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An efficient triazole-pyridine-bistetrazolate platform for highly luminescent lanthanide complexes†

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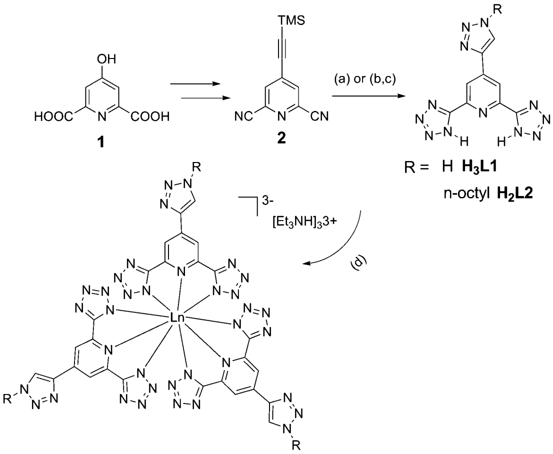
Two new triazole-pyridine-bistetrazolate ligands were synthesized *via* a versatile procedure that allows for further derivatization; their corresponding homoleptic tris-ligand nona-coordinated lanthanide complexes are highly luminescent in the solid state and in a PVA polymeric matrix with measured 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 materials 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 ditetrazolate 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 dicarboxylate derivatives such as dpa^{2-} for both the Eu and Tb ions while maintaining comparable stability with respect to dissociation.



Scheme 1 (a) NaN_3/NH_4Cl, DMF, (b, c) *n*-octyl-$N_3/K_2CO_3/CuSO_4$/sodium ascorbate/*t*-BuOH/H_2O and NaN_3/NH_4Cl/DMF, (d) Et_3N, 0.33 eq. $Ln(OTf)_3$.

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-ditetrazolate scaffold with a 1,2,3-triazole ring 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 $\mathbf{H_3L_1}$ and $\mathbf{H_2L_2}$ 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 ^1H NMR spectrum in d_6-DMSO shows, for both the ligands, the labile tetrazole protons and in the case of $\mathbf{L_1}$ also the triazole proton (Fig. S1, ESI†). The pK_a's of $\mathbf{L_1}$ ($pK_{a1} = 7.7(1)$ $pK_{a2} + pK_{a3} = 9.2(1)$) were determined in water by UV absorption spectroscopy. These values indicate that the tetrazole group can

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be deprotonated using triethylamine as a base while under these conditions the triazole remains protonated.

The UV-visible absorption spectra of $\mathbf{H_2L_1}$ and $\mathbf{H_2L_2}$ feature two main bands located at around 227 and 303 nm assigned to the $\pi \rightarrow \pi^*$ 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} (Fig. S3, ESI†). The complexation of Eu^{III} was monitored in MeOH (2.5×10^{-5} M) by UV spectroscopy and the titration data could be fitted to the following model with L_i = $\mathbf{L_1}$ and $\mathbf{L_2}$ (charges omitted for the sake of simplicity):

$$\mathrm{Eu} + {}_n\mathbf{L_i} \leftrightarrow \mathrm{Eu}(\mathbf{L_i})_n \qquad (1)$$

$$\log \beta_n = [\mathrm{Eu}(\mathbf{L_i})_n]/[\mathrm{Eu}]\cdot[\mathbf{L_i}]^n \qquad (2)$$

They are consistent with the presence of four absorbing species ($\mathbf{L_i}$, $[\mathrm{Ln}(\mathbf{L_i})_3]$, $[\mathrm{Ln}(\mathbf{L_i})_2]$ and $[\mathrm{Ln}(\mathbf{L_i})]$). The lower values of $\log\beta1$, $\log\beta2$, and $\log\beta3$ determined for $\mathbf{L_1}$ (6.3(2), 10.2(5), 17.2(3)) compared to $\mathbf{L_2}$ (7.2(3), 11.8(3), 18.6(4)) indicate slightly reduced stability of the complexes formed by $\mathbf{L_1}$. These values are similar to those reported for the trianionic homoleptic Eu(III) complexes of the dipicolinate ligand (dpa^{2-}).[6] These results are in line with those observed for terpyridine-based tetrazolate ligands[5a] 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 $\mathbf{L_1}$ and $\mathbf{L_2}$ compounds compared to the pyridine-bistetrazolate analogues (Fig. S3, ESI†).[5b]

The homoleptic complexes $[\mathrm{Ln}(\mathbf{L_i})_3](\mathrm{Et_3NH})_3$ (Ln = La, Pr, Eu, Tb, L_i = L1, L2) have been prepared by reacting three equivalents of $\mathbf{L_1}$ or $\mathbf{L_2}$ 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 $\mathbf{L_1}$ are also soluble in water while the *n*-octyl group in $\mathbf{L_2}$ renders its complexes highly soluble in CH_2Cl_2. The complexes have been characterized by proton NMR spectroscopy and mass spectrometry. The ^1H spectra of all complexes in MeOD (Fig. S4–S8, ESI†) show the presence of only one set of signals with two and six resonances, respectively, for $\mathbf{L_1}$ and $\mathbf{L_2}$. These features are consistent with the presence of the undissociated, rigid, D_3-symmetric $[\mathrm{Ln}(\mathbf{L_i})_3]^{3-}$ solution species on the NMR timescale. Similar features were found in the closely related homoleptic complex $[\mathrm{Ln}(\mathbf{pytz})_3](\mathrm{Et_3NH})_3$ ($\mathbf{H_2pytz}$ = 2,6-bis-tetrazolyl-pyridine).[5b]

