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Efficient Sensitization of Lanthanide Luminescence by Tetrazole-Based Polydentate Ligands

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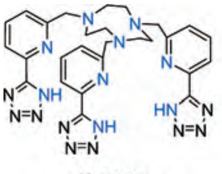
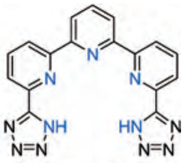
Tetrazolate groups have been included by a convenient synthetic route in diverse ligand topologies, which have allowed the incorporation of lanthanide ions into highly luminescent double- and triple-helical complexes, demonstrating their potential for the expansion of lanthanide chemistry and the development of lanthanide-based applications.

The fascinating optical and magnetic properties of lanthanide ions have promoted the use of their complexes in an increasing number of technological applications ranging from biomedical analysis (fluoroimmunoassays, MRI contrast agents, and cellular imaging) to materials science (lasers, optical fibers, light emitting diodes, and optical displays).[1–5] In particular, lanthanide ions present sharp characteristic emission in the visible and near-infrared (NIR) ranges, long luminescence lifetimes, and large Stokes shifts, which makes them very attractive candidates for the development of optical devices. Ligands that contain strongly absorbing chromophores can be conveniently used to sensitize lanthanide emission at low energy. Accordingly, numerous studies have been directed toward the design of ligands for the development of highly luminescent and robust lanthanide chelates.[2,6] However, current lanthanide chemistry, and its applications in material science and medical imaging, relies mostly on the poly(aminocarboxylate) class of ligands and related amide derivatives. Recently, new ligand scaffolds have been proposed to optimize the luminescence quantum yield in terbium and europium chelates[7] or to sensitize NIR luminescence.[8]

Tetrazolate groups are used as isosteric replacement of carboxylates in medicinal chemistry.[9] In spite of this and although two recent reports evoke the possibility of using tetrazole as lanthanide binding units,[10] the chemistry of lanthanide tetrazolates remains unexplored. Here we describe for the first time the incorporation of tetrazole in high-denticity architectures suitable for lanthanide chelation and the isolation of lanthanide complexes with an unusual coordination sphere containing only N-donor atoms. The different geometric and electronic features of these complexes with respect to carboxylate ones are likely to result in very interesting properties, as highlighted by their very efficient luminescence emission, and should lead to important applications not only in the field of optical devices but also in other areas such as MRI contrast agents or selective ion recognition.



H_3pytztcn



H_2terpytz

In order to show the versatility of the tetrazolate binding units for lanthanide complexation, we have introduced them in two selected ligand topologies: a terpyridine-based linear

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Table 1. Photophysical Characterization of the terpytz^{2-} and pytztcn^{3-} Complexes

	terpytz^{2-}			pytztcn^{3-}		
	Eu	Tb	Nd	Eu	Tb	Nd
λ_{max} (nm)	369	373	370	315	315	320
τ (ms)	2.500(7)	0.179(4)		1.13(4)	1.56(6)	0.569(2)
Φ (%)	35.3(2)	6.1(3)	0.22(1)	19.8(4)	56.1(3)	0.14(1)

ligand and a triazacyclonane-based tripodal ligand. The carboxylate analogues of these ligands have proven to be well suited to include lanthanide ions in mono- and polymetallic architectures with interesting properties.[11,12]

The linear podand H_2terpytz and the tripodal ligand H_3pytztcn containing only N-donor atoms were synthesized, and their europium complexes were isolated and crystallographically characterized, proving that tetrazole-based architectures can provide a stable coordination environment for lanthanide ions. Solid-state photophysical studies show that these tetrazole-based ligands can sensitize efficiently visible and NIR emission of lanthanide ions (Table 1). Furthermore, preliminary studies of the stability of [Eu(terpytz)$_2$]NHEt$_3$ in a methanol solution by UV−visible spectroscopy indicate for this complex containing only N donors a stability [log β = 10.5(5)] comparable to that of the analogous terpyridine dicarboxylate complex [log β = 11.8(4)].

Both tetrazole derivatives H_2terpytz and H_3pytztcn were prepared in good yield (60−90%) by the thermal cycloaddition reaction of sodium azide with the respective carbonitrile in anhydrous *N*,*N*-dimethylformamide in the presence of NH_4Cl. The versatility of this reaction, which uses easily accessible carbonitrile precursors, anticipates the facile inclusion of tetrazole motifs in a variety of ligand frameworks suitable for the development of new mono- and polymetallic lanthanide architectures. The pentadentate dianionic H_2terpytz ligand allows one to isolate the homoleptic cationic lanthanide complexes [Ln(terpytz)$_2$]NHEt$_3$ (Ln = Eu, **1**; Tb, **2**; Nd, **3**) in a pure form from a reaction with the lanthanide triflate salts in the ratio L:Ln = 2:1 in methanol and in the presence of triethylamine. X-ray-quality crystals of the europium complex formed overnight. The ORTEP view of the anion [Eu(terpytz)$_2$]$^-$ in **1** is shown in Figure 1.

