

SHORT COMMUNICATION

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Synthesis of 2,6-bis-(oxazolyl)pyridine ligands for luminescent Ln(III) complexes

Goreti Pereira,^a Miguel F. Ferreira,^a Elisabete M. S. Castanheira,^b José A. Martins,^{*a} Paula M.T. Ferreira^{*a}**Keywords:** Dehydroaminobutyric acid / dipicolinic acid / bis-oxazoles / Ln(III) complexes / Luminescence

New bis-(oxazolyl)pyridine ligands for Ln(III) ions were prepared using a expeditious methodology from threonine and dipicolinic acid chloride. The synthetic strategy includes a dehydration step to give a bis-dehydroaminobutyric acid derivative followed by bromination and cyclization with DBU.

Photophysical studies of Eu(III) and Tb(III) complexes of these ligands showed that the 2,6-bis-(oxazolyl)pyridine moiety acts as an effective sensitizer for lanthanide luminescence and indicate the formation of 3:1 complexes [Ln-(bis-(oxazole)pyridine)₃]³⁺.

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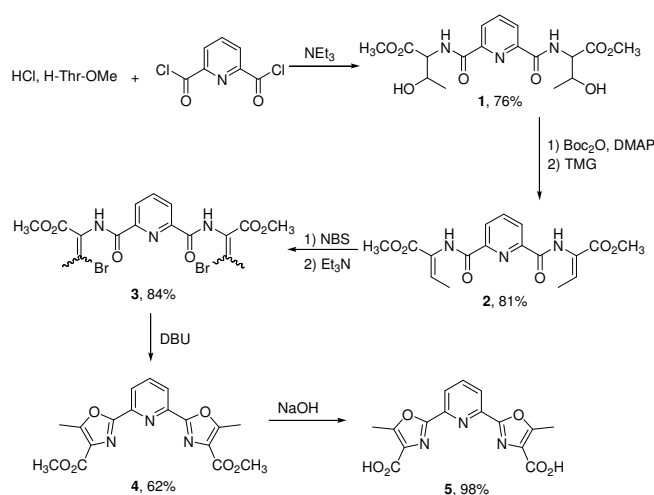
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Introduction

The unique photophysical properties of complexes of Ln(III) cations namely large Stokes shifts, narrow emission bands and long fluorescence lifetimes make them ideal as specific reporters.[1] However, direct excitation of these ions results in a very weak luminescence signal. This is due to the fact that absorption transitions within the 4f electron shell are parity forbidden and therefore the absorption coefficients for lanthanide ions are very low and also to the non-radiative deactivation of these ions by high energy vibration of the solvent molecules. The lanthanide luminescence can be effectively pumped by the use of a light absorbing coordinating ligand which sensitizes the lanthanide ion. This increase in the luminescence is the result of an efficient intramolecular energy transfer process from the excited triplet state of the ligand to the emitting level of the lanthanide ion.[2] In the last few years, a series of highly luminescent pyridine-bis(oxazoline) Ln(III) complexes has been described.[3] The 2,6-bis-(oxazolyl)pyridines coordinate readily to the lanthanide ions and sensitize the luminescence of Eu(III) and Tb(III), showing an efficient ligand-to-metal ion energy transfer process. Taking these results into account and the fact that we have recently developed a new and efficient method for the synthesis of oxazole derivatives,[4] we decided to prepare new 2,6-bis-(oxazolyl)pyridine ligands for Ln(III) ions.

Results and discussion

The new 2,6-bis-(oxazolyl)pyridine ligand was prepared from a bis-threonine derivative **1** using a methodology developed in our laboratories that involves a sequential dehydration reaction followed by halogenation and cyclization with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 1). Compound **1** was treated with *tert*-butylpyrocarbonate (Boc₂O) and 4-dimethylaminopyridine (DMAP) followed by *N,N,N',N'*-tetramethylguanidine (TMG) to afford stereoselectively the *Z*-isomer of the corresponding bis-dehydroaminobutyric acid derivative **2** in 81% yield.[5] This compound was then halogenated with *N*-bromosuccinimide (NBS) to give a mixture of the stereoisomers **3** which was treated without purification with a 2% solution of DBU in acetonitrile to give the bis-oxazole **4**. [4b] Basic hydrolysis of the methyl esters afforded the diacid **5** in good yield.



Scheme 1. Synthesis of 2,2'-(pyridine-2,6-diyl)bis(5-methyloxazole-4-carboxylates).

The ¹H NMR spectra of compounds **1-5** display as a characteristic feature a set of invariable signals due to the pyridine central core.

