# First diastereoselective formation of lanthanide triple helical complexes with a terdentate chiral $C_2$ symmetric ligand†

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**Steric interactions between three enantiopure terdentate ligands leads to the diastereoselective formation of luminescent triple helical lanthanide complexes.**

Enantiopure compounds are of fundamental interest in coordination chemistry. In addition to the classical separation of racemates, several approaches for the selective synthesis of desired stereoisomers have emerged in the last decade for transition metal complexes.[1] With lanthanide centers the situation is more delicate since only slight preferences for coordination number and coordination polyhedra exist along the series. Therefore even small changes in reaction conditions can lead to addition or loss of coordinated solvent molecules and/or counter ions, opening pathways for easy racemization.[2] The design of ligands predisposed to form only one of many possible stereoisomers is therefore a challenging task. Chiral luminescent lanthanide complexes can be envisoned as discriminating probes of local environments. For practical reasons, they should be highly emissive and be conformationally rigid on the timescale of the luminescence emission lifetime. We recently reported on complexes with chiral ligands derived from 2,6-pyridinedicarboxylic acid[3a] and bis(benzimidazolyl)pyridine[3b] displaying only slight diastereomeric excesses in solution. The first examples of enantiopure lanthanide complexes involving macrocyclic ligands were reported by Parker and coworkers[4] formed by chiral octadentate $C_4$ symmetric ligands of the DOTA family. Here we report on the first selective formation of a single stereoisomer in a mononuclear lanthanide coordination compound resulting from the interplay of three independent terdentate chiral $C_2$-symmetrical ligands.

The approach to introduce well defined carbon stereocenters derived from terpene sources into classical coordination ligands was pioneered by the group of von Zelewsky.[5] Most widely used is the pinene fragment which can be conveniently introduced in various positions in oligopyridine ligands by Kröhnke-type strategy. The steric bulk in the terpene fragments leads to the preferential formation of a limited number of stereoisomers.

We recently reported on the strong luminescence enhancement in lanthanide complexes obtained by alkylation of terpy ligands in the positions 4, 4′ and 4″.[6] Starting points for the present investigations were the questions if such an enhancing effect can also be produced by pinene fragments and whether a chiral discrimination in lanthanide complexes of pinene-substituted terpy ligands can be achieved. To test these

hypotheses, we have used the known enantiopure ligand **L(−)**.[7]



**L(-)**
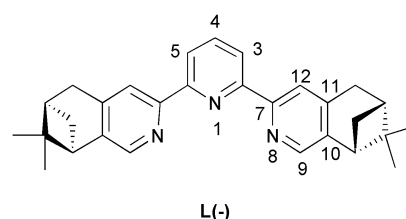
Preliminary studies with a chiral terpy containing the pinene group attached in positions 9 and 10 showed formation of only LnL$_2$ complexes (Ln = La, Eu, Lu).[8] Steric interactions most probably interfere with the coordination of a third ligand in mononuclear complexes as observed in related examples.[9] No such problems were encountered when the pinene moieties are facing away from the metal center (positions 10 and 11) and complexes [Ln(**L**(−))$_3$](ClO$_4$)$_3$ (Ln = La, Eu, Tb) have been isolated in good yields (80–90%, see ESI† for details). The $^1$H NMR spectra of solutions of $5 \times 10^{-3}$ M Ln(ClO$_4$)$_3\cdot x$H$_2$O (Ln = La or Eu and $x$ = 0.3–0.6) and three equivalents of **L**(−) in anhydrous CD$_3$CN display only one set of signals at 298 K. This indicates that on the NMR time scale the complexes adopt helical, nine-coordinate $C_3$ symmetric structures and the 1:3 species is strongly predominant. No additional peaks were detectable in temperature dependent studies in the range 243–298 K with [Ln(**L**(−))$_3$](ClO$_4$)$_3$ (Ln = La, Eu) in anhydrous CD$_3$CN. Fig. 1 displays the results of the experiment with the La complex. Further evidence for the stereoselective helical arrangement of the ligand strands is provided by the specific molar rotatory angle of solutions of $1 \times 10^{-3}$ M [Ln(**L**(−))$_3$](ClO$_4$)$_3$ (Ln = La, Eu, Tb). In all cases the value for the complexes ([ϕ] = −280 deg dm$^2$ mol$^{-1}$, La; −600, Eu; −935, Tb) is larger than the sum of three ligand molecules ([ϕ] = −68.9 deg dm$^2$ mol$^{-1}$)[7] pointing to the importance of the structural contribution by the chiral helicate.