The solution structure of the $[\mathrm{Eu}(\mathbf{L_1})_3]^{3-}$ anion was determined by paramagnetic NMR spectroscopy.[7] The proton and carbon resonances of the $[\mathrm{Ln}(\mathbf{L_1})_3](\mathrm{Et_3NH})_3$ (Ln = La, Pr, Eu) complexes were assigned using 1D- and 2D-NMR experiments (HSQC, HMBC, ^{13}C-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 by the "two lanthanide method" developed by Di Bari *et al.*[8] These PCS values were used together with the relaxation rates for the structural optimization by means of the PERSEUS program.[9]

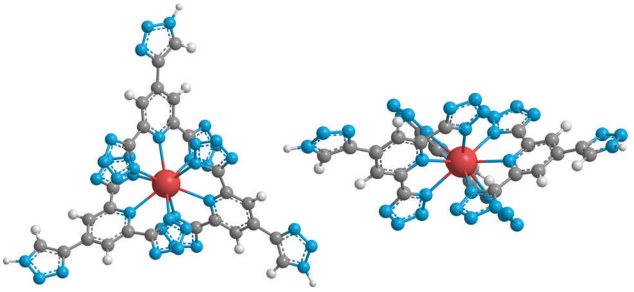

Fig. 1 Diagram of the PERSEUS optimized solution structure of $[\mathrm{Eu}(\mathbf{L_1})_3]^{3-}$ (colour code: europium, red; nitrogen, blue; carbon grey; hydrogen, white). View along the threefold symmetry axis (left) and perpendicular to it (right).

This structure (Fig. 1) compares well (see ESI†) with the solid state structure of the closely related $[\mathrm{Ln}(\mathbf{pytz})_3](\mathrm{Et_3NH})_3$ complexes reported by our group in 2012.[5b] The coordination polyhedron around the Eu cation is best described as a slightly distorted tricapped trigonal prism. The similarity of the chemical shifts of the paramagnetic $[\mathrm{Ln}(\mathbf{L_i})_3](\mathrm{Et_3NH})_3$ complexes 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 $[\mathrm{Ln}(\mathbf{L_i})_3](\mathrm{Et_3NH})_3$ (Ln = Eu, Tb, Nd, Yb, Fig. 2a and ESI†) and they show that ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ efficiently sensitize the lanthanide emission both in the visible and NIR ranges. In solution, the ligand emission levels were determined for $\mathbf{L_1}$ and $\mathbf{L_2}$ through UV excitation in the $(n,\pi) \rightarrow \pi^*$ absorption bands. For $\mathbf{L_2}$ the emission of the $^1\pi\pi^*$ and $^3\pi\pi^*$ states occur at 28 600 and 24 800 cm^{-1}, respectively. For $\mathbf{L_1}$ they are found at 28 450 and 23 900 cm^{-1} (23 100 cm^{-1} in the solid state),

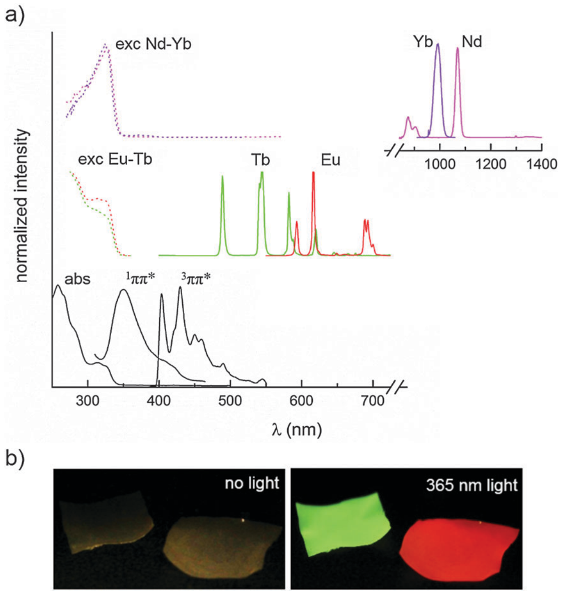

Fig. 2 (a) Absorption, excitation, singlet, triplet and emission spectra of $[\mathrm{Ln}(\mathbf{L_2})_3](\mathrm{Et_3NH})_3$ in MeOH (Ln = Eu, Tb, Nd, Yb, Gd); (b) flexible PVA films doped with $[\mathrm{Ln}(\mathbf{L_2})_3](\mathrm{Et_3NH})_3$ complexes excited or not using a UV lamp (Tb left and Eu right).

respectively, in agreement with the increased conjugation. The $^3\pi\pi^*$ mono-exponential luminescence decay is unusually long at 3.1(4) s, close to that obtained for benzoic acid.[10]