The ^1H NMR of compound **2** shows the signals of the β -CH and γ -CH₃ protons of dehydroaminobutyric acid at 6.97 and 1.91 ppm respectively and also the carboxamide NH protons at 9.27 ppm in CDCl₃. The stereochemistry of compound **2** was confirmed by NOE difference experiments by irradiating the α -NH proton and observing an NOE enhancement in the β -CH₃ protons. The spectrum of the mixture of *Z,Z*-**3**, *E,E*-**3** and *E,Z*-**3** shows three singlets due to the β -CH₃ protons, three singlets attributed to the OCH₃ protons, a complex signal in the aromatic region due to the pyridine protons and three broad singlets due the NH protons. Besides the aromatic protons, a common feature in ^1H NMR spectra of compounds **4** and **5** is the signal due to the methyl protons linked to the oxazole moiety at 2.81 and 2.42 ppm, respectively.

The photophysical properties of compounds **4** and **5** were studied in acetonitrile and Tris-HCl buffer (0.1 M, pH=7.45), respectively. Figure 1 shows the normalized absorption and emission spectra of these compounds. The maximum absorption (λ_{abs}) and emission wavelengths (λ_{em}), molar absorption coefficients (ϵ) and fluorescence quantum yields (Φ_{F}) are presented in Table 1.

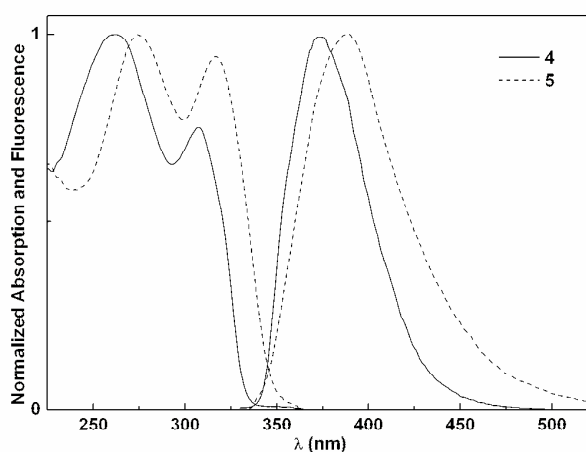


Figure 1. Normalized absorption and fluorescence spectra ($\lambda_{\text{exc}}=270$ nm) of compound **4** in acetonitrile and compound **5** in Tris-HCl buffer (0.1 M, pH=7.45) (1×10^{-5} M for absorption and 1×10^{-6} M for emission).

Table 1. Maximum absorption (λ_{abs}) and emission wavelengths (λ_{em}), molar absorption coefficients (ϵ) and fluorescence quantum yields (Φ_{F}) for compounds **4** and **5**.

Compound	Solvent	λ_{abs} (nm) ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	λ_{em} (nm)	Φ_{F} [a]
4	Acetonitrile	307 (1.66), 262 (2.21), 225 (1.42)	355	0.51
5	Tris buffer (pH=7.45)	316 (1.31), 273 (1.39)	390	0.50

[a] relative to naphthalene in cyclohexane ($\Phi_{\text{F}}=0.23$ at 25 °C [6]).

Both ligands **4** and **5** absorb strongly in the UV, with maxima at $\lambda=262$ nm for compound **4** and 273 nm for **5**. These bis-oxazoles are also strongly fluorescent, with emission quantum yields around 50%. A significant red-shift in emission is observed for compound **5** relative to **4** (Table 1) which could be ascribed, not only to solvent effects, but also to the additional intramolecular charge transfer (ICT) character of the excited state of bis-oxazole **5**, as observed previously for other compounds with carboxylic acid groups instead of methyl ester groups.[7]

Compounds **4** and **5** were then used for complexation with Eu(III) and/or Tb(III) ions and the photophysical properties of these complexes were studied. Upon excitation in the π,π^* absorption

band of **4** and **5**, lanthanide luminescence is observed (Figure 2), due to the energy transfer from the organic ligand to the Ln(III) ions. It is well known that by positioning the antenna chromophore in close proximity of the lanthanide ion enhances the efficiency of the intersystem crossing (ISC) as a result of an external heavy atom effect.[8,9] This has led to the application of fluorescent dyes which have very low intrinsic intersystem crossing quantum yields, as efficient sensitizers for near-infrared Ln(III) luminescence.

