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Photophysical and Chiroptical Properties of the Enantiomers of *N,N'*-Bis(1-phenylpropyl)-2,6-pyridinecarboxamide and their Chiral 9-Coordinate Ln^{3+} Complexes

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Abstract

The *R,R* and *S,S* enantiomers of *N,N'*-bis(1-phenylpropyl)-2,6-pyridinedicarboxamide, **L(Et)**, react with Ln^{3+} ions ($\text{Ln} = \text{La}, \text{Eu}, \text{Gd}, \text{and Tb}$) to give stable $[\text{Ln}((R,R)\text{-L(Et)})_3]^{3+}$ in anhydrous acetonitrile solution, as evidenced by various spectroscopic measurements, including NMR and luminescence titrations. In addition to the characteristic Eu^{3+} and Tb^{3+} luminescence bands, the steady-state and time-resolved luminescence spectra of the aforementioned complexes show the residual ligand-centered emission of the $^1\pi\pi^*$ to $^3\pi\pi^*$ states, indicating an incomplete intersystem crossing (ISC) transfer from the $^1\pi\pi^*$ to $^3\pi\pi^*$ and ligand-to- Ln^{3+} energy transfer, respectively. The high circularly polarized luminescence (CPL) activity of $[\text{Eu}(\text{L(Et)})_3]^{3+}$ confirms that using a single enantiomer of **L(Et)** induces the preferential formation of one chiral $[\text{Eu}(\text{L(Et)})_3]^{3+}$ complex, consistent with the $[\text{EuL}_3]^{3+}$ complexes formed with other ligands derived from a 2,6-pyridine dicarboxamide moiety. Furthermore, the CPL sign patterns of complexes with (*R,R*) or (*S,S*) enantiomer of **L(Et)** are consistent with the CPL sign pattern of related $[\text{LnL}_3]^{3+}$ complexes with the (*R,R*) or (*S,S*) enantiomer of the respective ligands in this family.

Graphical Abstract

The enantiomers of **L(Et)**, a ligand derived from the 2,6-pyridine dicarboxamide moiety, shows that its chiral $[Ln(L(Et))_3]^{3+}$ complexes preserve the favorable circularly polarized luminescence (CPL) activity with a CPL signal pattern consistent with the behavior of analogue Ln^{3+} compounds with other structurally similar ligands, supporting further a relationship between structure and chiroptical properties.

Keywords

Luminescence; Lanthanides; Circularly polarized; luminescence; Speciation; 2,6-Dicarboxamidopyridine moiety

Introduction

The lanthanides, Ln, or rare earth elements, are *f*-block metals with atomic numbers between 57 (lanthanum) and 71 (lutetium). They prefer the Ln^{3+} oxidation state.^[1] The *f* orbitals are deep-lying and shielded by higher filled orbitals,^[1b,2] so they do not play a major role in coordination to the ligands and are not as affected by bound ligands or by the solvent.^[1a] Therefore, the luminescence spectrum is characteristic of the metal center, corresponding to its *f-f* transitions.^[1b,3] This shielding also means that the *f-f* transitions are sharp, and may have long decay times. Eu^{3+} and Tb^{3+} typically have long luminescent lifetimes in the range of milliseconds.

The *f* → *f* transitions are Laporte forbidden, and as a consequence lanthanides are weak absorbers of light.^[1b,3] A way to counteract this is through the “antenna effect”, where ligands, often aromatic organic molecules, are coordinated to a lanthanide ion, Ln^{3+} . The bound ligand absorbs a photon, undergoes some ligand-centered energy transitions, and then energy is transferred from the ligand excited states to the metal acceptor levels of the coordinated Ln^{3+} center.^[4] This energy transfer from the ligand to the metal is Laporte

allowed, and therefore, indirectly exciting through coordinated ligands is an effective way to counteract the weak absorbance of the lanthanide $f \rightarrow f$ transitions.

Typically, the Ln^{3+} complexes are quite labile compared with their transition metal counterparts, and therefore if there is a racemic mixture of Δ and Λ structures in solution, traditional techniques for isolating a single diastereomer will not work as well with the Ln^{3+} complexes. Control of the structure of Ln^{3+} coordination complexes is possible through other approaches, including macrocyclic ligands, podands, and multidentate ligands.^[5]

Ligands derived from a 2,6-pyridine dicarboxamide moiety (Scheme 1) have a variety of interesting properties that make them promising in the development of luminescent chiral probes and self assembly structures.^[6] These properties can be modified by changing the substituents at the R_1 , R_2 , or R_3 positions. The coordination of these ligands to Ln^{3+} ions usually follows a predictable pattern.^[6a] Generally, three tridentate ligands coordinate to the Ln^{3+} center to the form of a 9-coordinate complex where the Ln^{3+} ion is shielded from the solvent by the ligand. The resulting 1:3 Ln^{3+} :ligand complexes generally have somewhat a D_3 symmetry and can be indirectly excited through the antenna effect.^[6]

Early studies of the structurally similar but simpler dipicolinic acid, **DPA**, also known as 2,6-pyridine-dicarboxylate (Scheme 1), and $[\text{Ln}(\text{DPA})_3]^{3-}$ complexes showed that three equivalent ligands must be coordinated to the Ln^{3+} center in order to form the complex with D_3 symmetry.^[7] Complexes with only one or two ligands bound to the Ln^{3+} center do not have D_3 symmetry, as solvent molecules coordinate to the Ln^{3+} center, and symmetry is lost. As **DPA** is achiral, the only chirality in the complexes results from the chiral environment at the Ln^{3+} center, from the arrangement of the ligands to form a structure with either Δ or Λ helicity. Thus, the **DPA** complexes exist as a racemic mixture of Λ and Δ metal complexes in solution.^[6b,8] Exciting the sample with circularly polarized light results in a measurable luminescence dissymmetry factor, g_{lum} , value (g_{lum} reports the degree of circularly polarized luminescence or CPL, see for further details in the Circularly Polarized luminescence section), where left circularly polarized excitation and right circularly polarized excitation give g_{lum} of equal magnitude but opposite sign.^[6b,8] This mixture can be perturbed by the addition of chiral molecules in solution (the “Pfeiffer effect”), to induce the formation of an excess of either Δ or Λ results in a net circular polarization in the luminescence. The resulting sample has a measurable g_{lum} value. However, changing the excitation polarization will change the g_{lum} value, indicating that there are multiple species of different symmetry in solution.^[6b,8]

Chirality can be introduced in the ligand itself, by attaching a chiral substituent at the R_1 , R_2 or R_3 position of the 2,6-pyridine dicarboxamide moiety. The (*R,S*) structure will be *meso*, but the (*R,R*) and (*S,S*) structures will be chiral. Using a single enantiomer of the ligand (e.g., (*R,R*) vs. (*S,S*)) may induce a chiral environment, where one enantiomer preferentially forms the Λ -metal complex, and the other enantiomer preferentially forms the Δ -metal complex.^[6] An early study of 3-[2,6-bis(diethylcarbamoyl)pyridine-4-yl]-*N*-(*tert*-butoxycarbonyl)alanine methyl ester (Scheme 1), henceforth to be known as **L(4p)**, showed that using a single enantiomer of **L(4p)** induced the formation of an excess of one diastereomer of the $[\text{LnL}_3]^{3+}$ complex in solution.^[9] **L(4p)** has a chiral group (*tert*-

butoxycarbonyl) attached at the 4-position of the pyridine ring, or the R_1 position of the 2,6-pyridinedicarboxamide moiety in Scheme 1.

