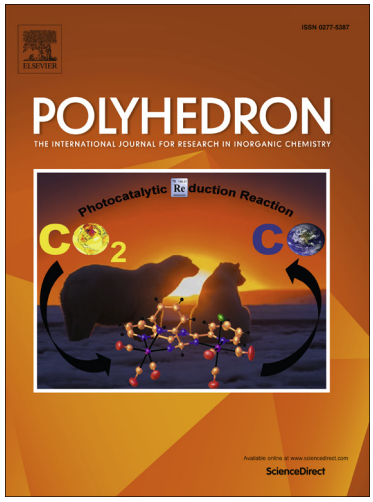

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Luminescent neutral lanthanide complexes of 5-aryl-2,2'-bipyridine-6-carboxylic acids, synthesis and properties

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Abstract

Luminescent lanthanide complexes of 4-aryl-1-(2-pyridyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine-3-carboxylic acids and 5-tolyl-2,2'-bipyridine-6-carboxylic acid were prepared. The ligands were synthesized using the "1,2,4-triazine" methodology. In one case, the opportunity of copper complex preparation, followed by exchange of the metal cation from copper to europium to overcome synthetic difficulties, was demonstrated. The ability of tuning the properties of the complexes by means of varying the structure of the ligands was demonstrated. In particular, the introduction of the cyclopentene moiety allowed the preparation of highly soluble complexes in non-polar organic solvents.

Keywords: 5-aryl-2,2'-bipyridine-6-carboxylic acids; luminescence; lanthanide complexes; aza-Diels-Alder reaction; 1,2,4-triazine.

1. Introduction

Nowadays, luminescent neutral lanthanide complexes represent a considerable practical interest,[1] and one of the important spheres of their applications is the creation of new electroluminescent materials (OLEDs). For this particular application, in addition to the most attractive features of luminescent lanthanide compounds, such as line-like emissions with high quantum efficiency, some specific additional properties are beneficial. Namely, such complexes have to be steady, capable of being sublimated in a vacuum or being soluble in non-polar organic solvents in order to dope semi-conductive polymers. In order to achieve these properties the formation of a neutral lanthanide complex with the whole inner coordination sphere (the coordination number of the lanthanide ion is 9) being occupied by organic ligands is required. As a consequence the quenching of the complex luminescence by the presence of water molecules

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in the inner coordination sphere due to non-radiative deactivation *via* interaction with O-H oscillators of the lanthanide cation is avoided.[1a]

Among the luminescent lanthanide coordination compounds, β-diketonate complexes are the most popular and the most intensively investigated[2] due to the commercial availability of β-diketones, easy synthesis and excellent luminescence properties of these complexes. Unfortunately, they usually suffer from poor photostability upon UV irradiation.[3] In addition, 2,2'-bipyridine-6-carboxylic acid derivatives or their aza-analogs are potentially useful as components for OLEDs since they form neutral complexes, [Ln(L)$_3$] (L = 2,2'-bipyridine-6-carboxylate), with a high quantum efficiency of lanthanide luminescence.[4,5] However, according to the literature, such complexes suffer from poor solubility in organic solvents. Therefore luminescent properties for some of these complexes were only studied in the solid state. Indeed, all of these facts considerably constrained the practical use of such chelates.

We analyzed the existing literature methods for the preparation of 2,2'-bipyridine-6-carboxylic acids from the viewpoint of possibly overcoming above mentioned disadvantages. In particular, 2,2'-bipyridine-6-carboxylic acids and their aza-analogues may be prepared directly using various heterocyclization reactions,[6] in particular by the Krönke method,[7] *via* the oxidation of methyl,[8] acetyl[9] or aldehyde[10] groups as well as 2-furyl moiety[11] in the C2 position of the pyridine ring, by the direct functionalization of 6-bromobipyridines,[12] and, finally, by the hydrolysis of cyanogroups.[13,14]

Analysis of these data showed that the most appropriate way to achieve our goal is the approach to 2,2'-bipyridine-6-carboxylic acids *via* their 1,2,4-triazine precursors, namely 6-aryl-3-(2-pyridyl)-5-cyano-1,2,4-triazines. Further synthesis can be carried out by the described earlier convenient methods,[14, 15] namely by means of the conversion of the 1,2,4-triazine ring into a pyridine one and the hydrolysis of the cyano group in acid medium. Fig. 1 shows the structure of the ligands that will be used for the neutral lanthanide complexes.

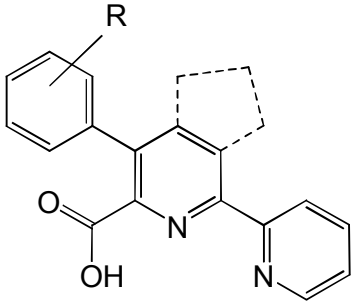


Fig. 1. The proposed structure of the ligands to produce neutral lanthanide complexes

The current approach was chosen among others for the following reasons: in this case, the preliminary introduction of various aromatic substituents in the C5 position of the 2,2'-bipyridine core can be used as a convenient tool for the tuning of the photophysical properties of the final complexes. Besides, increasing the conjugation degree of the whole ligand system and thus more effective intermolecular π-π–interactions improves energy transfer in the resultant OLED devise. The synthesis of these 1,2,4-triazine rings requires the use of commonly available reagents and simple synthetic procedures. It is worth mentioning that during the conversion of the 1,2,4-triazine ring into the pyridine one, by means of a very well-proven synthetic technique[16], the further functionalization of positions C3 and C4 of the newly formed pyridine ring is possible. For instance, in the case of enamines, used as dienophiles, the direct introduction of a fused cycloalkane moiety into the pyridine core is possible.[14,17] It should be noted that the synthesis of cycloalkene-annelated pyridine systems is very difficult using other synthetic approaches. In most cases such compounds have a much better solubility in organic solvents compared with their non-annelated pyridine analogues. Thus, it becomes possible to overcome the main disadvantage of most lanthanide complexes, namely low solubility in organic solvents.