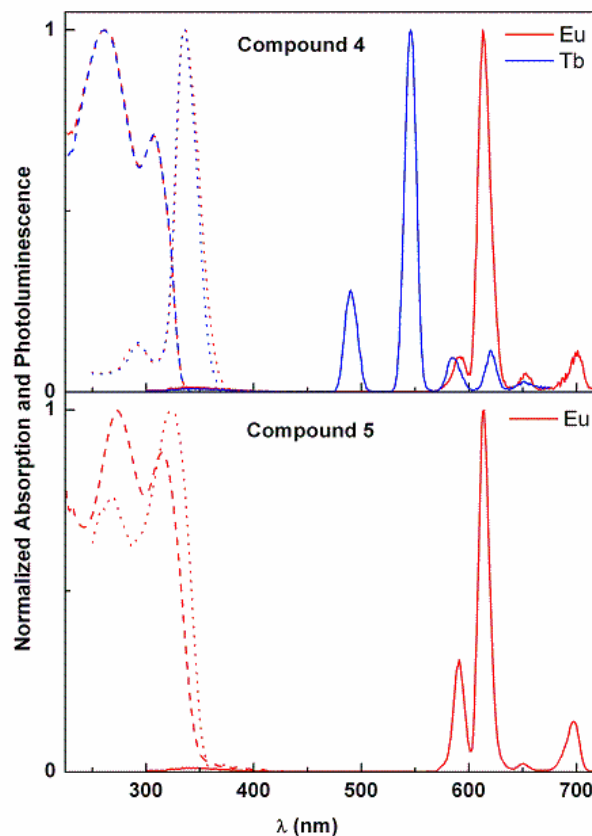


Figure 2. Normalized absorption (dashed), excitation (dotted) ($\lambda_{\text{em}}=613$ nm for Eu and 547 nm for Tb) and photoluminescence (solid) spectra of solutions of [3:1] complexes of compound **4** (1×10^{-4} M in acetonitrile) with EuCl₃ (red) and TbCl₃ (blue) and of compound **5** (1×10^{-5} M in Tris-HCl buffer) with EuCl₃.

The shapes of the absorption and excitation spectra are virtually identical for the complexes of both metals, which is consistent with sensitization of the lanthanide emission through absorption of light by the ligand and subsequent energy transfer to the lanthanide ion, in general occurring by an electron-exchange mechanism.[10]

The emission spectra exhibit the characteristic peaks for each metal ion, $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0, 1, 2, 3, 4$) for Eu(III) (578, 592, 614, 652, and 698 nm) and $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4, 3, 2, 1$) for Tb(III) (489, 545, 583, 620, 652, and 668 nm) (Figure 2).

It was described that for Eu(III) complexes, the relative intensities of the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (around 615 nm) and the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition (around 595 nm) can be related to the symmetry around the central metal ion.[11,12] In the two Eu(III) complexes, Eu-**4** and Eu-**5**, the ratio of the intensities of these transitions changes appreciably ($I_{7\text{F}2}/I_{7\text{F}1}=10.3$ for Eu-**4** and 3.2 for Eu-**5**), indicating that the first coordination sphere has different characteristics in the two species. The symmetry of the coordination sphere and the polarizability of the coordinating groups play a role in the hypersensitivity of certain Ln(III) transitions.[13] The methyl ester groups of ligand **4** are more polarizable than the carboxylic groups of **5** and this may contribute to the larger intensity of the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition in the Eu-**4** complex (Figure 2).

Luminescence titrations with anhydrous EuCl_3 and TbCl_3 were performed (Figures 3, 4 and 5) and indicate the formation of 3:1 complexes, $[\text{Ln}(\text{bis-oxazole})_3]^{3+}$. This behavior was also previously observed for other pyridine-bis(oxazoline) derivatives.[3]

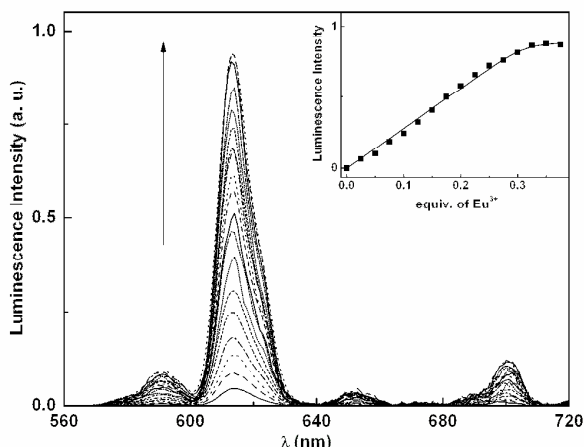


Figure 3. Luminescence titration experiment of the ligand **4** with Eu^{3+} in acetonitrile ($\lambda_{\text{exc}}=270$ nm). Inset: fit to the experimental data.