The chiral group in **L(4p)** is relatively distant from the coordinating region of the 2,6-pyridinedicarboxamide moiety. Ligands with a chiral substituent at R_2 and/or R_3 , directly attached to the coordinating amide region were explored as a way to increase the chiral directing power of the ligand. Pyridine-2,6-dicarboxylic acid-[1-naphthalen-1-yl-ethyl)-amide], **L(hh1)**,^[10] and pyridine-2,6-dicarboxylic acid-[1-naphthalen-2-yl-ethyl)-amide], **L(hh2)**,^[11] have one chiral substituent attached at R_2 (Scheme 1). Lincheneau et al. described **L(hh1)** and **L(hh2)** as “half helicates” because they have one chiral group at R_2 and an achiral carboxylic acid group on the other side.^[10]

Attaching chiral substituents at both R_2 and R_3 , created ligands with twice the chiral centers as the “half helicates”. Leonard et al. and Kotova et al., studied pyridine-2,6-dicarboxylic acid bis[1-naphthalen-1-yl-ethyl)-amide], **L(1yl)**,^[12] which is structurally similar to **L(hh1)**,^[10] and pyridine-2,6-dicarboxylic acid (R,R)-bis[-(1-naphthalen-2-yl-ethyl)-amide], **L(2yl)**,^[12a] which is structurally similar to **L(hh2)** (Scheme 1).^[11] The (R,R) enantiomer of **L(1yl)** and **L(2yl)** induced Λ chirality in the 1:3 Ln^{3+} :ligand complexes, and the (S,S) enantiomer of **L(1yl)** and **L(2yl)** induced Δ chirality.^[12b] The induced helicity of the Ln^{3+} complexes increased compared with the “half helicate” complexes, and higher g_{lum} values were observed (see later for further details in the Circularly Polarized Luminescence section).

While **L(1yl)** and **L(2yl)** have strong directing powers, the naphthalenyl groups are quite bulky, which may have an effect on helical structure and formation of the complexes. Bonsall et al. and Hua et al.,^[13] studied N,N' -bis(1-phenylethyl)-2,6-pyridinedicarboxamide, **L(Me)**, which has a less bulky phenyl group at the chiral carbon center (Scheme 1). Even with this change in structure, **L(Me)** also preferentially induces the formation of one diastereomer of the Ln^{3+} complex in solution, where the (R,R) enantiomer induces Δ chirality, and the (S,S) induces Λ chirality.^[13b]

As there is currently no method of predicting absolute chiral structure from chiroptical properties,^[4,6b] a family of ligands derived from a 2,6-pyridine dicarboxamide moiety may be a step towards chiral probes which display a consistent relationship between structure and spectroscopy. As discussed earlier, the chiral ligands **L(4p)**, **L(hh1)**, **L(hh2)**, **L(1yl)**, **L(2yl)**, and **L(Me)** form labile $[\text{LnL}_3]^{3+}$ complexes (where Ln^{3+} includes Eu^{3+} , Gd^{3+} , and Tb^{3+}) with somewhat a D_3 symmetry.^[6a] Additionally, it was shown that using one enantiomer of chiral ligand may induce the formation of a single diastereomer of the $[\text{LnL}_3]^{3+}$ complex, and there may be a relationship between structure of the complex (Δ and Λ) and the sign of the CPL.^[6] That is, a sequence of $(-, -)$ followed by $(+)$ for the various components (2 and 1) in the spectral range of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions was observed for the $[\text{EuL}_3]^{3+}$ complexes with the R,R enantiomers of the related ligands **L(4p)**, **L(hh1)**, **L(hh2)**, **L(1yl)**, **L(2yl)**, and **L(Me)**. Similarly an opposite trend was observed for the analogous $[\text{EuL}_3]^{3+}$ complexes with the S,S enantiomers of the aforementioned ligands.

Inspired by such a potential correlation between chiral structure of the ligand, the complex, and the sign of the CPL signal, we hereby report as a continued step of this project on the

photophysical, structural, and chiroptical properties of *N,N'*-bis(1-phenylpropyl)-2,6-pyridinedicarboxamide (Scheme 1), henceforth to be referred to as **L(Et)**, and $[\text{Ln}(\text{L(Et)})_3]^{3+}$ complexes ($\text{Ln}^{3+} = \text{Eu, Gd, and Tb}$). **L(Et)** is a chiral ligand which is structurally similar to the aforementioned family of ligands. **L(Et)** is in fact structurally most similar to **L(Me)**,^[13] where the only difference is that **L(Et)** contains an ethyl group at the chiral carbon centers and **L(Me)** has a methyl group at the chiral carbon centers. Minor structural changes in the ligand may have a larger impact on the photophysical and chiral properties of the $[\text{LnL}_3]^{3+}$ complexes.^[5,6,9,14] Thus, comparison with the properties of related ligands and $[\text{LnL}_3]^{3+}$ complexes is investigated for a broader understanding of the behavior of these complexes and the relationship between structure and chiroptical properties holds across similar ligand systems.

Of special interest, photophysical characterization will allow for the determination of the luminescent properties of **L(Et)** and $\text{Ln}^{3+}:\text{L(Et)}$ complexes. Ideally, an effective luminescent probe would have a high quantum yield value and efficient energy transfer. It is also important to ensure that the $[\text{Ln}(\text{L(Et)})_3]^{3+}$ species is formed in solution. Only the 1:3 species has D_3 symmetry, where the 1:1 and 1:2 species do not. Therefore, investigation includes electronic spectra in the UV/Visible region, steady-state and time-resolved luminescence at room temperature and 77 K (indirect excitation), laser excitation (direct excitation), NMR titration, and luminescence titration to determine stability constants. CPL of the $[\text{Eu}(\text{L(Et)})_3]^{3+}$ complex ($^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions) as well as the $[\text{Tb}(\text{L(Et)})_3]^{3+}$ complex ($^5D_4 \rightarrow ^7F_5$ transition) will be measured to determine if the sign pattern of the CPL also holds true for **L(Et)**.

Results and Discussion

Structure of **L(Et)**

The synthesis of the two isomers, namely (*R,R*)- and (*S,S*)-**L(Et)**, was done according to a procedure similar to the one reported for the preparation of the diamide stereoisomers of **L(Me)**, (*R,R*)- and (*S,S*)-**L(Me)**.^[13a] It is worth noting that the opposite optical rotations values of (*R,R*)- and (*S,S*)-**L(Et)** confirmed the preparation of each enantiomeric form of **L(Et)** and the chirality arising from the asymmetric C atoms, as also evidenced for (*R,R*)- and (*S,S*)-**L(Me)** (-191.4° and $+191.3^\circ$ vs. -213.4° and $+213.6^\circ$, respectively).

We resorted to density functional theory (DFT) calculations^[15] to determine the optimized molecular structures of (*R,R*)- and (*S,S*)-**L(Et)** as an alternative to X-ray, since it was difficult to obtain X-ray quality crystals of both isomers. Previous studies of the structurally similar ligand **L(Me)** found that results obtained via X-ray and DFT were consistent, which confirms that this is a valid method of verifying the structure of **L(Et)**.^[13b] The resulting equilibrium geometry and atom-numbering schemes of (*R,R*)- and (*S,S*)-**L(Et)** are shown in Fig. S1.

The conformation of the *R,R* and *S,S* enantiomers of **L(Et)** is important to consider because the geometry of the ligand may have an effect on the way the ligands arrange around the metal center. While there are limitations to these predicted conformations, namely that it is a gas-phase molecular mechanics calculation and the actual behavior of the ligand in solution

likely differs from the prediction, and also that there are likely conformational and electronic changes that occur upon coordination of the ligand to the metal center, these predicted conformations do still offer some insight. The predicted conformations of the (*R,R*) and (*S,S*) enantiomers of **L(Et)** are mirror images of each other. The bond lengths and angles of the (*R,R*) and (*S,S*) enantiomers of **L(Et)** are given in Tables S1 and S2. Both structures have the carbonyl groups bent away from each other – C28 and C21, and C14 and C21 in Fig. S1 – and out of the plane with the pyridine ring. The two phenyl groups are also out of the plane with the pyridine ring and with each other – C9–14 and C38–43, and C24–29 and C2–7 in Fig. S1. This structural pattern is similar to that of the conformations of (*R,R*)- and (*S,S*)-**L(Me)** predicted from the gas-phase DFT calculations, namely a syn,syn,*ZZ* conformation.^[13b] It also confirmed the enantiomeric nature of (*R,R*)- and (*S,S*)-**L(Et)**. It must be pointed out that this bent structure, as well as the steric bulk of the phenyl groups, will likely affect the arrangement of the ligands around the metal center. As there are three bulky ligands coordinated to the Ln³⁺ ion, they may need to distort their helical arrangement somewhat, to relieve some steric strain, and therefore it is likely that the [Ln(**L(Et)**)₃]³⁺ complex will have a perturbed D₃ geometry, rather than the near D₃ geometry Brittain observed in the [Ln(**DPA**)₃]^{3–} complex with the far less bulky **DPA** ligands.^[7a] This small structural change may have an effect on the CPL spectra of the [Eu(**L(Et)**)₃]³⁺ and [Tb(**L(Et)**)₃]³⁺ complexes (see later for further details in the Circularly Polarized Luminescence section).