2. Experimental

All chemicals and solvents were received from Aldrich/Merck as reagent grade and used without any further purification. NMR spectra were recorded on a Bruker Avance-400 spectrometer, at 298 K, digital resolution ± 0.01 ppm and using TMS as an internal standard. Infrared spectra were measured on a Bruker Alpha FTIR spectrometer with an ATR accessory (ZnSe). UV-Vis spectra were recorded on a Lambda 45 spectrophotometer (Perkin Elmer). Luminescence spectra were recorded on a Cary Eclipse spectrofluorometer (Varian). Mass spectra were recorded on a MicrOTOF-Q II mass spectrometer (Bruker Daltonics) with electrospray ionization (acetonitrile). Elemental analysis was performed on a PE 2400 II CHN-analyzer (Perkin Elmer). Compounds **2a** and **3b** were synthesized as described in the literature.[14]

6-(4-Fluorophenyl)-3-(2-pyridyl)-1,2,4-triazine-4-oxide (1d) was synthesized in accordance with the literature method[14] for similar compounds. Yield 50%. M.p. 217-219 °C. ^{1}H NMR (DMSO-d_6), δ, ppm: 7.34 (m, 2H, $CH_{arom.}$), 7.58 (m, 1H, H-5 (Py)), 8.00 (m, 2H, H-3,4 (Py)), 8.33 (m, 2H, $CH_{arom.}$), 8.78 (dd, 1H, ^3J = 4.9 Hz, ^4J = 1.7 Hz, H-6 (Py)), 9.41 (s, 1H, H-5). ESI-MS, *m/z*: found 269.08 $(M-H)^+$, required 269.08. Found, %: C 62.55, H 3.19, N 20.59. $C_{14}H_9FN_4O$ calculated, %: C 62.69, H 3.38, N 20.89.

5-Cyano-6-(4-fluorophenyl)-3-(2-pyridyl)-1,2,4-triazine (6d) was synthesized in accordance with the literature method[14] for similar compounds. Yield 80%. M.p. 124-126 °C. ^{1}H NMR (DMSO-d_6), δ, ppm: 7.45 (m, 2H, $CH_{arom.}$), 7.64 (m, 1H, H-5 (Py)), 8.08 (ddd, 1H, ^3J = 7.3, 7.3 Hz, ^4J = 1.7 Hz, H-4 (Py)), 8.18 (m, 2H, $CH_{arom.}$), 8.59 (dd, 1H, ^3J = 7.3 Hz, ^4J = 1.2 Hz, H-3 (Py)), 8.87 (dd, 1H, ^3J = 4.9 Hz, ^4J = 1.7 Hz, H-6 (Py)). ESI-MS, *m/z*: found 278.08 $(M-H)^+$, required 278.08. Found, %: C 64.80, H 2.77, N 24.98. $C_{15}H_8FN_5$ calculated, %: C 64.98, H 2.91, N 25.26.

4-Aryl-1-(2-pyridyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridines (2) were synthesized in accordance with the literature method[14] for similar compounds.

1-(2-Pyridyl)-4-tolyl-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine (2b). Yield 78%. M.p. 169-171 °C. ^{1}H NMR ($CDCl_3$), δ, ppm: 2.12 (m, 2H, CH_2-6), 2.44 (s, 3H, Me), 2.91 (t, 2H, ^3J = 7.6 Hz, CH_2-7), 3.58 (t, 2H, ^3J = 7.6 Hz, CH_2-5), 7.34 (m, 5H, H-5 (Py), Tol), 7.85 (ddd, 1H, ^3J = 7.3, 7.3 Hz, ^4J = 1.7 Hz, H-4 (Py)), 8.34 (dd, 1H, ^3J = 7.3 Hz, ^4J = 1.2 Hz, H-3 (Py)), 8.70 (dd, 1H, ^3J = 4.9 Hz, ^4J = 1.7 Hz, H-6 (Py)). ESI-MS, *m/z*: found 312.15 $(M-H)^+$, required 312.15. Found, %: C 83.62, H 6.21, N 9.54. $C_{20}H_{18}N_2$ calculated, %: C 83.88, H 6.34, N 9.78.

4-(4-Methoxyphenyl)-1-(2-pyridyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine (2c). Yield 84%. M.p. 164-166 °C. ^{1}H NMR ($CDCl_3$), δ, ppm: 2.12 (m, 2H, CH_2-6), 2.91 (t, 2H, ^3J = 7.6 Hz, CH_2-7), 3.57 (t, 2H, ^3J = 7.6 Hz, CH_2-5), 3.88 (s, 3H, OMe), 7.05 (m, 2H, C-H_{arom}), 7.33 (m, 1H, H-5 (Py)), 7.41 (m, 2H, C-$H_{arom.}$), 7.85 (ddd, 1H, ^3J = 7.3, 7.3 Hz, ^4J = 1.7 Hz, H-4 (Py)), 8.33 (dd, 1H, ^3J = 7.3 Hz, ^4J = 1.2 Hz, H-3 (Py)), 8.71 (dd, 1H, ^3J = 4.9 Hz, ^4J = 1.7 Hz, H-6 (Py)). ESI-MS, *m/z*: found 328.14 $(M-H)^+$, required 328.14. Found, %: C 79.19, H 5.77, N 9.13. $C_{20}H_{18}N_2O$ calculated, %: C 79.44, H 6.00, N 9.26.