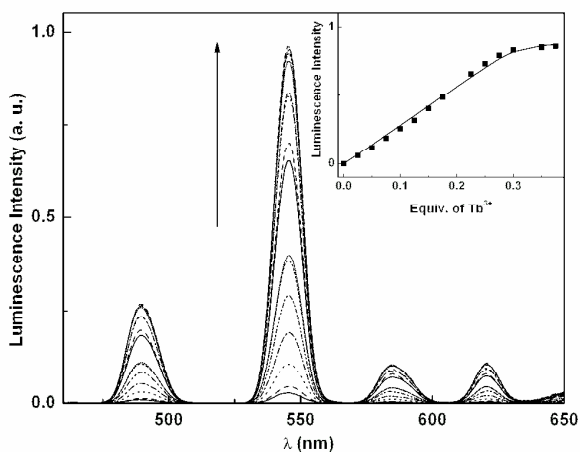


Figure 4. Luminescence titration experiment of the ligand **4** with Tb^{3+} in acetonitrile ($\lambda_{\text{exc}}=270$ nm). Inset: fit to the experimental data.

Using this stoichiometry, the stability constants were calculated for Eu-4 , Tb-4 and Tb-5 complexes, using the data from the photoluminescence titrations (insets of Figures 3, 4 and 5 show the fitting to the experimental results).

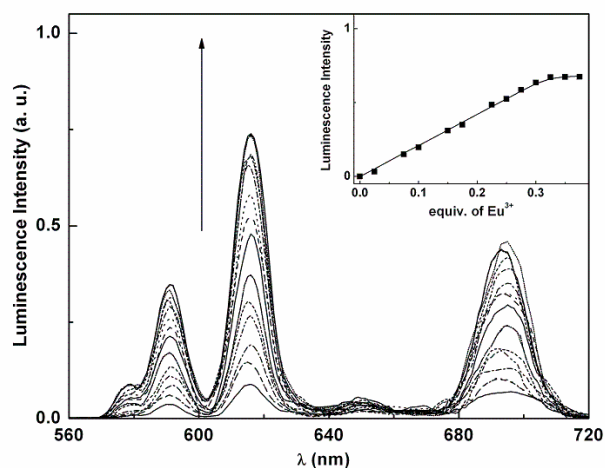


Figure 5. Luminescence titration experiment of the ligand **5** with Eu^{3+} in Tris-HCl buffer (0.1 M, pH = 7.45) ($\lambda_{\text{exc}}=270$ nm). Inset: fit to the experimental data.

The values obtained, $\log\beta=16.5\pm 0.4$ for $\text{Eu}(\mathbf{4})_3^{3+}$, $\log\beta=16.1\pm 0.5$ for $\text{Tb}(\mathbf{4})_3^{3+}$ and $\log\beta=17.3\pm 0.3$ for $\text{Eu}(\mathbf{5})_3^{3+}$, are similar or slightly higher than those for Ln(III) 1:3 complexes with other pyridine-bis(oxazoline) ligands.[3] The complex $\text{Eu}(\mathbf{5})_3^{3+}$ exhibits the largest stability constant, showing that the carboxylic groups enhance the stability of the Eu(III) complex, relative to the methyl ester groups.

All the three complexes are luminescent in both solid state and in solution. The luminescence quantum yields of the 3:1 complexes at room temperature were determined and the data are summarized in Table 2. Excited state lifetimes in solution and in the solid state were also measured (Table 2 and Figure 6).

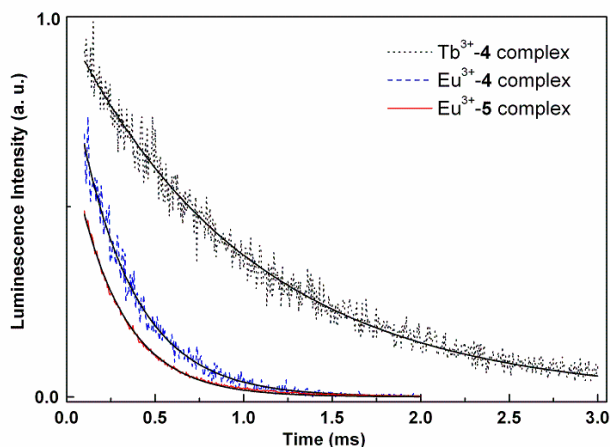


Figure 6. Decay traces (and corresponding fitting curves) for $\text{Tb}^{3+}\text{-4}$ and $\text{Eu}^{3+}\text{-4}$ complexes in acetonitrile and $\text{Eu}^{3+}\text{-5}$ complex in Tris-HCl buffer (0.1 M, pH = 7.45).