Like observed for **L(Me)**,^[13b] this conformation also prevails in solution, as evidenced by the ¹H NMR and ¹³C NMR spectra of the (*R,R*) and (*S,S*) enantiomers of **L(Et)** in CDCl₃. The ¹H NMR of the (*R,R*) enantiomer of **L(Et)** (numbering included in Figs. S2 and S3) shows peaks corresponding to the pyridine ring at 8.32 ppm (H on C1, C5) and 8.0 ppm (H on C6), as well as peaks corresponding to the H attached to N11 and N12 at 7.9 ppm. Also present is a multiplet at 7.36 ppm corresponding to the phenyl rings (C21–25 and C26–30), peaks at 5.07 ppm corresponding to the H directly attached to the chiral centers (C13, C14), as well as peaks corresponding to the aliphatic carbons at 1.95 ppm (C17, C18) and 1.92 (C19, C20). The ¹³C NMR of the (*R,R*) enantiomer of **L(Et)** shows peaks corresponding to the carbonyl carbons (C7, C8) at 162.8 ppm, the pyridine ring at 148.8 ppm (C4) and 125.2 ppm (C1, C5), at 126.66–136.3 corresponding to the phenyl rings (C15,16, C21–25 and C26–30), a peak at 55.3 ppm corresponding to the chiral centers (C13,C14), and peaks corresponding to the aliphatic carbons at 29.4 ppm (C17, C18) and 19.2 ppm (C19, C20). The positions of the peaks are relatively identical between the (*R,R*) enantiomer of **L(Et)** and the (*S,S*) enantiomer of **L(Et)**, as expected for enantiomers.

Speciation in Solution

For the [Ln(**L(Et)**)₃]³⁺ complexes studied, the speciation changes as the ratio of ligand to Ln³⁺ increases. The species formed will be the Ln³⁺ ion coordinated to 1, 2, or 3 ligand molecules, forming 1:1, 1:2, and 1:3 complexes of Ln³⁺:**L(Et)**, respectively. The formation of the [Ln(**L(Et)**)_{*n*}]³⁺ complexes follow the equilibria described in Equation (1), (2), and (3).

where β_n are cumulative stability constants for the formation of the complex with n ligands coordinated to the Ln^{3+} ion.

These species were studied using solutions of varying ratios of **L(Et)** and $[\text{Ln}(\text{NO}_3)_3] \cdot n\text{H}_2\text{O}$ in anhydrous acetonitrile. Anhydrous solvents were used to reduce decomplexation due to water directly bound to the Ln^{3+} center and quenching due to water indirectly connected or present in the outer sphere. Spectroscopic measurements (including lifetime measurements, direct excitation spectra...) were taken to determine the species present at various ratios of Eu^{3+} to ligand in solution. The formation of the complex can be observed in a variety of ways: a shift in ligand-centered excitation, an increase in Ln^{3+} -centered emission due to the antenna effect, and/or a sharp increase in lifetime. Luminescence titrations of $\text{Eu}(\text{NO}_3)_3$ with **L(Et)** in anhydrous acetonitrile under argon were performed in order to determine stability constants (see below for a luminescence discussion). Additionally, NMR titration of $\text{La}(\text{CF}_3\text{SO}_3)_3$ with **L(Et)** confirmed that using an excess of ligand will drive the coordination of three ligands to the Ln^{3+} center, but no further – the four ligand complex is not formed (see below for an NMR discussion). In the presence of an excess of ligand, peaks correlating with the free ligand were observed in addition to peaks correlating with the 1:3 species. As **L(Et)** is a bulky ligand, therefore it is unlikely that a four ligand complex, $[\text{Ln}(\text{L}(\text{Et}))_4]^{3+}$, would be formed for steric reasons. For this reason, in order to form the desired complex in solution, all $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ solutions used in luminescence and CPL measurements were prepared with an excess of ligand, unless otherwise stated.

The stability constants, β_n , for the formation of the various species of $[\text{Ln}(\text{L}(\text{Et}))_n]^{3+}$ were determined through time-resolved luminescence titrations. The complex was indirectly excited and the Ln^{3+} -centered emission was taken, allowing for observation of the changing metal environment as the species in solution changed. As the ligand does not phosphoresce at room temperature, the observed luminescence is solely a result of the metal emission. An example of the resulting time-resolved luminescence spectra for titration of Eu^{3+} into **L(Et)** illustrates the change in the bands as the titration progressed (Fig. S4). Note that the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (ca. 610.0–625.0 nm) of Eu^{3+} , which is sensitive to the metal environment, exhibits a change in intensity and shape as the ratio of Eu^{3+} to **L(Et)** changes during the titration. This change in intensity is illustrated in a plot of R , the ratio of $\text{Eu}^{3+}/\text{L}(\text{Et})$, vs. the luminescence intensity (Fig. S5). Analysis of R vs. intensity shows two breaks, the first at $R = 0.37$, similar to the break found at $R = 0.33$, for the Eu^{3+} to **L(Me)** titration,^[13b] attributed to the $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ complex. The positions of the second break are also similar, around $R = 0.55$ for the Eu^{3+} to **L(Et)** titration, and at 0.5 for the Eu^{3+} to **L(Me)** titration,^[13b] attributed to the 1:2 complex. The titration data were fitted to the equilibria (1), (2), and (3), using *Hyperquad2006* software with refinement and single species correction for Eu^{3+} , and the stability constants were determined. Details of titration procedure, and further information about the calculation of $\log \beta_n$ values, can be found in the Experimental section.

The log β values determined for **L(Et)** were log $\beta_1 = 8.6$, log $\beta_2 = 16.5$, and log $\beta_3 = 22.0$. These values are consistent with the pattern observed in the stability constants for formation of $[\text{EuL}_n]^{3+}$ for other related ligands. The log β values are similar for the $[\text{Eu}(\text{L(Et)})_n]^{3+}$ and $[\text{Eu}(\text{L(Me)})_n]^{3+}$ complexes,^[13b] with log β_3 lower for $[\text{EuL}_3]^{3+}$ (22.0 for **L(Et)** vs. 23.8 for **L(Me)**). This makes sense given that **L(Et)** is slightly bulkier than **L(Me)**, as **L(Et)** has ethyl groups attached at the chiral carbons as opposed to methyl groups for **L(Me)**. Previous studies noted that steric hindrance had an effect on the formation of $[\text{EuL}_3]^{3+}$ and other related complexes with Eu^{3+} and derivatives of 2,6-dicarboxamidopyridine.^[13b] **L(4p)** also has slightly lower log β values, with log β_3 for $[\text{EuL}_3]^{3+}$ being 22.0 for **L(Et)** vs. 19.7 for **L(4p)**.^[9] Even though **L(4p)** is less bulky at the coordinating nitrogen groups of the 2,6-dicarboxamidopyridine moiety, a study of related ligands showed that the group attached at the 4-position of the pyridine ring has a steric and electronic destabilization effect. **L(1ly)** and **L(2ly)** are much bulkier than **L(Et)** and **L(Me)** due to the larger naphthyl groups at the chiral centers,^[12] and they have lower log β values than both **L(Et)** and **L(Me)**, further supporting this observation. The “half helicate” **L(hh1)** is very bulky at the chiral center, as it has a naphthyl group,^[10] but it is less bulky overall, because it only has one chiral center with the aromatic group. Interestingly, **L(hh1)** also has lower log β values consistent with those of **L(1ly)** and **L(2ly)**, suggesting that the bulkiness at the chiral center has a larger effect on the stability constant than the overall sterics of the compound. Table S3 summarizes the stability constants for the related $[\text{EuL}_n]^{3+}$ species.

In order to confirm the formation of the 1:3 species in solution, an NMR titration of La^{3+} with **L(Et)** was performed in deuterated acetonitrile. Successive equivalents of the *S,S* enantiomer of **L(Et)** were titrated with a solution of $\text{La}(\text{CF}_3\text{SO}_3)_3$ to obtain ^1H NMR spectra of solutions where *R*, the ratio of the concentration of La^{3+} to the concentration of **L(Et)**, varies from 1 to 1, 1 to 2, 1 to 3, and 1 to 5. The successive spectra are shown in Fig. S6. As the titration proceeds, and the complex is formed, the position of the peaks associated with hydrogens close to the binding sites shift, and it is possible to see the appearance of the 1:1, 1:2, and 1:3 complexes. These peaks are labeled in the figure. For reference, the assignment of peaks in the ^1H NMR of **L(Et)** can be found in Figs. S2 and S3.

