. M.; Kozhevnikov, V. N.; Kopchuk, D. S.; Bernard, H.; Le Bris, N.; Tripier, R.; Handel, H.; Köenig, B.; Kozhevnikov, D. N. *Tetrahedron* **2011**, *67*, 597; (b) Krinochkin, A. P.; Kopchuk, D. S.; Kozhevnikov, D. N. *Polyhedron* **2015**, *102*, 556; (c) Kopchuk, D. S.; Krinochkin, A. P.; Kozhevnikov, D. N.; Slepukhin, P. A. *Polyhedron* **2016**, *118*, 30.
15. (a) Pabst, G. R.; Pfüller, O. C.; Sauer, J. *Tetrahedron* **1999**, *55*, 8045; (b) Rykowski, A.; Branowska, D.; Kielak, J. *Tetrahedron Lett.* **2000**, *41*, 3657; (c) Kopchuk, D. S.; Nikonov, I. L.; Zyryanov, G. V.; Kovalev, I. S.; Rusinov, V. L.; Chupakhin, O. N. *Chem. Heterocycl. Compds.* **2014**, *50*, 907.
16. Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.
17. Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229.
18. McMahon, B. K.; Gunnlaugsson, T. *Tetrahedron Lett.* **2010**, *51*, 5406.
19. Wang, Y.; Wang, H.; Zhao, X.; Jin, Y.; Xiong, H.; Yuan, J.; Wu, J. *New J. Chem.* **2017**, *41*, 5981.
20. Yip, Y.-W.; Law, G.-L.; Wong, W.-T. *Dalton Trans.* **2016**, *45*, 928.
21. Pope, S. J. A.; Laye, R. H. *Dalton Trans.* **2006**, 3108.
22. Hanaoka, K.; Kikuchi, K.; Kojima, H.; Urano, Y.; Nagano, T. *J. Am. Chem. Soc.* **2004**, *126*, 12470.



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