Table 2. Maximum absorption (λ_{abs}) and emission (λ_{em}) wavelengths, molar absorption coefficients (ϵ), luminescence quantum yields (Φ_L) and lifetimes (τ) for Ln(III) complexes with ligand **4** in acetonitrile and with ligand **5** in Tris buffer (0.1 M, pH=7.45) at T=293 K (lifetimes in solid state are also shown).

Complex	λ_{abs} (nm) ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	λ_{em} (nm)	τ (ms)	$\Phi_L^{[a]}$
$[\text{Eu}(\mathbf{4})_3]\text{Cl}_3$	308 (5.59), 261 (6.43)	577, 591, 614, 652, 698	0.46 0.19 (solid)	0.0008
$[\text{Tb}(\mathbf{4})_3]\text{Cl}_3$	307 (3.65), 262 (5.15)	489, 545, 583, 620, 652, 668	1.04 0.24 (solid)	0.00027
$[\text{Eu}(\mathbf{5})_3]\text{Cl}_3$	315 (1.61), 273 (1.82)	578, 591, 614, 651, 698	0.27 0.31 (solid)	0.0008

[a] Relative to $\text{Cs}_3[\text{Eu}(\text{dipic})_3]$ for Eu(III) complexes and $\text{Cs}_3[\text{Tb}(\text{dipic})_3]$ for Tb(III) complexes in Tris-HCl buffer (0.1M, pH=7.45) [14].

The luminescence quantum yields in solution (Table 2) measured at room temperature are low, but very similar to the ones reported for Ln(III) complexes with calix[4]azacrown ligands at the same temperature.[15]

The lifetime values are again similar to the ones reported for Eu and Tb complexes with calixarenes [15], the complex with Tb³⁺ exhibiting a significantly higher lifetime. Eu(III) luminescence, generated by excitation in the π,π^* absorption band of **4** and **5**, is characterized by comparably short lifetimes, pointing to the participation of a charge transfer (CT) state. This is supported by the observation of a clear additional band with maximum at *ca.* 340 nm in the excitation spectrum of Eu-**4** and Tb-**4** complexes (Figure 2 – top). This band is also present but in a lower extent in the excitation spectrum of Eu-**5** complex (Figure 2 - bottom). The involvement of a CT state as an efficient nonradiative deactivation channel has been demonstrated for several other Ln(III) complexes that exhibit very low luminescence quantum yields.[15-17] This CT state could be formed between the carbonyl groups of the ligands and the Ln(III) ions. Additionally, nonradiative quenching by OH groups [18] could justify the lower lifetime of Eu-**5** relative to Eu-**4** complex in solution.

Conclusions

New highly fluorescent 2,6-bis-(oxazolyl)pyridine derivatives (**4** and **5**) were synthesized in good yield using a simple and efficient methodology from a threonine derivative and dipicolinic acid chloride. Upon excitation in the π,π^* absorption band of the 2,6-bis-(oxazole)pyridine derivatives, Eu³⁺ and Tb³⁺ luminescence is observed. Therefore, the bis-(oxazole)pyridine moiety acts as a sensitizer for lanthanide(III) luminescence. The complexes of the bis-oxazole **4** with Tb(III) and Eu(III) and of the bis-oxazole **5** with Eu(III) are luminescent at room temperature, both in solution and in the solid state.

Experimental Section

Melting points (°C) were determined in a Gallenkamp apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Varian Unity Plus at 300 and 75.4 MHz, respectively or on a Bruker Avance II⁺ at 400 and 100.6 MHz, respectively. ¹H-¹H spin-spin decoupling and DEPT θ 45° were used. Chemical shifts are given in ppm and coupling constants in Hz. MS and HRMS data were recorded by the mass spectrometry service of the University of Vigo, Spain; elemental analysis was performed on a LECO CHNS 932 elemental analyser.

The reactions were monitored by thin layer chromatography (TLC). Column chromatography was performed on Macherey-Nagel silica gel 230-400 mesh. Petroleum ether refers to the boiling range 40-60 °C. When solvent gradient was used, the increase of polarity was made from neat petroleum ether to mixtures of diethyl ether/petroleum ether, increasing 10% of diethyl ether each time until the isolation of the product.

All metal complexes were prepared in a similar manner in air by mixing stoichiometric amounts of ligand and LnCl₃ (Ln=Eu, Tb) in acetonitrile. After stirring for 1 h, the solvent was removed under reduced pressure, and a minimum amount of acetonitrile form a saturated solution. The solution was filtered giving the complexes as white solids.