One set of peaks corresponding to the 1:3 species can be seen in the spectrum for the solution with ratio *R* = 0.33. The presence of one set of peaks for the 1:3 species is an indication that the three ligands bound to the Ln^{3+} center are equivalent and coordinated to the Ln^{3+} in the same way. If they were not equivalent, the individual ligands would have different shifts and multiple sets of peaks would be present. In conjunction with the lifetime values, longer than 1 ms, which show that there are no solvent molecules coordinated to the Ln^{3+} center, this confirms the formation of the D_3 complex in solution. The direct excitation g_{lum} results (see later for further details in the Circularly Polarized Luminescence section), which show that the g_{lum} values are independent of the polarization of the excitation beam, indicate the presence of a single diastereomer of the D_3 complex when a single enantiomer of the ligand is used.

Two of the binding sites on the ligand are the amide oxygen atoms, and as the oxygen binds to the positively charged La^{3+} center, electron density is withdrawn from the amide nitrogen, leading to deshielding of the attached hydrogen. A doublet corresponding to the 1:3 species

can be seen at 8.72 ppm in the spectrum for the solution with ratio $R = 0.33$. To probe into whether a 1:4 species forms, excess ligand is added, to a ratio $R = 0.2$, where there are five times as many ligand mol as metal in solution. The amide peak does not shift, rather, the peak corresponding to the 1:3 species is present at 8.72 ppm and a peak corresponding to the free ligand appears at 8.55 ppm. This indicates that additional ligands do not bind directly to the metal and instead have more of an outer sphere effect, consistent with the behavior of $\mathbf{L(Me)}$.^[13b]

The peak corresponding to the hydrogen directly attached to the chiral center also shifts upon complexation, as the chiral center is also close to the binding sites. In the solution with ratio $R = 1$, a peak corresponding to the 1:1 species is present at 5.21 ppm and a peak corresponding to the 1:2 species is present at 4.84 ppm. In the solution with ratio $R = 0.5$, the peaks corresponding to the 1:1 and the 1:2 species are both present, along with a peak corresponding to the 1:3 species at 4.46 ppm. In the solution with ratio $R = 0.33$, the 1:3 species peak is present, and in the solution with ratio $R = 0.2$, the 1:3 species peak is present, and a peak corresponding to the free ligand appears at 5.07 ppm.

Most of the photophysical studies are done with the usual method of indirectly exciting via the antenna effect, but it is also possible to study $[\text{Eu}(\mathbf{L(Et)})_n]^{3+}$ speciation by directly exciting the Eu^{3+} center, which is very sensitive to its environment. The observation of the formation of different species in solution is possible with specific emission and excitation transitions of Eu^{3+} .^[3a,13a] Since the Laporte forbidden $f-f$ transitions are weak, a laser was used as the direct excitation source. Emission was monitored at 615 nm, which corresponds to the characteristic Eu^{3+} luminescent emission in the range of 610.0–625.0 nm of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is especially sensitive to the environment, as it is one of the “hypersensitive transitions”, which follows the selection rule $J = 2$, and this transition can be an indicator that the metal environment is chiral as it is “hypersensitive; absent if the ion lies on an inversion center”.^[3a] The excitation range used is 578.0–582.0 nm, which corresponds to the $\text{Eu}^{3+} ^5\text{D}_0 \leftarrow ^7\text{F}_0$ transition. This is a very useful transition, because both the initial $^7\text{F}_0$ state and the final lowest excited $^5\text{D}_0$ state are nondegenerate, which means that for a “given chemical environment”, the transition itself is nondegenerate and there is a single corresponding excitation peak.^[3a] Eu^{3+} is the only Ln^{3+} ion with this unique transition. This allows for the observation of $[\text{Eu}(\mathbf{L(Et)})_n]^{3+}$ speciation, because each observed peak or shoulder must correspond to a different Eu^{3+} -containing species.

As the ratio of Eu^{3+} to ligand changes, so do the species in solution, 1:1, 1:2, and 1:3 $\text{Eu}^{3+}:\mathbf{L(Et)}$, forming as described in the equilibria (1), (2), and (3). This is reflected in the observed peaks (Figure 1). In instances where there were overlapping peaks, for example, in the 1:2 species solution, deconvolution was performed using the *Peakfit* software (see for further details in the Experimental section). At the lowest ratio, 1:0.5 $\text{Eu}^{3+}:\mathbf{L(Et)}$, the major peak has a maximum at ca. 579.7 nm, corresponding to the formation of the first species $[\text{Eu}(\mathbf{L(Et)})]^{3+}$. As the ratio increases to 1:1, then 1:2, the maximum shifts to ca. 580.0, corresponding to the formation of the second species $[\text{Eu}(\mathbf{L(Et)})_2]^{3+}$. As the ratio increases further, to 1:3, 1:5, and 1:10, the ca. 580.6 peak corresponding to the formation of the third species, $[\text{Eu}(\mathbf{L(Et)})_3]^{3+}$, is observed. This is the desired species with D_3 symmetry, and it can be observed to form in solution with excess ligand. For this reason, studies of the

photophysical and chiroptical properties of $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ were performed using solutions with an excess of ligand to ensure that the desired complex is formed in solution.

It is also possible to observe the change in speciation due to change in concentration. As concentration increases, an increase in the presence of $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ is observed, which follows Le Châtelier's principle, which states that increasing the concentration of reactants shifts the equilibrium towards formation of product.^[16] In the spectrum for the 2.00 mM solution, the predominant peak is the ca. 579.9 nm peak, corresponding to the 1:2 species, and a shoulder at ca. 580.6 nm corresponding to the 1:3 species is present. In the spectrum for the 3.33 mM solution, the ca. 580.6 nm shoulder is more developed, and in the spectrum for the 6.67 mM solution, there are two distinct peaks, the one at ca. 579.9 nm corresponding to the 1:2 species and the one at ca. 580.6 nm corresponding to the 1:3 species.

The general trend of the peak corresponding to the 1:3 $\text{Eu}^{3+}:\text{L}(\text{Et})$ species having a longer wavelength compared with that of the 1:1 $\text{Eu}^{3+}:\text{L}(\text{Et})$ species holds across different complexes as well (e.g., 579.7, 580.0, and 580.6 vs. 579.2, 579.8, and 580.4 for the 1:1, 1:2, and 1:3 $\text{Eu}^{3+}:\text{L}$ species with $\text{L} = \text{L}(\text{Et})$ and $\text{L}(\text{Me})$, respectively).^[13b] However, the effect of a small structural difference on photophysical properties can be observed by comparing the structurally similar $\text{L}(\text{Et})$ and $\text{L}(\text{Me})$ systems. The positions of the observed excitation peaks for the $[\text{Eu}(\text{L}(\text{Et}))_n]^{3+}$ species is shifted compared with the positions of the $[\text{Eu}(\text{L}(\text{Me}))_3]^{3+}$ species,^[13a] due to the change in ligand from $\text{L}(\text{Et})$ to $\text{L}(\text{Me})$.

Further confirmation that an excess of ligand leads to the formation of the desired $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ species was obtained by obtaining steady-state and time-resolved luminescence excitation spectra for solutions of $\text{Eu}^{3+}:\text{L}(\text{Et})$ with ratios ranging from 1:0.5 to 1:10. Emission was monitored at 615.0 nm, corresponding to the characteristic $\text{Eu}^{3+} {}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. As the ratio of ligand to metal increases, the ligand centered excitation is redshifted, moving from 308 nm for the 1:0.5 ratio, to 318.0 nm for the 1:10 ratio. Fig. S7 (left) depicts this shift in steady-state luminescence excitation spectra, and Fig. S7 (right) depicts this shift in the time-resolved luminescence excitation spectra. This shift is a sign that the predominant species in solution is changing as the ratio changes, which is consistent with the ligand-centered measurements of $\text{L}(\text{Et})$ and $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$ (see below for the photophysical properties discussion), where the excitation maximum of the complex was redshifted compared with the ligand alone, as well as with the results obtained through ${}^5\text{D}_0 \leftarrow {}^7\text{F}_0$ excitation of $[\text{Eu}(\text{L}(\text{Et}))_n]^{3+}$, previously discussed.