4-(4-Fluorophenyl)-1-(2-pyridyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine (2d). Yield 85%. M.p. 174-176 °C. ^{1}H NMR ($CDCl_3$), δ, ppm: 2.12 (m, 2H, CH_2-6), 2.89 (t, 2H, ^3J = 7.6 Hz, CH_2-7), 3.59 (t, 2H, ^3J = 7.6 Hz, CH_2-5), 7.22 (m, 2H, $CH_{arom.}$), 7.34 (m, 1H, H-5 (Py)), 7.45 (m, 2H, $CH_{arom.}$), 7.86 (ddd, 1H, ^3J = 7.3, 7.3 Hz, ^4J = 1.7 Hz, H-4 (Py)), 8.34 (dd, 1H, ^3J = 7.3 Hz, ^4J = 1.2 Hz, H-3 (Py)), 8.70 (dd, 1H, ^3J = 4.9 Hz, ^4J = 1.7 Hz, H-6 (Py)). ESI-MS, *m/z*: found 316.13 $(M-H)^+$, required 316.13. Found, %: C 78.41, H 5.36, N 9.31. $C_{19}H_{15}FN_2$ calculated, %: C 78.60, H 5.21, N 9.65.

*General method for the synthesis of acids **4** and **5***

The corresponding cyanobipyridine **2** or **3** (3 mmol) was suspended in sulfuric acid (50%, 6 mL) and the resulting mixture was stirred at 140 °C for 10 h. The mixture was then cooled to room temperature and water (20 mL) was added. The obtained precipitate was filtered

off, washed with water and dissolved in an aqueous solution of NaOH (1M, 5 mL). The undissolved part was filtered off, then hydrochloric acid (5N) was added to the filtrate to adjust the pH value to 2. The resulting precipitate was filtered off, washed with water and dried under vacuum.

4-Phenyl-1-(2-pyridyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine-3-carboxylic acid (4a). Yield 0.55 g (1.74 mmol, 58%). M.p. 209-210 °C. ^{1}H NMR (DMSO-d_6), δ, ppm: 2.11 (m, 2H, CH_2-6), 2.84 (t, 2H, ^3J = 7.6 Hz, CH_2-7), 3.48 (t, 2H, ^3J = 7.6 Hz, CH_2-5), 7.39 (m, 5H, Ph), 7.82 (m, 1H, H-5 (Py)), 8.41 (m, 2H, H-3,4 (Py)), 8.88 (d, 1H, ^3J = 4.8 Hz, H-6 (Py)). IR, υ/cm^{-1}: 1736 (CO). ESI-MS, *m/z*: found 315.12 (M-H)$^-$, required 315.11.

1-(2-Pyridyl)-4-tolyl-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine-3-carboxylic acid (4b). Yield 0.6 g (1.82 mmol, 61%). M.p. 195-197 °C. ^{1}H NMR (DMSO-d_6), δ, ppm: 2.12 (m, 2H, CH_2-6), 2.41 (s, 3H, Me), 2.85 (t, 2H, ^3J = 7.6 Hz, CH_2-7), 3.47 (t, 2H, ^3J = 7.6 Hz, CH_2-5), 7.23 (m, 4H, Tol), 7.71 (m, 1H, H-5 (Py)), 8.27 (m, 1H, H-4 (Py)), 8.45 (d, 1H, ^3J = 8.0 Hz, H-3 (Py)), 8.84 (d, 1H, ^3J = 4.8 Hz, H-6 (Py)). ^{13}C NMR (DMSO-d_6), δ, ppm: 21.3, 25.1, 32.6, 33.4, 125.3, 125.8, 128.9, 129.5, 133.5, 133.6, 137.9, 141.6, 142.9, 145.0, 146.1, 148.8, 152.2, 157.2, 167.9 (CO). IR, υ/cm^{-1}: 1737 (CO). ESI-MS, *m/z*: found 329.13 (M-H)$^-$, required 329.13.

4-(4-Fluorophenyl)-1-(2-pyridyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine-3-carboxylic acid (4d). Yield 0.55 g (1.65 mmol, 55%). M.p. 208-210 °C. ^{1}H NMR (DMSO-d_6), δ, ppm: 2.12 (m, 2H, CH_2-6), 2.84 (t, 2H, ^3J = 7.6 Hz, CH_2-7), 3.50 (t, 2H, ^3J = 7.6 Hz, CH_2-5), 7.20 (m, 2H, C-H_{arom}), 7.36 (m, 2H, C-H_{arom}), 7.71 (m, 1H, H-5 (Py)), 8.26 (m, 1H, H-4 (Py)), 8.46 (d, 1H, ^3J = 8.0 Hz, H-3 (Py)), 8.84 (d, 1H, ^3J = 4.4 Hz, H-6 (Py)). IR, υ/cm^{-1}: 1735 (CO). ESI-MS, *m/z*: found 333.10 (M-H)$^-$, required 333.10.

5-Tolyl-2,2'-bipyridine-6-carboxylic acid (5). Yield 0.5 g (1.72 mmol, 57%). M.p. > 250 °C. ^{1}H NMR (DMSO-d_6), δ, ppm: 2.41 (s, 3H, Me), 7.27 (m, 2H, Tol), 7.38 (m, 2H, Tol), 7.64 (m, 1H, H-5'), 8.01 (d, 1H, ^3J = 8.4 Hz, H-3), 8.18 (m, 1H, H-4'), 8.64 (m, 2H, H-4,3'), 8.76 (d, 1H, ^3J = 4.4 Hz, H-6'). IR, υ/cm^{-1}: 1737 (CO). ESI-MS, *m/z*: found 289.10 (M-H)$^-$, required 289.10.