In contrast to alkylation in the pyridine 4-position[6] the pinene moiety leads to no strong enhancement of the metal-centered luminescence upon ligand excitation, as demonstrated by the determined quantum yields $Q^{Eu}$ = 4% and $Q^{Tb}$ = 0.022%. Measurements at 77 K with [La(**L**(−))$_3$](ClO$_4$)$_3$ indicate that an inefficient intersystem crossing in the ligand strands ($I$(triplet)/$I$(singlet) = 0.033) is probably one of the main factors leading to such low values. Other processes such as photo induced electron transfers may also be involved.[10] The excitation spectrum of [Eu(**L**(−))$_3$]$^{3+}$ in acetonitrile recorded at 295 K in the spectral range of the $^5D_0 \leftarrow ^7F_0$ transition shows the presence of a symmetrical band at 17 228 cm$^{-1}$ with a small shoulder at lower wavelength. The emission was monitored at wavelengths corresponding to the $^5D_0 \rightarrow ^7F_1$ or $^7F_2$ transition, and identical spectra were obtained. This result is consistent with the presence of a dominant species in solution. A broader asymmetrical band is observed at 17 238 cm$^{-1}$ at 10 K for a

powdered sample. The solid state result is indicative of a range of distorted Eu(III) environments which may be due to packing effects, or other structural changes occurring at low temperature (Fig. S1, ESI). More details on the photophysical properties will be described elsewhere.

Total luminescence and circularly polarized luminescence spectra for a solution of $5 \times 10^{-3}$ M [Eu(L(−))$_3$]$^{3+}$ in CH$_3$CN are shown in Fig. 2. The Eu(III) luminescence is fairly intense when excited at 361 nm into the ligand states. The observation of only two components for the $^5D_0 \rightarrow {}^7F_1$ transition is compatible with a trigonal symmetry of the complex.

The latter transition is particularly well suited for the measurement of circularly polarized luminescence (CPL), since it satisfies the magnetic-dipole selection rule, $\Delta J = 0, \pm 1$.[11] In the spectra shown, however, the magnitude of the luminescence dissymmetry ratio, $g_{lum}$, defined as follows: $g_{lum} = 2\Delta I/I = 2(I_L - I_R)/(I_L + I_R)$, where $I_L$ and $I_R$ refer, respectively, to the intensity of left and right circularly polarized light, is approximately the same (0.028 and 0.020 at the intensity maxima) for both transitions. To date there is no reliable quantitative relationship between the sign or magnitude of $g_{lum}$ for Eu(III) transitions and molecular structure, and, for this reason, CPL measurements are most useful in studies aimed at simply verifying the existence of pure enantiomers or racemic mixtures.

A useful experiment to determine whether or not the solution contains a mixture of species is to excite directly the Eu(III) ion with circularly polarized laser light. We have used laser excitation at 557 nm, corresponding to the $^5D_1 \leftarrow {}^7F_2$ transition. Even though the initial state is only 1% populated at room temperature, this transition satisfies the selection rule given above and may lead to a large chiral discrimination. At this excitation wavelength, $g_{lum}$ is *independent* of the polarization of the excitation light. Since it is known that the primary source of chirality for Ln(III) ions is the $\Delta$ or $\Lambda$ helical configuration of the chelating ligands, this result is consistent with the presence of only one diastereomer in solution[12] during the lifetime of the excited state which for Eu(III) is in the ms regime. If the solution contained a mixture of diastereomers or enantiomers, the CPL should have been dependent on excitation polarization, as previously observed for 1:3 complexes with related terdentate ligands.[3] In these cases, the CPL results were interpreted in terms of the coexistence of 1:2 and 1:3 species in solution.