Synthesis of compound 1

Triethylamine (4.4 equiv.) was added to a solution of the methyl ester of the threonine hydrochloride (11 mmol) in dichloromethane (0.1 M). 2,6-Pyridinedicarbonyl dichloride (5 mmol) was then slowly added with vigorous stirring and cooling in an ice bath. After stirring at 0 °C for 30 min, the solution was stirred at room temperature overnight. The reaction mixture was then concentrated and partitioned between ethyl acetate (200 mL) and KHSO₄ (1 M, 100 mL) and washed with water and brine (3x50

mL). After drying over MgSO₄, the extract was taken to dryness at reduced pressure to afford compound **1** (1.40g, 76%) as an oil. ¹H NMR (400 MHz, CDCl₃): δ =1.24-1.27 (m, 6 H, γ CH₃), 3.75 (s, 6 H, OCH₃), 4.45-4.48 (m, 2 H, β CH), 4.77-4.81 (m, 2 H, α CH), 7.98-8.03 (m, 1 H, HAR), 8.30 (d, *J* = 7.6 Hz, 2 H, HAR), 8.91 (d, *J* = 9.2 Hz, 2 H, NH) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 20.00 (γ CH₃), 52.62 (OCH₃), 57.88 (α CH), 68.06 (β CH), 125.38 (2CH), 138.99 (CH), 148.28 (C), 164.10 (C=O), 171.59 (C=O) ppm. HRMS (micrOTOF): calcd. for C₁₇H₂₃N₃NaO₈ 420.1383; found 420.1377.

Synthesis of compound 2

DMAP (0.11 equiv.) was added to a solution of compound **1** (0.80 g, 2 mmol) in dry acetonitrile (1 M), followed by di-*tert*-butyl dicarbonate (1.1 equiv.) with rapid stirring at room temperature. The reaction was monitored by TLC (diethyl ether/petroleum ether, 1:1) until all the reactant had been consumed. TMG (2% in volume) was then added, stirring was continued, and the reaction was followed by TLC. When all the reactant had been consumed, evaporation at reduced pressure gave a residue that was partitioned between dichloromethane (100 mL) and KHSO₄ (1 M, 30 mL). The organic phase was thoroughly washed with KHSO₄ (1 M) and brine (2x30 mL) and dried with MgSO₄. Removal of the solvent afforded the compound **2** (0.59 g, 81%) as a white solid. M.p. 165.0-166.0 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.91 (d, *J* = 7.2 Hz, 6 H, γ CH₃), 3.83 (s, 6 H, OCH₃), 6.97 (q, *J* = 7.5 Hz, 2 H, β CH), 8.10 (t, *J* = 7.8 Hz, 1 H, HAR), 8.42 (d, *J* = 7.5 Hz, 2 H, HAR), 9.27 (s br, 2 H, NH) ppm. ¹³C NMR (75.4 MHz, CDCl₃): δ = 15.11 (γ CH₃), 52.48 (OCH₃), 125.67 (α C), 125.70 (β CH), 134.48 (CH), 139.41 (C), 161.11 (C=O), 164.93 (C=O) ppm. C₁₇H₁₉N₃O₆ (361.35): calcd. C 56.51, H 5.30, N 11.63; found C 56.05, H 5.27, N 11.64.

Synthesis of the mixture of stereoisomers 3

To a solution of compound **2** (0.687 g, 1.9 mmol) in dichloromethane (0.1 mol dm⁻³) 1.5 equiv. of *N*-bromosuccinimide was added with vigorous stirring. After reacting for 16 hours, triethylamine (1.5 equiv.) was added and stirring continued for an additional hour. Dichloromethane (50 cm³) was added and the organic phase was washed with water and brine (3x30 cm³ each). After drying over MgSO₄, the extract was taken to dryness at reduced pressure. Dry flash using diethyl ether/petroleum ether (2:1) give a mixture of stereoisomers **3** (0.830 g, 84%), as a white solid. ¹H NMR (400 MHz, CDCl₃): δ = 2.51, 2.52 and 2.64 (s, γ CH₃), 3.87, 3.88 and 3.90 (s, OCH₃), 7.82 and 8.02 (t, *J* = 8.0 Hz, ArH), 8.10 (d, *J*=8.0 Hz, ArH), 8.29-8.33 (m, ArH) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 24.76, 26.08 and 26.27 (γ CH₃), 52.58, 52.61 and 52.88 (OCH₃), 123.75, 124.39 and 124.87 (C), 125.38, 125.70 and 126.62 (C), 125.54, 125.89 and 125.96 (CH), 139.10 and 139.49 (CH), 147.63, 147.68 and 147.70 (C), 160.64, 160.68 and 161.01 (C=O), 162.99, 164.32 and 165.24 (C=O) ppm. C₁₇H₁₇BrN₃O₆ (357.32): calcd. C 39.33, H 3.30, N 8.09; found C 39.19, H 3.80, N 7.441.