In addition, lifetimes data taken of solutions of Eu^{3+} and $\text{L}(\text{Et})$ with varying molar ratios and concentration fit with earlier results determining that the desired $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ species is formed in solution with excess ligand. As the ratio of ligand to metal increased, the overall trend was an increase in lifetime, and as the concentration increased, the lifetime also increases. Table S4 summarizes the lifetimes results, and the trend of increasing lifetimes is evident, with a sharp increase in the lifetime as the ratio of ligand to Eu^{3+} is increased. These trends of an increasing lifetime are likely due to the formation of longer lifetime complexes of $\text{Eu}^{3+}:\text{L}(\text{Et})$ as well as the displacement of solvent molecules by ligand, as this

reduces nonradiative quenching processes (see later for a lifetime discussion in the Ln^{3+} -Centered Luminescence section).

In summary, direct excitation spectra, indirect excitation spectra and lifetimes measurements taken of solutions of varying ratios and concentrations of $\text{Eu}^{3+}:\text{L}(\text{Et})$ confirmed that the desired $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ species is formed when there is an excess of ligand (1:5 or 1:10 ratio $\text{Eu}^{3+}:\text{L}(\text{Et})$) and a higher concentration (6.67 mM). Therefore, solutions with 6.67 mM concentration and 1:5 or 1:10 $\text{Ln}^{3+}:\text{L}(\text{Et})$ ratio were used to obtain the luminescence and CPL results for all of the $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ species studied. This is in line with the observations resulting from the various speciation studies conducted (see above for further details) that showed the in situ formation of the $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ complexes when an excess of ligand was used. As a result, these complexes were not isolated but only prepared in situ using anhydrous conditions for the purpose of the photophysical studies discussed thereafter, especially as the complex solutions were prepared with an excess of the ligand. A similar approach was reported for the photophysical studies of some of the $[\text{Ln}(\text{L}(\text{Me}))_3]^{3+}$ complexes.^[13]

Ligand-Centered Emission

Since the photophysical properties for both enantiomeric forms of $\text{L}(\text{Et})$, (*R,R*)- and (*S,S*)- $\text{L}(\text{Et})$, are identical within experimental errors, we only reported the photophysical data of the (*R,R*) enantiomer of $\text{L}(\text{Et})$ thereafter. Previous studies of the structurally similar ligand $\text{L}(\text{Me})$ also found that the photophysical properties of the (*R,R*) enantiomer and the (*S,S*) enantiomer were similar.^[13] The same approach was applied to the discussion of the photophysical properties of the $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ complexes.

Investigation of the ligand of interest, $\text{L}(\text{Et})$, began with photophysical characterization of $\text{L}(\text{Et})$. The $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$ complex was used to observe the effects of complexation on the position of the ligand bands, as the observed luminescence is ligand-centered, because the Gd^{3+} acceptor bands are not accessible for energy transfer from ligand excited states.

Electronic spectra of $\text{L}(\text{Et})$ and $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ ($\text{Ln}^{3+} = \text{Eu}$, Tb , and Gd) complexes in solution are shown in Fig. S8. $\text{L}(\text{Et})$ shows broad absorbance maxima around 228.0, 275.0 and 285.0 nm, which are likely associated with pyridinedicarboxamide $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.^[13b] The maxima are somewhat redshifted for $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$, indicating that complexation has occurred, and the position of the transitions has shifted. This shift upon complexation is also observed in other $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ complexes, namely $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ and $[\text{Tb}(\text{L}(\text{Et}))_3]^{3+}$.

The absorbance maxima for related ligands is summarized in Table S5. As $\text{L}(\text{Et})$ is structurally very similar to $\text{L}(\text{Me})$, only differing in an ethyl group vs. a methyl group at the chiral centers, it is likely that these pyridinedicarboxamide-centered transitions would be similarly positioned for both compounds, and in fact, the observed absorbance maxima for the $\pi \rightarrow \pi^*$ transition for $\text{L}(\text{Me})$, 276.0 and 284.0 nm, are only slightly redshifted compared with those of $\text{L}(\text{Et})$, 275.0 and 285.0 nm.^[13b] In contrast, the absorbance maxima for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of $\text{L}(\text{1yl})$, $\text{L}(\text{2yl})$, $\text{L}(\text{hh1})$, and $\text{L}(\text{hh2})$ have a larger shift compared to the bands of $\text{L}(\text{Et})$.^[10–12] This makes sense as $\text{L}(\text{1yl})$, $\text{L}(\text{2yl})$, $\text{L}(\text{hh1})$, and

L(hh2) are more electronically different from **L(Et)** than **L(Me)**,^[13b] especially in the aromatic groups present. **L(Et)** and **L(Me)** have the central 2,6-pyridine dicarboxamide moiety as well as two phenyl groups, one attached at each chiral carbon center, and the maximum around 285.0 nm is associated with the phenyl groups. **L(1yl)** and **L(2yl)** also have the central 2,6-pyridine dicarboxamide moiety,^[12] but they have two naphthyl groups instead of two phenyl groups, one attached at each chiral carbon center, and the maximum around 281 nm is likely associated with the naphthyl group. **L(hh1)** and **L(hh2)** have the central 2,6-pyridine dicarboxamide moiety and only one aromatic group (naphthyl) attached at its only chiral carbon center.^[10,11] The largest difference from **L(Et)** is seen in the electronic spectrum of **L(4p)**, where the pyridine transitions are observed at 267.0 nm.^[9] This difference makes sense as **L(4p)** has a substituent directly attached to the pyridine at the 4-position, in contrast to **L(Et)**, which is unsubstituted at this position.

Ligand-centered emission of **L(Et)** and $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$ also showed the effects of complexation. The excitation maximum of **L(Et)** is around 280.0 nm, whereas the excitation maximum of $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ complexes is around 310.0 nm. The change in the excitation maximum is explored in more detail in the discussion of speciation (see above). Room temperature fluorescence emission from the $^1\pi\pi^*$ state is shown in Fig. S10. The fluorescence band of **L(Et)** consists of a broad band, centered around 315.0–330.0 nm, while the fluorescence band of $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$ is redshifted, centered around 400 nm. This change in the position of the $^1\pi\pi^*$ state of the ligand in the 1:3 $\text{Gd}^{3+}:\text{L}(\text{Et})$ solution is indicative of the formation of the complex.

As the ligand does not exhibit observable phosphorescence at room temperature, in order to observe its $^3\pi\pi^*$ state emission, the sample must be cooled to 77 K (frozen anhydrous acetonitrile solution) to reduce nonradiative decay processes. The observed emission corresponds to the phosphorescence of the $^3\pi\pi^*$ state (Figure 2). The phosphorescence band of **L(Et)** is centered around 415.0 nm, while the one of $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$ is blueshifted, centered around 390.0 nm.

As with the $^1\pi\pi^*$ state, the change in the position of the $^3\pi\pi^*$ state of the ligand in the 1:3 $\text{Gd}^{3+}:\text{L}(\text{Et})$ solution is indicative of the formation of the complex. The energy gap between the $^1\pi\pi^*$ and $^3\pi\pi^*$ states, $E(^1\pi\pi^* - ^3\pi\pi^*)$, was 8,250 cm^{-1} for the ligand, and decreased significantly after complexation with Gd^{3+} , to 6,402 cm^{-1} . $E(^1\pi\pi^* - ^3\pi\pi^*)$ of the Gd^{3+} complex is closer to the ideal energy gap, which is in the range of 5,000 cm^{-1} .^[17] However, $E(^1\pi\pi^* - ^3\pi\pi^*)$ of the Gd^{3+} complex with **L(Et)** is still further from the ideal energy gap than that of the $[\text{Gd}(\text{L}(\text{Me}))_3]^{3+}$ complex. While $E(^1\pi\pi^* - ^3\pi\pi^*)$ is 6,402 cm^{-1} for $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$, it is 5,070 cm^{-1} for $[\text{Gd}(\text{L}(\text{Me}))_3]^{3+}$, and $E(^1\pi\pi^* - ^3\pi\pi^*)$ is 8,250 for **L(Et)**, and 4,190 cm^{-1} for **L(Me)**.^[13b]

