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Two new triazole-pyridine-bistetrazolate ligands were synthesized via a versatile procedure that allows for further derivatization; their corresponding homoleptic tris-ligand nona-coordinated lanthanide complexes are highly luminescent in the solid state and in a PVA polymeric matrix with measured values for the luminescence quantum yield of 70(7) and 98(9)% for Eu\(^{III}\) and Tb\(^{III}\), respectively.

Due to their remarkable intrinsic photophysical properties (narrow emission lines, large quantum yields and high resistance to photobleaching), lanthanide ions have attracted increasing attention for a broad range of applications ranging from material science to bioanalysis.\(^1\) However, due to their low absorption coefficients, the stable complexation of lanthanide ions with sensitizing ligands such as β-diketonates, aromatic carboxylates or heterocyclic compounds, capable of efficient energy-transfer to the lanthanide excited state, is essential for the development of such applications.\(^2\) Numerous efforts have been directed towards the understanding of the energy transfer between ligands and lanthanide ions with the aim of obtaining high luminescence quantum yields. Indeed high photoluminescence quantum yields and reasonable stability are crucial for the technological application of lanthanide complexes in the areas of energy conversion (luminescent dyes or solar concentrators) or in devices such as light emitting diodes.\(^3\) However, lanthanide complexes showing a quantitative ligand to metal energy transfer leading to luminescence quantum yields higher than 90%, remain extremely rare.\(^4\) Recently we have reported a new class of di-tetrazolate ligands containing bipyridine, terpyridine, hydroxyquinoline and pyridine chromophores.\(^5\) These complexes demonstrated an extension of the absorption windows and higher luminescence quantum yields compared to analogous diketonate derivatives such as dpa\(^{2-}\) for both the Eu and Tb ions while maintaining a comparable stability with respect to dissociation.

Here we report two new triazole-pyridine-bistetrazolate ligands prepared via a versatile synthetic procedure (Scheme 1) which show that the derivatization of the pyridine-di tetrazolate scaffold with a 1,2,3-triazole using click chemistry leads to an optimized energy transfer, affording lanthanide complexes with very high luminescent quantum yields, up to 70% for Eu and 98% for Tb. The ligands \(L_1\) and \(L_2\) were synthesized in six and seven steps from chelidamic acid with global yields of 38 and 22% respectively. The chosen synthetic route allows the synthesis of both ligands from the same alkyne intermediate in just one or two steps based on click chemistry. We anticipate that this versatile route can be used for the synthesis of a wide range of N-substituted triazole derivatives. The \(^1\)H NMR in d6-DMSO shows, for both the ligands, the labile tetrazole protons and in the case of \(L_1\) also the triazole proton (Figure S1). The pK\(_a\)'s of \(L_1\) (pK\(_{a_1}\) = 7.7(1) pK\(_{a_2}\) = 9.2(1)) were determined in water by UV absorption spectroscopy. These values indicate that the tetrazole group can be deprotonated using triethylamine as a base while in these conditions the triazole remains protonated.

The UV-visible absorption spectra of \(L_1\) and \(L_2\) feature two main bands located around 227 and 303 nm assigned to the π→π* transitions mainly located on the pyridine. Upon ligand deprotonation these bands are slightly shifted with the appearance of an additional absorption band at 250 nm. The absorption bands of the deprotonated ligands are slightly red-shifted by ca. 15-20 nm upon complexation to Eu\(^{III}\) (Figure S7). The complexation of Eu\(^{III}\) was monitored in MeOH (2.5x10^{-5} M) by UV spectroscopy and the titration data could be fitted to the following model with \(L_1\) = \(L_{1a}\) and \(L_2\) = \(L_{2a}\) (charges omitted for the sake of simplicity):

\[
\text{Eu} + \alpha L_i \Leftrightarrow \text{Eu}(L_i)_\alpha \quad \log \beta_\alpha = \frac{[\text{Eu}(L_i)_\alpha]}{[\text{Eu}][L_i]_\alpha} (1)
\]

consistent with the presence of four absorbing species (\(L_{ia}\), [Ln(L_{ia})], [Ln(L_{ia})] and [Ln(L_{ia})]). The lower values of logβ1, logβ2, and logβ3 determined for \(L_1\) (6.3(2), 10.2(5), 17.2(3)) compared to \(L_2\) (7.2(3), 11.8(3), 18.6(4)) indicates a slightly...
reduced stability of the complexes formed by L₁. These values are similar to those reported for the trianionic homoleptic Eu(III) complexes of the dipicolinate ligand (dpa⁺). These results are in line with that observed for terypyridine based tetrazolate ligands and indicate that tetrazolate and carboxylate-based ligands afford lanthanide complexes of comparable stability. A sizeable increase of both the absorbance red-shift and the absorption coefficient is also observed for the triazole-substituted L₁ and L₂ compounds compared to the pyridine-bistetrazolate analogues (Figure S8).