The luminescence emission spectra of the Ln^{III} complexes of $\mathbf{L_1}$ and $\mathbf{L_2}$ are consistent with the empirical rules defined for an optimal ligand-to-metal transfer process,[2b,11] since emissions from 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 with $\Delta E(^3\pi\pi^*–^5D_0) \approx 6600$ for $\mathbf{L_1}$ and 7560 cm^{-1} for $\mathbf{L_2}$. The energy gap between the Tb^{III} accepting level and the $\mathbf{L_1}$ and $\mathbf{L_2}$ triplet state is optimum for a quantitative energy transfer with $\Delta E(^3\pi\pi^*–^5D_4) \approx 3410$ and 4310 cm^{-1}, respectively.[2b] The emission spectra of $[Eu(\mathbf{L_i})_3](Et_3NH)_3$ in MeOH (see Fig. 2a and ESI†), through direct excitation of the ligand, exhibit the characteristic $^5D_0 \rightarrow {}^7F_J$ transitions and in spite of the low resolution of the emission spectrum, the crystal field splitting can be interpreted in terms of an average D_3 symmetry point group (in which $^7F_0$ 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 $[Eu(\mathbf{L_i})_3](Et_3NH)_3$ are mono-exponential 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_{tot}^{Eu} measured in MeOH amount to 40–42% and increase from 41 to 70% passing from $\mathbf{L_1}$ to $\mathbf{L_2}$ in the solid state. The latter value is among the highest reported in the literature for europium complexes (60–76%).[5b,12] Since $\Phi_{tot}^{Eu} = n_{sens} \cdot \Phi_{Eu}^{Eu}$, we have determined the intrinsic quantum yield Φ_{Eu}^{Eu} of Eu^{III} upon direct f–f excitation, in order to better understand the origin of the high measured absolute quantum yields.[6a,13,14]

The obtained values of n_{sens} at 0.9 and 0.73 in the solid state and MeOH, respectively, for $\mathbf{L_2}$ (0.65 and 0.71 for $\mathbf{L_1}$) are in perfect agreement with a very efficient metal-centred emission.

The $[Tb(\mathbf{L_i})_3](Et_3NH)_3$ complexes display the typical lanthanide emission spectrum $^5D_4 \rightarrow {}^7F_J$ transitions (Fig. 2a and ESI†) and monoexponential luminescence decays (1.6 ms in MeOH and 0.93–1.29 ms in the solid state for $\mathbf{L_1}$ and $\mathbf{L_2}$, respectively). The values of the absolute luminescence quantum yield of $[Tb(\mathbf{L_2})_3](Et_3NH)_3$ both in MeOH and in the solid state are very high at 98(9)%. Only one example of a ligand architecture leading to a quantitative quantum yield for terbium emission has been reported to date.[4] The value of the luminescence quantum yield measured for $[Tb(\mathbf{L_1})_3](Et_3NH)_3$ 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 $\Delta E(^3\pi\pi^*–^5D_4)$ energy gaps going from solution to the solid state, allowing the mixing of the $^3\pi\pi^*$ states with the 4f levels and a subsequent back-transfer from the excited state of the metal to the ligand (decrease of the lifetime).[12a,15] 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 the 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. 2a) with sizeable measured luminescence quantum yields of 0.023 and 0.13%.

Table 1 Lifetimes (ms for Eu–Tb and s for Gd complexes) and absolute quantum yields (%) measured at 298 K in the solid state, MeOH (λ_{ex} = 325 nm) and in PVA films (λ_{ex} = 335 nm)

L_i	Ln	τ_{solid}	τ_{PVA}	τ_{MeOH}	Φ_{solid}	Φ_{PVA}	Φ_{MeOH}
$\mathbf{L_2}$	$Gd(^3\pi\pi^*)$	—	—	1.85(1)	—	—	3.4(1)
	$Eu(^5D_0)$	2.68(4)	2.80(6)	2.98(9)	70(7)	70(3)	43(4)
	$Tb(^5D_4)$	1.29(2)	1.29(3)	1.61(5)	98(9)	96(4)	94(9)
$\mathbf{L_1}$	$Gd(^3\pi\pi^*)$	—	—	2.05(2)	—	—	3.4(1)
	$Eu(^5D_0)$	2.21(3)	—	3.02(5)	42(4)	—	41(5)
	$Tb(^5D_4)$	0.93(2)	0.70(2)	1.62(2)	9(1)	18(1)	79(8)

The $[Ln(\mathbf{L_2})_3](Et_3NH)_3$ complexes (Ln = Eu and Tb) are easily incorporated within flexible PVA films affording doped polymers (Fig. 2b) with photophysical properties matching those obtained for the pure complexes in the solid state (Table 1). Thus, the excellent brightness of these systems is preserved in the polymer and could be useful for photonic device applications.

In conclusion, we have shown that $\mathbf{L_1}$ and $\mathbf{L_2}$ 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 of ~100% 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 $\mathbf{L_1}$ and $\mathbf{L_2}$ 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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