As $E(^1\pi\pi^* - ^3\pi\pi^*)$ for the Gd^{3+} complex is closer to $E \approx 5,000 \text{ cm}^{-1}$, considered the ideal energy gap for an efficient intersystem crossing, or ISC, energy transfer,^[17] it is predicted that the ISC is more efficient in the Gd^{3+} complex. If true, this would be reflected in the magnitude of the ratio between the integrated $^3\pi\pi^*$ and $^3\pi\pi^*$ state emissions, I^T/I^S . I^T/I^S of **L(Et)** is 4.25×10^{-3} , while I^T/I^S for $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$ is 4.04×10^{-2} . I^T/I^S is 10 times greater for the Gd^{3+} complex, suggesting an increase in the efficiency of the ISC from the

lowest $^1\pi\pi^*$ state to the lowest $^3\pi\pi^*$ state of the ligand when it is complexed to the Gd^{3+} metal. As the $E(^1\pi\pi^* - ^3\pi\pi^*)$ of the $[\text{Gd}(\text{L}(\text{Me}))_3]^{3+}$ complex is closer to the ideal value of $5,000\text{ cm}^{-1}$ than the $E(^1\pi\pi^* - ^3\pi\pi^*)$ of $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$, it also makes sense that I^T/I^S would be higher for the $[\text{Gd}(\text{L}(\text{Me}))_3]^{3+}$ (Table 1). This correlation between a more favorable $E(^1\pi\pi^* - ^3\pi\pi^*)$ and a higher I^T/I^S also holds true with **L(4p)**,^[9] where there is a change to the substituent attached to the pyridine. As the ligand itself is “essentially nonluminescent”, Muller et al. could only measure these values for the complexes, and they studied complexes of **L(4p)** with La^{3+} and Lu^{3+} . $E(^1\pi\pi^* - ^3\pi\pi^*)$ of the $[\text{La}(\text{L}(\text{4p}))_3]^{3+}$ complex was $6,800\text{ cm}^{-1}$, closer to $5,000\text{ cm}^{-1}$ than $E(^1\pi\pi^* - ^3\pi\pi^*)$ of the $[\text{Lu}(\text{L}(\text{4p}))_3]^{3+}$ complex, which was $7,545\text{ cm}^{-1}$. This correlated to a higher I^T/I^S for the $[\text{La}(\text{L}(\text{4p}))_3]^{3+}$ complex of 8.0×10^{-3} compared with 4.7×10^{-3} for the $[\text{Lu}(\text{L}(\text{4p}))_3]^{3+}$ complex.^[9]

The quantum yield, Φ , which is a measure of a fluorophore's emission efficiency, of **L(Et)** was determined using a concentration and an excitation wavelength where Lambert–Beer is obeyed.^[2] In addition to these requirements, it was important to ensure that the quantum yield of $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$, and all following $[\text{LnL}_3]^{3+}$ complexes, was determined in conditions that ensure the formation of the desired $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$ complex where the Gd^{3+} ion is coordinated to three ligand molecules. This is discussed in further detail in the Speciation in Solution section (see above). $\Phi(\text{L(Et)})$ was determined to be 22.0 %, which is very close to the quantum yield of **L(Me)** 21.2 %.^[13b] The luminescence from the ligand is much weaker once it is complexed to Gd^{3+} . The fluorescence quantum yield of **L(Et)** is approximately ten times greater than the quantum yield of $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$, which was 2.8 %. This is consistent with the **L(Me)**, which also shows a ten-fold drop in the quantum yield of $[\text{Gd}(\text{L}(\text{Me}))_3]^{3+}$, compared with the ligand alone.^[13b] The luminescence from the **L(4p)** ligand is also weak when it is complexed, as the fluorescence quantum yield of $[\text{La}(\text{L}(\text{4p}))_3]^{3+}$ is $5.5 \times 10^{-2}\%$ and $[\text{Lu}(\text{L}(\text{4p}))_3]^{3+}$ is $6.5 \times 10^{-2}\%$.^[9]

Ln³⁺-Centered Luminescence

In contrast to Gd^{3+} , the Eu^{3+} and Tb^{3+} metal acceptor bands are accessible for energy transfer from ligand excited states, so it is possible to observe metal-centered emission through indirect excitation. The ligand transfers energy to the Ln^{3+} center through the antenna effect and allows for observation of the metal environment through metal-centered emission.

The presence of the characteristic emission bands in the luminescence spectra of $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ and $[\text{Tb}(\text{L}(\text{Et}))_3]^{3+}$ indicate that the complex has formed and energy is being transferred from the ligand to the metal via the antenna effect.

The peaks corresponding to the long-lived Eu^{3+} transitions (the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions, for example, $J = 1$ ca. 590.0 nm, $J = 2$ ca. 615.0 nm, $J = 3$ ca. 645.0 nm, and $J = 4$ ca. 700.0 nm) can be observed in the time-resolved luminescence emission spectra taken at room temperature and 77 K (Figs. S9 and 2), with the ca. 580.0 nm peak, corresponding to the sometimes weak nondegenerate $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition, observable in the spectrum taken at 77 K (Figure 2). The strongest peak at ca. 615.0 nm corresponds to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. Other transitions are also visible, and the stronger peaks originate from $^5\text{D}_0$,

notably the band around 590.0 nm corresponding to the $^5D_0 \rightarrow ^7F_1$ transition, the small peak/shoulder around 580.0 nm, corresponding to the $^5D_0 \rightarrow ^7F_0$ transition, the small peak around 645 nm corresponding to the $^5D_0 \rightarrow ^7F_3$ transition, and the peak around 700.0 nm corresponding to the $^5D_0 \rightarrow ^7F_4$ transition. Sometimes visible are the weaker peaks around 530.0 and 550.0 nm, corresponding to the $^5D_1 \rightarrow ^7F_0$ and $^5D_1 \rightarrow ^7F_1$ transitions.

In addition to the characteristic metal emission bands, the ligand emission bands may also be observed, which is an indication of incomplete energy transfer in either ISC or ligand-to- Ln^{3+} energy transfer. In the steady-state luminescence spectra at room temperature (Fig. S10), the ligand band is present as a broad band around ca. 330.0–360.0 nm, and indicates $^1\pi\pi^*$ emission from the ligand. The presence of $^1\pi\pi^*$ emission implies incomplete ISC transfer from the $^1\pi\pi^*$ to $^3\pi\pi^*$ states. The residual emission of the ligand-centered $^1\pi\pi^*$ state observed in the $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ and $[\text{Tb}(\text{L}(\text{Et}))_3]^{3+}$ complexes is redshifted compared to the ligand only emission, in line with the results obtained for $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$.

In the steady-state luminescence emission spectra obtained at 77 K (frozen anhydrous acetonitrile solution, Figure 2), both the $^1\pi\pi^*$ state band and the $^3\pi\pi^*$ state band may be observed, while only the $^3\pi\pi^*$ state band is observed in the time-resolved luminescence emission spectra at 77 K (frozen anhydrous acetonitrile solution, see Figure 2), due to the shorter lifetime of the $^1\pi\pi^*$ state emission. The presence of emission around ca. 395–425 nm, corresponding to the $^3\pi\pi^*$ state emission, indicates incomplete ligand-to- Ln^{3+} energy transfer. The peak area of the $^3\pi\pi^*$ emission band is smaller than the $^1\pi\pi^*$ emission band, indicating that the ligand-to- Ln^{3+} energy transfer is relatively efficient, as confirmed by the I^T/I^S measurement (see above and Table 1). Note that ligand-centered bands are significantly more prominent in the $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ spectrum than in the $[\text{Tb}(\text{L}(\text{Et}))_3]^{3+}$ spectrum, indicating that ligand-to- Ln^{3+} energy transfer is less efficient in $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ vs. $[\text{Tb}(\text{L}(\text{Et}))_3]^{3+}$. This will have the effect of lowering the overall quantum yield of $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$, as discussed thereafter.