General method for the synthesis of the lanthanide complexes

The corresponding acid (0.35 mmol) was suspended in methanol (40 mL), then sodium hydroxide (14 mg, 0.35 mmol) was added and the resulting mixture was refluxed until a clear solution was obtained. The mixture was cooled to room temperature and the chloride of the corresponding lanthanide (0.117 mmol) was added. The mixture was kept at room temperature for 2 h. Solvent was removed under reduced pressure, then water (20 mL) was added to the residue. The precipitate was filtered off, washed with water, dried under vacuum and dissolved

in a mixture of methanol-DCM (1:1, 30 mL). The undissolved part was filtered off and solvents were removed under reduced pressure. The resulting product was dried under a vacuum.

Eu*4a. Yield 80 mg (0.067 mmol, 57%). IR, υ/cm^{-1}: 1643 (CO). ESI-MS, *m/z*: found 1099.26 $(M+H)^+$, required 1099.27. Found, %: C 61.47, H 4.01, N 6.90. $C_{60}H_{45}EuN_6O_6*CH_2Cl_2$, calculated, %: C 61.94, H 4.00, N 7.10.

Eu*4b. Yield 90 mg (0.076 mmol, 64%). IR, υ/cm^{-1}: 1644 (CO). ESI-MS, *m/z*: found 1141.32 $(M+H)^+$, required 1141.32. Found, %: C 64.44, H 4.29, N 7.23. $C_{63}H_{51}EuN_6O_6 \cdot 0.5CH_2Cl_2$ calculated, %: C 64.50, H 4.43, N 7.11.

Eu*4d. Yield 80 mg (0.065 mmol, 57%). ESI-MS, *m/z*: found 1153.25 $(M+H)^+$, required 1153.24. Found, %: C 58.78, H 3.12, N 6.67. $C_{60}H_{42}EuF_3N_6O_6 \cdot CH_2Cl_2$ calculated, %: C 59.23, H 3.59, N 6.79.

Tb*4d. Yield 85 mg (0.071 mmol, 61%). ESI-MS, *m/z*: found 1159.24 $(M+H)^+$, required 1159.24. Found, %: C 60.31, H 3.49, N 6.91. $C_{60}H_{42}TbF_3N_6O_6 \cdot 0.5CH_2Cl_2$ calculated, %: C 60.48, H 3.61, N 7.00.

Eu*5. Yield 70 mg (0.063 mmol, 55%). ESI-MS, *m/z*: found 1021.22 $(M+H)^+$, required 1021.22. Found, %: C 59.38, H 3.53, N 7.21. $C_{54}H_{39}EuN_6O_6 \cdot CH_2Cl_2$ calculated, %: C 59.79, H 3.74, N 7.61.

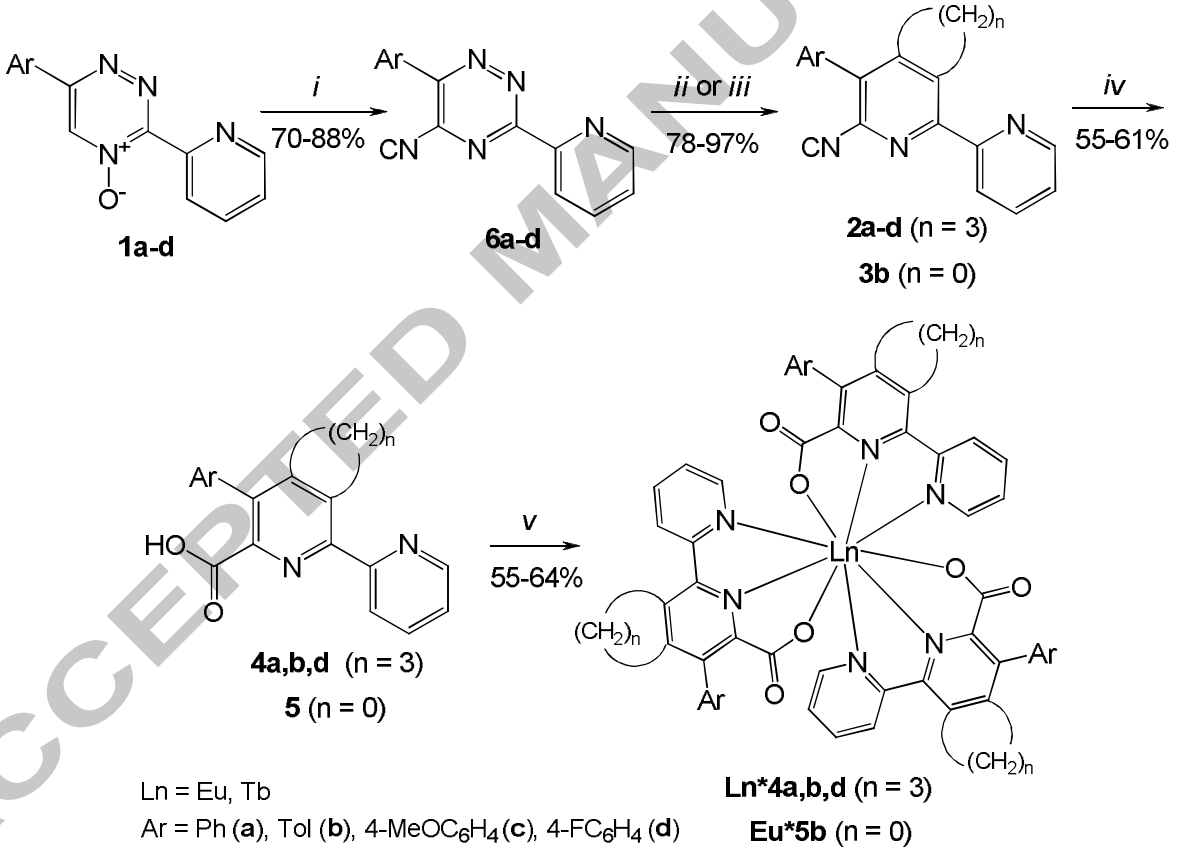
Cu*4c. Cyanobipyridine **1c** (175 mg, 0.54 mmol) was dissolved in an ethanol (30 mL), solution of $CuCl_2 \cdot 2H_2O$ (92 mg, 0.54 mmol) in water (30 mL) was added and the resulting mixture was refluxed for 8 h. Solvents were removed under reduced pressure, then water (20 mL) was added to the residue. The precipitate was filtered off, washed with water and dried. Yield 150 mg (0.34 mmol, 63%). ESI-MS, *m/z*: found 443.04 (M^+), required 443.02. Found, %: C 56.88, H 3.53, N 6.07. $C_{21}H_{17}ClCuN_2O_3$ calculated, %: C 56.76, H 3.86, N 6.30.