Synthesis of compound 4

To a solution of the mixture of **3** (0.140 g, 0.27 mmol) in acetonitrile (10⁻² mol dm⁻³), 2% of DBU was added with stirring at room temperature. The reaction was followed by TLC until all the starting material was consumed (approximately 3 hours.). The reaction mixture was filtered giving compound **4** (60 mg, 62%) as a white solid, M.p. 225.0-226.0 °C (from ethyl acetate/petroleum ether). ¹H NMR (400 MHz, CDCl₃): δ = 2.81 (s, 6 H, CH₃), 3.98 (s, 6 H, OCH₃), 7.99 (t, *J* = 8.0 Hz, 1 H, HAR), 8.35 (d, *J* = 8.0 Hz, 1 H, HAR) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ = 12.43 (CH₃), 52.17 (OCH₃), 123.71 (CH), 129.08 (C), 138.25 (CH), 145.57 (C), 157.62 (C), 158.19 (C), 162.47 (C=O) ppm. C₁₇H₁₅N₃O₆ (357.32): calcd. C 57.14, H 4.23, N 11.76; found C 56.76, H 4.54, N 11.78.

Synthesis of compound 5

To a solution of the mixture of **4** (30 mg, 0.084 mmol) in methanol (1 mL), 3 equiv. of NaOH (1 mol.dm⁻³) were added with stirring at room temperature. The reaction was followed by tlc until all the starting material was consumed (approximately 3 hours). The methanol was removed and the reaction mixture was acidified to pH 2-3 with KHSO₄ 1 mol dm⁻³. The solid formed was filtered, giving compound **5** (27 mg, 98%) as a white

solid, M.p. 342.0-345.0 °C. ¹H NMR (400 MHz, D₂O): δ= 2.42 (s, 6 H, CH₃), 7.50-7.68 (m, 3 H, HAR) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ= 11.40 (CH₃), 122.62 (CH), 132.95 (C), 138.92 (CH), 143.95 (C), 154.74 (C), 155.71 (C), 168.65 (C=O) ppm. HRMS (ESI-TOF): calcd. for C₁₅H₁₁N₃NaO₆ 352.0540; found 352.0523.

Spectroscopic measurements

The solutions were prepared using spectroscopic grade solvents. The solutions for all the photophysical measurements were allowed to equilibrate for 2 to 3 hours before being used. All measurements were performed at 20.0±0.5 °C. Absorption spectra were recorded in a Shimadzu UV-3101PC UV-Vis-NIR spectrophotometer. Fluorescence measurements were performed using a Spex Fluorolog 2 spectrofluorimeter, equipped with double monochromators in both excitation and emission. Fluorescence spectra were corrected for the instrumental response of the system. For fluorescence quantum yield determination, the solutions were previously bubbled for 30 minutes with ultrapure nitrogen. The fluorescence quantum yields (Φ_s) were determined using the standard method (equation 1) [19]

$$\Phi_s = \frac{A_r F_s n_s^2}{A_s F_r n_r^2} \Phi_r \quad (1)$$

where *A* is the absorbance at the excitation wavelength, *F* the integrated emission area and *n* the refraction index of the solvents used. Subscripts refer to the reference (r) or sample (s) compound. The excitation wavelengths of the samples were chosen to ensure that there is a linear relationship between the intensity of emitted light and the concentration of the absorbing/emitting species (*A* ≤ 0.05).

For phosphorescence measurements, the data were collected with Spex Fluorolog 2 equipped with phosphorimeter accessory, with a delay of 0.1 ms, a cycle time of 20 ms and a gate time of 0.05 ms. All reported data are the average of at least three independent measurements.

Acknowledgments

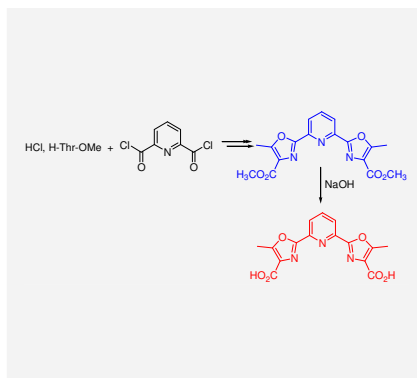
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[1] a) J. Georges, *Analyst* **1993**, 118, 1481-1486. b) J. Rocha, L. D. Carlos, F. A. Almeida Paz, D. Ananias, *Chem. Soc. Rev.* **2011**, 40, 926-940.