Finally, it should be mentioned that the corresponding Tb(III) complex is much less luminescent than the Eu(III) analogue, presumably due to deactivation through energy back transfer to
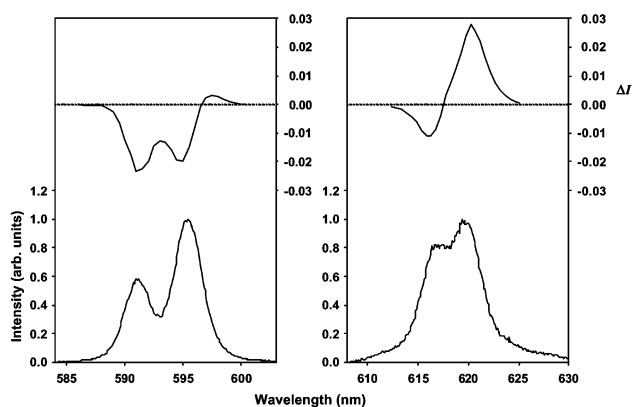


**Fig. 2** Total luminescence (bottom) and CPL (top) spectra of the transitions $^5D_0 \rightarrow {}^7F_1$ (left) and $^5D_0 \rightarrow {}^7F_2$ (right) of $5 \times 10^{-3}$ M [Eu(L(−))$_3$]$^{3+}$ in anhydrous MeCN at 295 K, upon excitation at 361 nm.

the ligand, consistent with the temperature dependence of the Tb($^5D_4$) lifetime (from 1.34 to 0.22 ms between 20 and 295 K). Although it was not possible to record a complete CPL spectrum due to very low emission intensity, we were able to measure the luminescence dissymmetry ratio, $g_{lum}$, for the $^5D_4 \rightarrow {}^7F_5$ transition of Tb(III) upon indirect excitation of the ligand. The result at the peak wavelength obtained was 0.06, a value three times higher than that observed for a corresponding complex with a derivative of 2,6-pyridinedicarboxylic acid.[3a]

In conclusion, we have shown the strength of the pinene approach in controlling the stereochemistry of luminescent lanthanide coordination compounds. The resultant emitted light is polarized in a direction determined by the helicity of the metal complex, which in turn is controlled by the absolute configuration at the remote carbon centers in the pinene moieties. Taken into account the easy synthetic availability of both pinene enantiomers, and well-known strategies to generate water robust complexes with a terpy framework,[13] this opens further opportunities for the synthesis of chiral luminescent probes.

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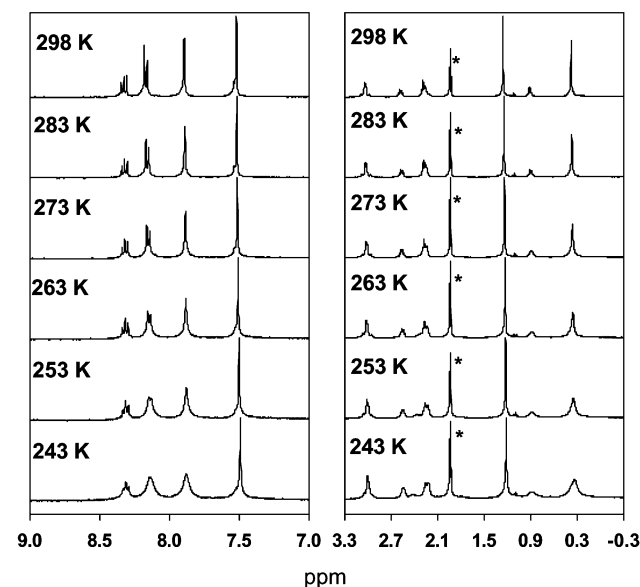
**Fig. 1** $^1$H NMR spectra of $5 \times 10^{-3}$ M [La(L(−))$_3$]$^{3+}$ in anhydrous CD$_3$CN, measured as a function of temperature; asterisks correspond to the signal of the solvent.