Eu*4c. Complex **Cu*4c** (135 mg, 0.3 mmol) was dissolved in a mixture of water-ethanol (1:1, 20 mL). A mixture of acetone cyanohydrin (0.28 mL, 3 mmol), KOH (170 mg, 3 mmol) and water (5 mL) was added and the resulting mixture was kept at 50 °C for 30 min. The solution was then cooled to room temperature, followed by adding $EuCl_3 \cdot 6H_2O$ (39 mg, 0.11 mmol). The resulting mixture was kept at room temperature for 1 h. The product was extracted with DCM (3 x 20 mL) and dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure. Yield 55 mg (0.045 mmol, 45%). ESI-MS, *m/z*: found 1189.30 $(M+H)^+$, required 1189.30. Found, %: C 59.89, H 3.94, N 6.47. $C_{63}H_{51}EuN_6O_9 \cdot CH_2Cl_2$ calculated, %: C 60.38, H 4.20, N 6.60.

3. Results and discussion

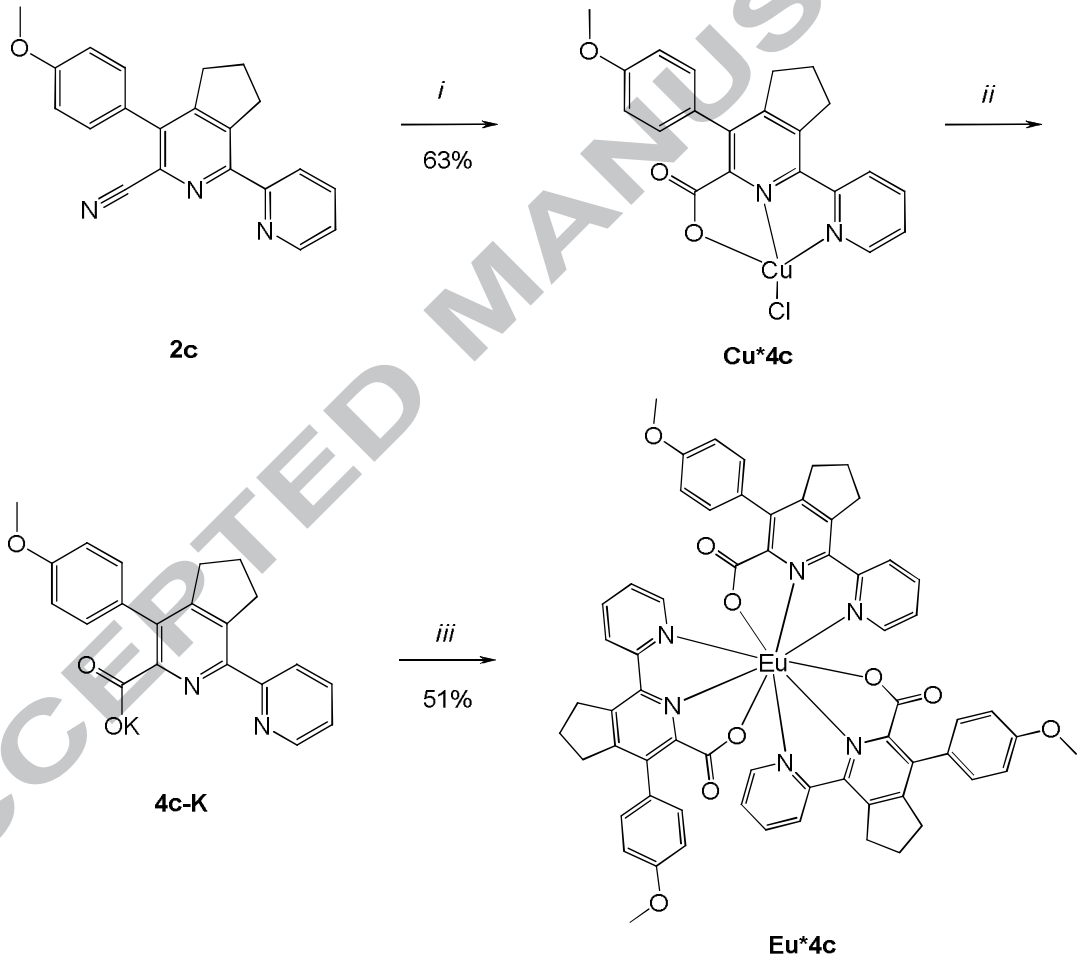
As starting compounds for the preparation of the target ligands, the previously described 6-aryl-3-(2-pyridyl)-1,2,4-triazine-4-oxides **1**[14] were obtained. The subsequent nucleophilic substitution of a hydrogen atom by the cyanide anion generated *in situ* and the following aza-Diels-Alder reaction with 2,5-norbornadiene or 1-morpholinocyclopentene, used as dienophiles, afforded the cyano-substituted precursors **2** and **3**[14] of the target ligands. The final products, the 5-aryl-2,2'-bipyridine-6-carboxylic acids **4** and **5**, were obtained by the acidic hydrolysis of the cyano group in a media of 50% sulfuric acid. Such reaction conditions allow the one-step synthesis without isolation of the intermediate amide, unlike in the previously reported method.[14]