The quantum yield, Φ , is a measure of a fluorophore's emission efficiency^[2] and, therefore, reflects the efficiency of processes such as the previously discussed ISC. Additionally, for $[\text{EuL}_3]^{3+}$ complexes, it is possible to measure the luminescence sensitization (η_{sens}),^[18] which in this case is a measure of the efficiency by which the coordinated ligand transfers energy to the Eu^{3+} . Further details about the calculations used to determine these values can be found in the Experimental section. The quantum yield values for $[\text{LnL}_3]^{3+}$ complexes, and the luminescence sensitization values for $[\text{EuL}_3]^{3+}$ complexes are summarized in Table 2. The presence of residual ligand-centered emission in the $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ complex spectra indicates incomplete energy transfer, where the presence of $^1\pi\pi^*$ state emission indicates inefficient ISC and the presence of $^3\pi\pi^*$ state emission indicates incomplete energy transfer from ligand bands to Ln^{3+} acceptor bands. By inspection, when the ligand bands are more prominent in the $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ complex spectrum, it is likely an indication of inefficient ISC and ligand-to- Ln^{3+} energy transfer, and quantum yield values will likely be lower. For example, the ligand bands are more prominent in the $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ complex spectra compared with the $[\text{Tb}(\text{L}(\text{Et}))_3]^{3+}$ complex spectra, and the $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ complex had a relatively low quantum yield value of 1.4 % compared with 8.1 % for the $[\text{Tb}(\text{L}(\text{Et}))_3]^{3+}$ complex. The related $[\text{Eu}(\text{L}(\text{Me}))_3]^{3+}$ complex also had an incomplete ISC and ligand-to-

Ln^{3+} energy transfer, and a lower quantum yield value for $[\text{Eu}(\text{L}(\text{Me}))_3]^{3+}$ (1.0 %) vs. $[\text{Tb}(\text{L}(\text{Me}))_3]^{3+}$ (8.6 %).^[13b] Although these quantum yield values are not especially high, it can be noted that the $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ and $[\text{Ln}(\text{L}(\text{Me}))_3]^{3+}$ complexes have a significantly higher quantum yield when compared to the respective $[\text{Ln}(\text{L}(\text{4p}))_3]^{3+}$ complexes – $[\text{Eu}(\text{L}(\text{4p}))_3]^{3+}$ 2.2×10^{-1} % and $[\text{Tb}(\text{L}(\text{4p}))_3]^{3+}$ 1.2 %, ^[9] largely due to more efficient energy transfer of ligand and complex transitions in the $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ and $[\text{Ln}(\text{L}(\text{Me}))_3]^{3+}$ complexes.

However, the efficiency of energy transfer is not the only factor contributing to the relatively low value of the quantum yield of the $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ complex. An additional explanation for the lower quantum yield of the $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ complex is that Eu^{3+} is more susceptible than Tb^{3+} to certain quenching processes.^[3b] In addition, the luminescence sensitization value for **L(Et)**, η_{sens} , is 4.1×10^{-5} , indicating weak efficiency. In comparison, for **L(1yl)** η_{sens} is the much higher value of 4.9×10^{-1} ,^[12a] which corresponds to the much higher quantum yield for $[\text{Eu}(\text{L}(\text{1yl}))_3]^{3+}$, 7.3 %, compared with $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$, 1.0 %. Kotova et al. attributed the higher quantum yield value at least partially to the naphthalene groups attached to the chiral carbons,^[12a] as they are more able to shield the Eu^{3+} centers than the phenyl groups attached to the chiral carbons of **L(Et)** and **L(Me)**.

Lifetimes values for $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ species were obtained at room temperature and 77 K (frozen anhydrous acetonitrile solution). The $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ lifetime values were 1.53 ms at room temperature, and 1.76 ms at 77 K, and the observed lifetime for the $[\text{Tb}(\text{L}(\text{Et}))_3]^{3+}$ species was 1.60 ms at room temperature and 1.85 ms at 77 K. The lifetime values are typically higher at 77 K than at room temperature because there is less nonradiative decay due to vibration at 77 K. There is a larger difference for the $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ lifetimes at 77 K vs. room temperature than for the $[\text{Ln}(\text{L}(\text{Me}))_3]^{3+}$ lifetimes,^[13b] which means that nonradiative decay processes have a larger effect on the $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ complexes than the $[\text{Ln}(\text{L}(\text{Me}))_3]^{3+}$ complexes. The observed lifetime for the $[\text{Tb}(\text{L}(\text{Et}))_3]^{3+}$ species in acetonitrile was 1.60 ms at room temperature and 1.85 ms at 77 K, and for the $[\text{Tb}(\text{L}(\text{Me}))_3]^{3+}$ species was 1.89 ms at room temperature and 1.95 ms at 77 K.^[13b] The $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ lifetime values were 1.53 ms at room temperature, and 1.76 ms at 77 K, and the $[\text{Eu}(\text{L}(\text{Me}))_3]^{3+}$ lifetime values were 1.75 ms at room temperature and 1.84 ms at 77 K.

The high lifetime values, greater than 1 ms, are indicative of the preference for the species with three ligands coordinated to the Ln^{3+} center, without partial decomplexation or quenching due to solvent interaction, as the coordinated ligand molecules protect the Ln^{3+} center and therefore result in longer luminescent lifetimes.^[3b,13b] This is also corroborated by the NMR data because the latter do not point to a partial decomplexation of one of the arms of the coordinated ligand molecules through the binding of an acetonitrile molecule. A similar observation was seen for the analogous complex with **L(Me)**. The lifetimes of the $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ complexes are comparable to previously reported values, though the lifetimes of the **L(Et)** related species are slightly lower than those of the **L(Me)**- and **L(1yl)**-based species,^[12,13b] indicating that there may be some quenching of the **L(Et)** related species. At room temperature, the observed lifetimes for the $[\text{EuL}_3]^{3+}$ species are 1.53 ms for the **L(Et)** complex, 1.75 ms for the **L(Me)** complex,^[13b] 1.85 ms for the **L(1yl)** complex,

^[12] 1.79 ms for the **L(2yl)** complex,^[12a] 1.76 ms for the **L(hh1)** complex,^[14a] and 1.95 ms for the **L(hh2)** complex.^[11]

Circularly Polarized Luminescence (CPL)

We have resorted to CPL,^[6b,8,19] the emission analog to circular dichroism (CD), to study the chiroptical properties of the complex solutions of $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ ($\text{Ln}^{3+} = \text{Eu}$ and Tb) in anhydrous acetonitrile. CPL involves the emission of circularly polarized luminescence from a chiral compound. Unlike the CD spectroscopy, CPL is only dependent on the active CPL species and free of potentially interfering background signals. The degree of CPL is commonly reported in terms of the luminescence dissymmetry factor, $g_{\text{lum}}(\lambda) = 2 \frac{I - I_0}{I + I_0}$, where I_L and I_R refer to the intensity of left and right circularly polarized light of well-resolved $f-f$ emission lines and each line splitting into several Stark levels. The spectrum of CPL measures a g_{lum} value for each wavelength, and is reported as change in intensity (I) vs. the wavelength. A combination of positive and negative CPL signs ensures the splitting of narrow emission lines of the Ln^{3+} ions which provide unique chiroptical properties that can be used to probe for target proteins and biomolecules.^[20] Thus, the CPL activity serves as a “fingerprint” to indicate any structural changes within the Ln^{3+} -containing system and/or around the local environment of the Ln^{3+} metal.

Two sources of chirality exist for the $[\text{Ln}(\text{L}(\text{Et}))_3]^{3+}$ ($\text{Ln}^{3+} = \text{Eu}$ and Tb) complexes studied. One is the helical arrangement of ligands around the metal center, where left-handed helical arrangement of the ligands results in the formation of the Λ structure, and right-handed helical arrangement results in the formation of the Δ structure. An excess of one of the two forms (Δ or Λ) could lead to CPL activity. Previous studies of complexes with achiral ligands, for example $[\text{LnDPA}_3]^{3-}$ complexes,^[6b,8] showed that a racemic mixture of Δ and Λ structures formed in solution. Such a racemic mixture would lead to no CPL activity. Another source of chirality is the ligands themselves, for example the chiral pyridine dicarboxamide derivatives discussed in this work. The chirality of the ligand may induce the preferential formation of either the Δ or Λ helical environment over the other. As this helical arrangement affects the chiral environment at the metal center, preferential formation of one helical structure would result in observable CPL activity.