The homoleptic complexes [Ln(L₃)₃](Et₃NH)₃ (Ln = La, Pr, Eu, Tb, L₁ = L₁, L₂) have been prepared by reacting three equivalents of L₁ or L₂ with one equivalent of lanthanide triflate in methanol solution in the presence of triethylamine as shown in Scheme 1. Both complexes are soluble in methanol, those of L₁ are also soluble in water while the n-octyl group in L₂ renders its complexes highly soluble in CH₂Cl₂. The complexes have been characterized by proton NMR spectroscopy and mass spectrometry. The ¹H spectra of all complexes in MeOD (Figure S2-S6) show the presence of only one set of signals with two and six resonances respectively for L₁ and L₂. These features are consistent with the presence of the undissociated, rigid, D₃ symmetric [Ln(L₃)₃]⁺ solution species on the NMR timescale. Similar features were found in the closely related homoleptic complex [Ln(pytz)₃](Et₃NH)₃ (H_pytz=2,6-bis-tetrazolylpyridine).

**Figure 1.** Diagram of the PERSEUS optimized solution structure of [Eu(L₁)₃]⁺ (colour code: europium, red; nitrogen, blue; carbon grey; hydrogen, white). View along the threefold symmetry axis (left) and perpendicular to it (right).

The solution structure of the anion [Eu(L₁)₃]⁻ was determined by paramagnetic NMR spectroscopy. The proton and carbon resonances of the [Ln(L₃)₃](Et₃NH)₃ (Ln = La, Pr, Eu) complexes were assigned using ¹D and ²D-NMR experiments (HSQC, HMBC, ¹³C-NMR) with Ln = La, Pr and Eu. The separation of the PCS terms from the FC term, crucial for the structural determination, was achieved using the NMR data of the Pr and Eu complexes with the "two lanthanide method" developed by Di Bari et al. These PCS values were used together with the relaxation rates for the structural optimization by means of the program PERSEUS.

This structure (Figure 1) compares well (see ESI) with the solid state structure of the closely related complexes [Ln(L₃)₃](Et₃NH)₃ reported by our group in 2012. The coordination polyhedron around the Eu cation is best described as a slightly distorted trigonal prism. The similarity of the chemical shifts of the paramagnetic complexes [Ln(L₃)₃](Et₃NH)₃ indicates that, as anticipated, the presence of the n-octyl substituent on the triazole does not significantly affect the solution structure.

Photophysical data have been collected both in the solid state and in methanol solution for the [Ln(L₃)₃](NHET₃)₃ (Ln = Eu, Tb, Nd, Yb, Figure 2a and ESI) and they show that the ligands L₁ and L₂ efficiently sensitize the lanthanide emission both in the visible and NIR range. In solution, the ligand emission levels were determined for L₁ and L₂ through UV excitation in the (n,π*) absorption bands. For L₁, the emission of the 1ππ* and 3ππ* states occur at 28 600 cm⁻¹ and 24 800 cm⁻¹, respectively. For L₂ they are found at 28 450 and 23 900 cm⁻¹ (23 100 cm⁻¹ in solid state), respectively, in agreement with the increased conjugation. The 3ππ* mono-exponential luminescence decay is unusually long at 3.4(1) s, close to that obtained for benzoic acid.

The luminescence emission spectra of the Ln(III) complexes of both the singlet and triplet states are not observed. It is worth noting that the metal-centered luminescence is efficiently sensitized, in spite of the relatively large energy gaps between the ligand triplet state and the Eu(III) accepting level (ΔE(3ππ*) = 5500 cm⁻¹ for Tb(III), ΔE(3ππ*) = 6600 cm⁻¹ for L₁ and 7560 cm⁻¹ for L₂). The energy gap between the Tb(III) accepting level and the L₁ and L₂ triplet state is optimum for a quantitative energy transfer with ΔE(1ππ* - 3ππ*) ≈ 3410 and 4310 cm⁻¹, respectively. The emission spectra of [Eu(L₁)₃](Et₃NH)₃ in MeOH (see Figure 2a and ESI), through direct excitation of the ligand, exhibit the characteristic ⁵D₉→⁷F₇ transitions and in spite of the low resolution of the emission spectrum, the crystal field splitting can be interpreted in terms of an average D₃ symmetry point group (in which ⁷F₀ is forbidden), in agreement with the solution structure determined by NMR. The solid state emission spectra are identical to those observed in solution both in shape and intensity, indicating the presence of the same structure for all the complexes.

The luminescence decays for [Eu(L₁)₃](Et₃NH)₃ are monoexponential in the 2.21-3.02 ms range and confirm the absence of solvent in the first coordination sphere of the lanthanide ion. The values of the absolute luminescence quantum yield Φ_Eu tot measured in MeOH amounts to 40–42% and increase from 41 to 70% passing from L₁ to L₂ in solid state. The latter value is among the highest reported in the literature for europium complexes (60-76%). Since Φ_Eu tot = Φ_sens × Φ_Eu, we have determined the intrinsic quantum yield Φ_Eu in Eu(III) upon direct f-f excitation, in order to better understand the origin of the high measured absolute quantum yields. 