- [2] S. V. Eliseeva, J.-C. G. Bunzli, *Chem. Soc. Rev.* **2010**, 39, 189-227.
- [3] A. de Bettencourt-Dias, P. S. Barber, S. Viswanathan, D. T. de Lill, A. Rollett, *Inorg. Chem.* **2010**, 49, 8848-8861.
- [4] a) P. Ferreira, L. S. Monteiro, *Eur. J. Org. Chem.* **2008**, 27, 4676-4683. b) P. M. T. Ferreira, E. M. S. Castanheira, L. S. Monteiro, G. Pereira, H. Vilaça, *Tetrahedron* **2010**, 45, 8672-8680.
- [5] P. Ferreira, L. S. Monteiro, G. Pereira, L. Ribeiro, J. Sacramento, L. Silva, *Eur. J. Org. Chem.* **2007**, 35, 5934-5949.
- [6] I. B. Berlman in *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, London, **1965**.
- [7] B. F. Hermenegildo, G. Pereira, A.S. Abreu, E.M.S. Castanheira, P.M.T. Ferreira, M.-J.R.P. Queiroz, *J. Photochem. Photobiol. A: Chem.* **2011**, 221, 47-57.
- [8] a) S. Tobita, M. Arakawa, I. Tanaka, *J. Phys. Chem.* **1984**, 88, 2697-2702. b) S. Tobita, M. Arakawa, I. Tanaka, *J. Phys. Chem.* **1985**, 89, 5649-5654.
- [9] S. I. Klink, L. Grave, D. N. Reinhoudt, F. C. J. M. van Veggel, M. H. V. Werts, F. A. J. Geurts, *J. Phys. Chem. A* **2000**, 104, 5457-5468.
- [10] W. Streck, M. Wierczaczewski, *Chem. Phys.* **1981**, 58, 185-193.
- [11] A. L. Gassner, C. Duhot, J.-C. G. Bünzli, A.-S. Chauvin, *Inorg. Chem.* **2008**, 47, 7802-7812.
- [12] S. I. Klink, G. A. Hebbink, L. Grave, P. G. B. Oude Alink, F. C. J. M. van Veggel, M. H. V. Werts, *J. Phys. Chem. A* **2002**, 106, 3681-3689.
- [13] B. R. Judd, *J. Chem. Phys.* **1979**, 70, 4830-4833.
- [14] a) A.-S. Chauvin, F. Gumy, D. Imbert, J.-C. G. Bünzli, *Spectrosc. Lett.* **2004**, 37, 517-532. b) A.-S. Chauvin, F. Gumy, D. Imbert, J.-C. G. Bünzli, *Spectrosc. Lett.* **2007**, 40, 193.
- [15] I. Oueslati, R. A. Sá Ferreira, L. D. Carlos, C. Baleizão, M. N. Berberan-Santos, B. de Castro, J. Vicens, U. Pischel, *Inorg. Chem.* **2006**, 45, 2652-2660.
- [16] F. de María Ramírez, S. Varbanov, C. Cécile, G. Muller, N. Fatin-Rouge, R. Scopelliti, J.-C. G. Bünzli, *J. Chem. Soc., Dalton Trans.* **2002**, 4505-4513.
- [17] F. de María Ramírez, L. Charbonnière, G. Muller, J.-C. G. Bünzli, *Eur. J. Inorg. Chem.* **2004**, 2348-2355.
- [18] A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. de Sousa, J. A. G. Williams, M. Woods, *J. Chem. Soc., Perkin Trans. 2* **1999**, 493-503.
- [19] a) J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, 75, 991-1024; b) S. Fery-Forgues, D. Lavabre, *J. Chem. Educ.* **1999**, 76, 1260-1264.

Layout 1:

New bis-(oxazole)pyridine ligands for Ln(III) ions were prepared using an expeditious methodology from threonine and dipicolinic acid chloride. Photophysical studies of the Eu(III) and Tb(III) complexes with this ligand showed that the 2,6-bis-(oxazolyl)pyridine moiety acts as an effective sensitizer for lanthanide luminescence and indicate the formation of 3:1 complexes [Ln-(bis-(oxazole)pyridine)₃]³⁺.



Luminescent Ln(III) complexes

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Synthesis of 2,6-bis-(oxazolyl)pyridine ligands for luminescent Ln(III) complexes

Keywords: Dehydroaminobutyric acid / dipicolinic acid / bis-oxazoles / Ln(III) complexes / Luminescence