At the final step, the *in situ* prepared sodium salts of acids **4** and **5** were reacted with europium(III) or terbium(III) chloride in a solution of methanol at room temperature to form the corresponding complexes **Ln*4** and **Ln*5** (Scheme 1, Table. 1).



Scheme 1. Synthesis of neutral lanthanides chelates of acids **4** and **5**. Reagents and conditions: *i*) Acetone cyanohydrin, DCM, 40 °C, 30 min; *ii*) 1-morpholinocyclopentene, toluene, 110 °C, 1.5 h, then acetic acid, 118 °C, 2 min; *iii*) 2,5-norbornadiene, toluene, 110 °C, 7 h; *iv*) H_2SO_4 (50%), 140 °C, 10 h; *v*) NaOH (1 eq.), ethanol, 78 °C, 5 min, then $LnCl_3 \cdot 6H_2O$ (0.33 eq.), 20 °C.

In the case of the 2,2'-bipyridine **2c**, containing a strong electron donor methoxy group, during the hydrolysis of the cyano-group in 50% sulfuric acid a side reaction of sulfonation of the 4-methoxyphenyl moiety, as well as the demethylation reaction, occurred. Attempts at the hydrolysis of **2c** under basic conditions, even after boiling for several hours, did not result in the formation of the carboxylic acid either. However, according to the literature, the formation of complexes with transition metals cations considerably facilitates the reaction of nitriles with various nucleophiles.[18] In particular, such effects were previously reported for 2-cyanopyridines[19] and 5-aryl-6-cyano-2,2'-bipyridines.[20] The hydrolysis of the cyano group in the latter case takes place in aqueous ethanol under reflux in the presence of 1 equivalent of copper dichloride. The main disadvantage of this method is the formation of a sufficiently stable copper complex as the reaction product.



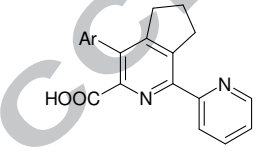
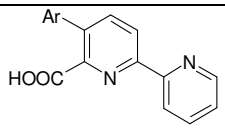
Scheme 2. Preparation of **Eu*4c**. Reagents and conditions: *i*) $CuCl_2 \cdot 2H_2O$, EtOH/H_2O (1:1), 85 ºC, 8 h; *ii*) KCN, EtOH/H_2O (1:1), 50 ºC, 30 min; *iii*) $EuCl_3 \cdot 6H_2O$, EtOH/H_2O (1:1), 20 ºC, 2 h.

This approach was used in the current work for the hydrolysis of cyanopyridine **2c**, and by reacting of **2c** with $CuCl_2 \cdot 2H_2O$ the copper complex of bipyridine carboxylic acid, **Cu*4c**, was isolated (Scheme 2). The extremely high stability of the complex prevented the isolation of the acid **4c** in its pure form. On the other hand, the dissociation of **Cu*4c** in the presence of *in situ* generated KCN followed by the addition of europium(III) chloride to the reaction mixture afforded the target complex **Eu*4c**, after the extraction of the aqueous reaction mixture with methylene chloride.

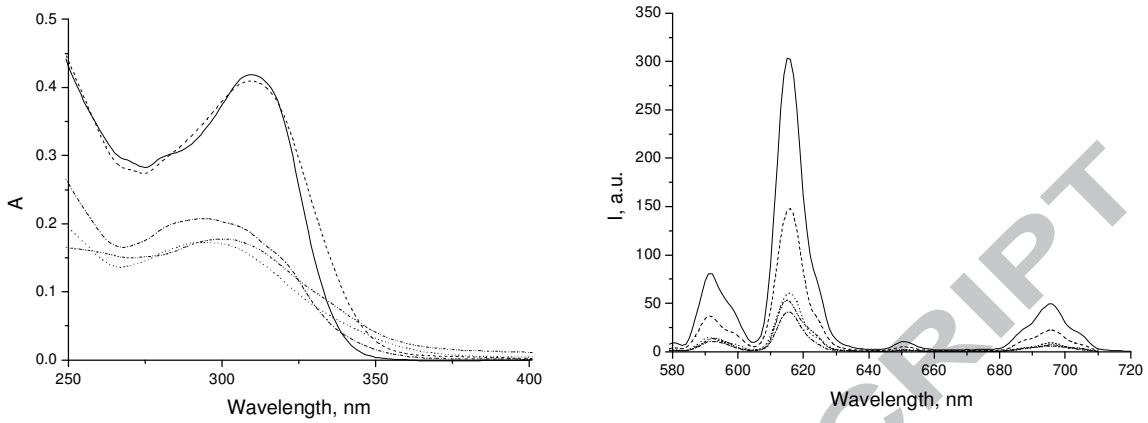
The structures of the obtained complexes were confirmed by elemental analysis, mass spectrometry (ESI-MS) and IR spectroscopy. In particular, upon chelating of the europium cation the ligand carbonyl group vibration band shifts from 1720 to 1640 cm^{-1}, which directly indicates the participation of the carboxyl group in the complexation of the lanthanide cation. In addition, assignment of peaks and their intensities by mass spectrometry match the expected isotopic distribution of the europium complexes.