### Table 1. Lifetimes (ms for Eu-Tb and s for Gd complexes) and absolute quantum yields (%) measured at 298K in solid state, MeOH (λex = 325 nm) and in PVA film (λex = 335 nm).

<table>
<thead>
<tr>
<th></th>
<th>Ln</th>
<th>τ_{sens}</th>
<th>τ_{τVA}</th>
<th>τ_{Dmol}</th>
<th>Φ_{sens}</th>
<th>Φ_{τVA}</th>
<th>Φ_{Dmol}</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁</td>
<td>Gd(1ππ*)</td>
<td>-</td>
<td>-</td>
<td>1.85(1)</td>
<td>-</td>
<td>3.4(1)</td>
<td></td>
</tr>
<tr>
<td>L₂</td>
<td>Eu(D₉)</td>
<td>2.68(4)</td>
<td>2.80(6)</td>
<td>2.98(9)</td>
<td>70(7)</td>
<td>70(3)</td>
<td>43(4)</td>
</tr>
<tr>
<td></td>
<td>Tb(D₉)</td>
<td>1.29(2)</td>
<td>1.29(3)</td>
<td>1.61(5)</td>
<td>98(9)</td>
<td>96(4)</td>
<td>94(9)</td>
</tr>
<tr>
<td>L₁</td>
<td>Gd(ππ*)</td>
<td>-</td>
<td>-</td>
<td>2.05(2)</td>
<td>-</td>
<td>3.4(1)</td>
<td></td>
</tr>
<tr>
<td>L₂</td>
<td>Eu(D₉)</td>
<td>2.21(3)</td>
<td>-</td>
<td>3.02(5)</td>
<td>42(4)</td>
<td>-</td>
<td>41(5)</td>
</tr>
<tr>
<td>L₁</td>
<td>Tb(D₉)</td>
<td>0.93(2)</td>
<td>0.70(2)</td>
<td>1.62(2)</td>
<td>9(1)</td>
<td>18(1)</td>
<td>79(8)</td>
</tr>
</tbody>
</table>
The obtained values of \( n_{\text{em}} \) at 0.9 and 0.73 in the solid state and MeOH respectively for \( L_2 \) (0.65 and 0.71 for \( L_1 \)) are in perfect agreement with a very efficient metal-centred emission. The \([\text{Tb}(L_2)](\text{Et}_3\text{NH})_3\) complexes display the typical lanthanide emission spectrum \( ^4\text{D}_{4,5} \rightarrow ^2\text{F}_{j} \) transitions (Figure 2a and ESI) and monoexponential luminescence decays (1.6 ms in MeOH and 0.93-1.29 ms in the solid state for \( L_1 \) and \( L_2 \), respectively). The values of the absolute luminescence quantum yield of \([\text{Tb}(L_2)](\text{Et}_3\text{NH})_3\) both in MeOH and in solid state are very high at 98(9)%. Only one example of a ligand architecture leading to quantitative quantum yield for terbium emission has been reported to date.\(^4\) The values of the luminescence quantum yield measured for \([\text{Tb}(L_1)](\text{Et}_3\text{NH})_3\) is very high at 79% in MeOH but is dramatically reduced to 9% in the solid state. This can be explained by the decrease of the \( \Delta E(\pi\pi^* - ^4\text{D}_4) \) energy gaps going from solution to solid state, allowing the mixing of the \( \pi\pi^* \) states with the \( ^4f \) levels and a subsequent back-transfer from the excited state of the metal to the ligand (decrease of the lifetime).\(^12\)\(^a\)

Additional molecular packing interactions in the solid state might also lead to quenching effects as suggested by the increase of the quantum yields (9 to 18%) from solid to PVA (polyvinyl acetate) films. Preliminary studies show that these ligands can also sensitize the Nd\(^{III}\) - and Yb\(^{III}\) centered NIR luminescence emission in MeOH (Fig. 3) with sizeable measured luminescence quantum yields of 0.023 and 0.13%.

In conclusion, we have shown that \( L_1 \) and \( L_2 \) form soluble and stable homoleptic 3:1 complexes and sensitize very efficiently the emission of Eu\(^{III}\) and Tb\(^{III}\). For the Tb complex, the measured value of the absolute quantum yield at \( \sim100\% \) indicates the presence of a quantitative energy transfer from the ligand to the metal which has only been observed once before. The versatile procedure developed for the synthesis of \( L_1 \) and \( L_2 \) allows access to complexes with different solubilities and provides a facile route for grafting or encapsulating these complexes in different substrates. Thus, the triazole-pyridine-bistetrazolate motif provides a very attractive platform with optimum energy transfer which is crucial for the application of lanthanide complexes in optical devices.

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Notes and references


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