In **1**, two pentadentate dianionic terpytz^{2-} ligands wrap around the Eu ion in a helical manner so as to minimize the interaction between the terminal tetrazole rings. The two ligands arrange orthogonally to yield a C_2-symmetric, double-helical mononuclear complex with Δ or Λ metal stereochemistry. Both enantiomers are present in the racemic crystal (space group *C*2/*c*). While the metal-driven assembly of helical structures continues to promote a large number of studies, less attention has been directed to lanthanide-based helical structures, although several fascinating polymetallic[13] architectures have been obtained. A plethora of triple-helical mononuclear complexes have also been reported,[14] but complex **1** is the first example of a double-helical mononuclear lanthanide complex. The packing structure is dominated by π−π interactions between pyridine−tetrazole units from different complexes. The 10 N atoms interact strongly with the lanthanide ion [Eu−N distances range from 2.569(3) to 2.704(3) Å], providing an efficiently protected environment, which should prevent the deexcitation of the Ln^{III} excited states. Furthermore, ^{1}H NMR studies show the presence of only a bisligand species in a methanol solution. Accordingly, intense luminescence was observed for the europium complex in both solution and solid state with luminescence quantum yields (35% in the solid state and 28% in methanol) comparable to those reported for the bisligand Eu^{III} complexes of terpyridine monocarboxylate (27% in methanol).[15] Furthermore, good emission efficiencies were also found for the [Tb(terpytz)$_2$]$^-$ (6.1%) and [Nd(terpytz)$_2$]$^-$ (0.22%) complexes, indicating that tetrazole-based ligands can effectively sensitize the luminescence emission of different lanthanide ions. The excitation spectra reproduce the shape of the components of the absorption spectra. This indicates an efficient intramolecular energy-transfer process from the ligand to the lanthanide ion levels. Moreover, the excitation maximum is displaced at longer (20 nm) wavelength with respect to the carboxylate analogue.

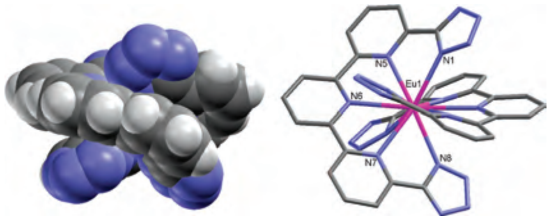

Figure 1. Space-filling representation (left) and wire diagram (right) of the [Eu(terpytz)$_2$]$^-$ anion in **1** showing the helical arrangement of the two pentadentate ligands.

To validate the efficiency of the pyridine−tetrazole unit as a sensitizer of lanthanide luminescence, we have also included it in a tripodal scaffold, which has previously afforded highly luminescent picolinate-based complexes of terbium.[12] The reaction of the nonadentate H_3pytztcn ligand with lanthanide triflates in water at pH = 7 led to the isolation of the neutral [Ln(pytztcn)] (Ln = Nd, **4**; Eu, **5**; Tb, **6**) complexes.

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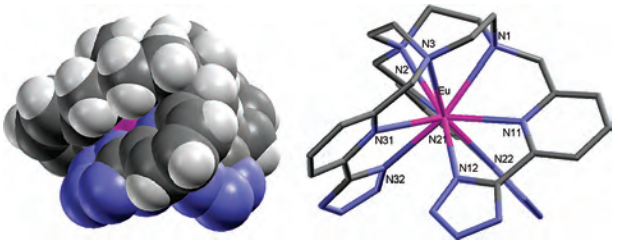

Figure 2. Space-filling representation (left) and wire diagram (right) of [Eu(pytztcn)] (**5**).

The X-ray diffraction study of [Eu(pytztcn)] revealed the presence of an Eu ion nonacoordinated by nine N atoms of the tripodal ligand, which wrap around the metal in a helical fashion. An ORTEP view of complex **5** is presented in Figure 2. The complex adopts a distorted tricapped trigonal-prism geometry with Eu−N distances ranging from 2.523(8) to 2.649(8) Å. While the low solubility of the [Ln(pytztcn)] complexes in common solvents prevented their solution characterization, the solid-state luminescence measurements showed high emission efficiencies for the $\mathrm{Tb^{III}}$ (56%) and $\mathrm{Eu^{III}}$ (20%) complexes and a sizable quantum yield for $\mathrm{Nd^{III}}$ (0.14%) accompanied by long luminescence lifetimes (Table 1). These high quantum yield values compare favorably to those found for analogous tripodal and tetrapodal ligands based on picolinate chromophores in water (45% for Tb and 7% for Eu).[12] The facile derivatization of the pyridine−tetrazole unit[10] should allow easy tuning of the complex properties (including solubility) for specific applications.

In summary, we have shown that the tetrazole group can be easily introduced in different scaffolds to afford a new class of ligands suitable for lanthanide complexation and which can efficiently sensitize lanthanide emission. Furthermore, the attractive electronic and geometric properties of these tetrazole-based ligands should prove useful in expanding lanthanide chemistry and its application to the development of lanthanide-based devices including MRI contrast agents and catalysts.

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Supporting Information Available: Full experimental procedures and spectroscopic and X-ray crystallographic (CIF) data. This material is available free of charge via the Internet at http://pubs.acs.org.

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