The complexes **Eu*4** and **Eu*5** show the typical photoluminescence of europium chelates (Table 1). At room temperature in solutions of methylene chloride, upon excitation of these complexes at the absorption maximum, i.e. in the range 294-309 nm, which corresponds to the π–π* transitions of the ligand, a strong luminescence is observed. The luminescence spectra show the typical narrow bands of the europium cation emission (591, 615 and 695 nm). The europium cation luminescence quantum yields of these complexes are in the range 3.2-11%. The data obtained are summarized in Table 1 and the absorption and emission spectra are shown in Fig. 2.

Table 1. Photophysical properties of the lanthanide complexes of ligands **4** and **5**

Ligand structure	Ar	Lanthanide complex	Absorption, λ_{max}, nm (ε, 10^{-3} M^{-1} $см^{-1}$)[a]	Φ[b]	τ[c], ms
	Ph	**Eu*4a**	309 (41.9)	0.064	
	Tol	**Eu*4b**	309 (41.0)	0.11	
	4-$MeOC_6H_4$	**Eu*4c**	232 (34.5), 295 (17.3)	0.057	1.1
	4-FC_6H_4	**Eu*4d**	232 (42.6), 294 (20.7)	0.042	0.95
	4-FC_6H_4	**Tb*4d**	232 (42.7), 296 (21.8)		
	Tol	**Eu*5b**	300*	0.032	0.8

[a]In a solution of CH_2Cl_2 at room temperature; [b]Europium cation luminescence quantum yields were measured in CH_2Cl_2 solution using $[Ru(bpy)_3]Cl_2$ as a standard[21]; [c]Europium cation luminescence lifetime; *Due to the low solubility, the extinction coefficient could not be measured

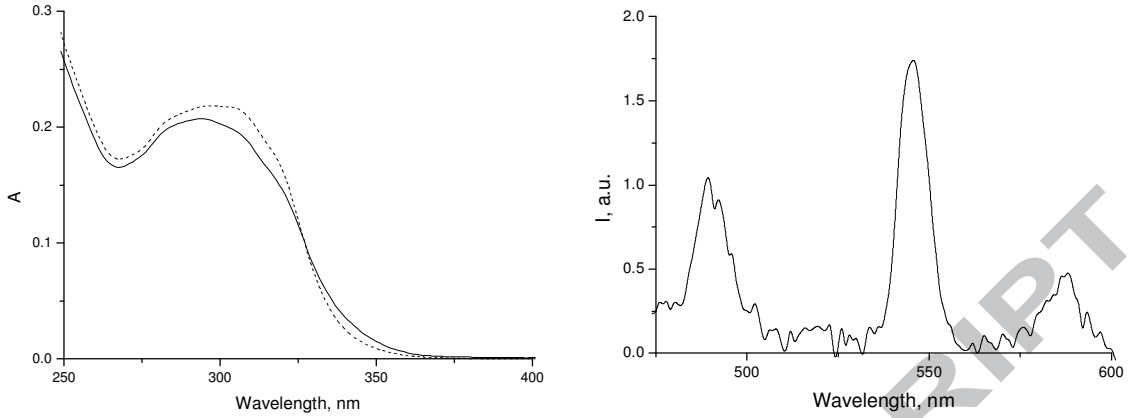


a) **b**)

Fig. 2. The absorption spectra (**a**) and europium cation luminescence spectra (**b**) of complexes **Eu*4** (**Eu*4a** – solid lines; **Eu*4b** – dash lines; **Eu*4c** – dot lines; **Eu*4d** – dash dot lines) and **Eu*5** (dash dot dot lines) in CH_2Cl_2 solution at room temperature.

The D_{2d} site symmetry of the Eu^{3+} cation was determined from the luminescent spectra, in accordance with the number of components in the transitions $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$.[22]

Complex **Tb*4d** showed a very weak terbium cation luminescence in CH_2Cl_2 solution at room temperature, with two major bands at 490 and 545 nm. Apparently, an increase of the conjugation system of the ligand due to the introduction of an aromatic substituent reduces the energy of the excited state of the ligand, which greatly complicates the energy transfer to the higher in energy $^5D_4$ level of the terbium cation, followed by sensitization of the terbium cation luminescence. In the europium complexes, the ligand-to-metal energy transfer takes place on the $^5D_0$ level, which is much lower in energy, therefore significant sensitization of europium cation luminescence is observed. The absorption spectra of the complexes **Eu*4d** and **Tb*4d** (Fig. 3a) actually do not differ in shape. The terbium cation luminescence spectrum of the complex **Tb*4d** is shown in Fig. 3b.



a) **b**)

Fig. 3. The absorption spectra of the complexes **Eu*4d** (solid line) and **Tb*4d** (dash line) (**a**) and the terbium cation luminescence spectrum of the complex **Tb*4d** (**b**) in CH_2Cl_2 solution at room temperature.

As was expected, analysis of the photophysical data clearly demonstrates the significant influence of the nature of the aromatic substituent in position C5 of the pyridine ring on the efficiency of the luminescence of the europium cation. Thus, complex **Eu*4b** showed the most intense luminescence, having a ligand with the tolyl moiety.

A comparison of the solubility of complexes **Eu*5b** and **Eu*4** in non-polar solvents showed that it was much higher for the latter case (up to 10g/L in CH_2Cl_2), which is due to the annelution of the cyclopentene fragment. Thus, the "1,2,4-triazine" approach to 2,2'-bipyridine ligands can largely eliminate the low solubility drawback of the majority of such complexes. Especially notable is the fact that the europium cation luminescence of complex **Eu*5b** is less effective compare to **Eu*4**.

Compare to the previously reported photophisycal data for similar neutral lanthanide complexes, i.e. a luminescence quantum yield of 85%[4b] and a luminescence lifetime of 2.81 ms[5b], both the luminescence quantum yields and the luminescence lifetimes of europium complexes **Eu*4** and **5** are lower in value (up to 11% and up to 1.1 ms, respectively). However, the good solubility of complexes **Eu*4** in organic non-polar solvents suggests that this work approach is potentially promising from the standpoint of obtaining lanthanide complexes with acceptable properties, and further research is required in this direction for improving the photophysical properties.

4. Conclusions

In summary, in this work the synthetic approach to 4-aryl-1-(2-pyridyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine-3-carboxylic acids and 5-aryl-2,2'-bipyridine-6-carboxylic acids has been optimized, as compared with the previously described methods. The range of compounds was substantially expanded, and at first they were used as ligands for neutral lanthanide complexes. It is shown that upon varying the structure of the ligands (i.e. by varying of the nature of the aromatic substituent in the C5 position of the pyridine ring, and by the introduction of a fused cyclopentene fragment into the pyridine core) the turning of the photophysical properties of the lanthanide complexes, namely the luminescence efficiency, is possible. In addition, due to the direct annulation of the cyclopentene moiety onto the central pyridine ring, the solubility of such complexes in non-polar solvents has been improved dramatically compared with the previously reported analogs. Despite the lower values of both the luminescence quantum yields and the luminescence lifetimes of the obtained lanthanide complexes, further research for new synthetic possibilities to 2,2'-bipyridine ligands using the "1,2,4-triazine" methodology seems promising, since only in this case may highly soluble cycloalkane-annulated bipyridine ligands be obtained, which are useful for the preparation of highly soluble lanthanide chelates that are valuable for practical use.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version.

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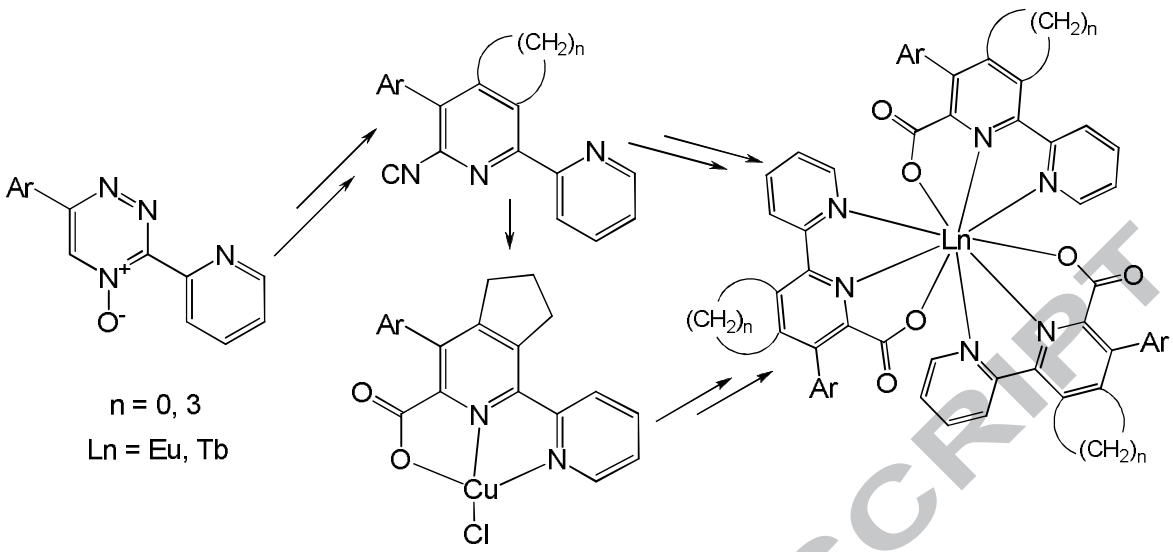

Graphical abstract

Luminescent neutral lanthanide complexes of 5-aryl-2,2'-bipyridine-6-carboxylic acids, synthesis and properties

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Abstract

Phosphorescent lanthanide complexes of 4-aryl-1-(2-pyridyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine-3-carboxylic acids and 5-tolyl-2,2'-bipyridine-6-carboxylic acid were prepared. The ligands were synthesized using the "1,2,4-triazine" methodology. In one case, the opportunity for copper complex preparation, followed by exchange of the metal cation from copper to europium to overcome synthetic difficulties, was demonstrated. The ability of tuning the properties of the complexes by means of varying the structure of the ligands was demonstrated. In particular, the introduction of the cyclopentene moiety allowed the preparation of highly soluble complexes in non-polar organic solvents.

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