The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions of $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ with both (*R,R*) and (*S,S*) enantiomers show mirror image CPL spectra with strong CPL activity (Figure 3). Like for **L(Me)**,^[13a] the chiral centers in the amide substituents control the helicity of the Eu^{3+} , which then influences the direction of the polarization of the Eu^{3+} -centered emitted light observed. Table 3 summarizes the CPL values for $[\text{Eu}((R,R)\text{-L}(\text{Et}))_3]^{3+}$, and compares them to the values for the $[\text{Eu}(R,R)\text{-L}_3]^{3+}$ complexes of the other previously mentioned ligands **L(Me)**, **L(p4)**, **L(1yl)**, **L(2yl)**, **L(hh1)**, and **L(hh2)**. It is worth noting that Starck et al. recently described an analog of $[\text{Eu}(\text{L}(\text{Me}))_3]^{3+}$ with the ligand **L(MeOrBu)**.^[22] The latter differs from **L(Me)** by having a *para*-substituted pyridinyl group at the R_1 position (Scheme 1 and Scheme 2). They showed that $[\text{Eu}(\text{L}(\text{MeOrBu}))_3]^{3+}$ preserved the favorable CPL activity of $[\text{Eu}(\text{L}(\text{Me}))_3]^{3+}$ with the advantage of having an efficient lower-energy wavelength excitation capability (ca. 365 nm vs. 308 nm for $[\text{Eu}(\text{L}(\text{Me}))_3]^{3+}$).^[13] Similarly, Bradberry et al. designed a water-soluble chiral ligand, **L'(1yl)**, analog to **L(1yl)**,^[12] which

contains a water-solubilizing sulfonate motif at the R_1 position (Scheme 1 and Scheme 2).^[21] In addition, to preserve the promising CPL activity of $[\text{Eu}(\text{L}(\mathbf{1yl}))_3]^{3+}$, the authors showed that the introduction of this water-solubilizing center at the *para*-position of the pyridyl unit led to almost a three-fold increase in the efficiency of the ligand-to- Eu^{3+} energy transfer, which resulted in a higher quantum yield of the Eu^{3+} -centered luminescence in the aqueous medium (ca. 10.9–11.8 %) compared to organic media (ca. 3.4–4.5 %).

The g_{lum} values for $[\text{Eu}((R,R)\text{-L}(\mathbf{Et}))_3]^{3+}$ are -0.16 for the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, and $+0.10$ for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. This sign pattern corresponds with the CPL sign pattern of the $[\text{Eu}(R,R)\text{-L}_3]^{3+}$ complexes with the ligands $\text{L}(\mathbf{Me})$, $\text{L}(\mathbf{1yl})$, $\text{L}(\mathbf{2yl})$, $\text{L}(\mathbf{hh1})$, $\text{L}(\mathbf{hh2})$, $\text{L}'(\mathbf{1yl})$, and $\text{L}(\mathbf{MeOrBu})$, that is, $(-)$ for the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, and $(+)$ for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition.^[6a,22] This indicates the (R,R) enantiomer of these ligands induces the same chirality at the Eu^{3+} center of the complexes, with structural data from these studies showing that it is the Λ structure.^[10–13] Indeed, the magnitude of the g_{lum} values for $\text{L}(\mathbf{Et})$ are high ($^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition $|g_{\text{lum}}| = 0.16$) and consistent with the high g_{lum} values observed for the $\text{L}(\mathbf{Me})$ ($|g_{\text{lum}}| = 0.19$), $\text{L}(\mathbf{1yl})$ ($|g_{\text{lum}}| = 0.24$), $\text{L}(\mathbf{2yl})$ ($|g_{\text{lum}}| = 0.16$), $\text{L}'(\mathbf{1yl})$ ($|g_{\text{lum}}| = 0.18$), $\text{L}(\mathbf{MeOrBu})$ ($|g_{\text{lum}}| = 0.16$) which indicates that the chiral ligand induces the formation of the single Λ diastereomer of the $[\text{Eu}(R,R)\text{-L}_3]^{3+}$ complex (Table 3). In contrast, the ligand $\text{L}(\mathbf{4p})$, where the chiral group is more distant from the coordinating region of the 2,6-pyridinedicarboxamide moiety, induces only a small excess of one diastereomer of the $[\text{EuL}_3]^{3+}$ complex in solution, thus resulting in weak CPL activity, $|g_{\text{lum}}| = 0.02$.^[9]

Indirect excitation through the ligand bands was used to take the CPL spectra in Figure 3. It is also possible to directly excite the Eu^{3+} center, and g_{lum} values obtained via direct excitation of $[\text{Eu}(\text{L}(\mathbf{Et}))_3]^{3+}$ species were consistent with those obtained via indirect excitation, that is, the sign of the g_{lum} was $(+)$ for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. Additionally, the magnitude of the g_{lum} values is consistent regardless of the direction of polarization of the excitation beam, since identical g_{lum} values were obtained using a plane-polarized excitation beam, a left circular polarization in the excitation beam, or a right circular polarization in the excitation beam. Since the CPL activity of the $[\text{Eu}(\text{L}(\mathbf{Et}))_3]^{3+}$ species is independent of direct or indirect excitation and independent of the polarization of the excitation beam, this indicates that a single diastereomer of the metal complex is present in solution.^[23]

The CPL spectrum for the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of $[\text{Tb}(\text{L}(\mathbf{Et}))_3]^{3+}$ with both (R,R) and (S,S) enantiomers was taken (Figure 3). Similarly to its analogue Eu^{3+} -containing complex, mirror image CPL spectra with strong CPL activity were observed for $[\text{Tb}(\text{L}(\mathbf{Et}))_3]^{3+}$ (g_{lum} values of -0.11 , $+0.02$, -0.23 , $+0.14$, and $+0.08$ at 539.2, 540.8, 543.6, 546.8, and 551.2 nm). As with the previously discussed $[\text{Eu}(\text{L}(\mathbf{Et}))_3]^{3+}$, the high $|g_{\text{lum}}|$ of 0.23 indicates that $(R,R)\text{-L}(\mathbf{Et})$ induces the formation of a single diastereomer of the $[\text{Tb}(\text{L}(\mathbf{Et}))_3]^{3+}$ complex. In comparison, the $[\text{Tb}(\text{L}(\mathbf{4p}))_3]^{3+}$ complex, where only a small excess of one diastereomer is formed, has a much weaker CPL activity with $|g_{\text{lum}}| = 0.01$.^[9]

The strong CPL activity of the $[\text{Eu}(\text{L}(\mathbf{Et}))_3]^{3+}$ and $[\text{Tb}(\text{L}(\mathbf{Et}))_3]^{3+}$ complexes supports our hypothesis that using only one enantiomer, (R,R) , of $\text{L}(\mathbf{Et})$ will induce the formation of one chiral structure in solution, resulting in strong CPL activity. Additionally, comparison with other $[\text{EuL}_3]^{3+}$ complexes of related ligands shows the CPL sign pattern is consistent (Table

3). This means that using the (*R,R*) enantiomer results in the formation of a chiral $[\text{EuL}_3]^{3+}$ structure with consistent chiroptical properties across similar ligand systems and $[\text{LnL}_3]^{3+}$ complexes with somewhat a D_3 symmetry.

In summary, the chiral structure of the ligands induced the chiral or Λ helical environment of the metal complexes. The Δ and Λ complexes have mirror image CPL spectra. There is a consistent correlation between the $[\text{EuL}_3]^{3+}$ complexes and the CPL sign pattern – that is, (–, –) then (+) for the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions, which held across this family of ligands.^[10–13,21,22] This is the mirror image of the pattern found across related ligands for the $[\text{Eu}((S,S)\text{-L})_3]^{3+}$ complexes of (+, +) then (–) for the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions.^[6b] This shows that there is a correlation from the chiral structure in the ligand to the chiral environment of the metal complex to the CPL signal, and is extremely promising, as it supports a relationship between structure and spectroscopy. Such a pattern is also evidenced for the analog Tb^{3+} -containing complexes, confirming that the use of the CPL signal is not only limited to the one from Eu^{3+} complexes.

Conclusion

We have studied the photophysical and chiroptical properties of **L(Et)** and the chiral $[\text{Ln}(\text{L(Et)})_n]^{3+}$ complexes it forms with Ln^{3+} ions, e.g., Eu^{3+} , Gd^{3+} , and Tb^{3+} , in solution. Comparison of **L(Et)** with related ligands derived from the 2,6-pyridine dicarboxamide moiety, showed that the small structural change in the ligand did result in some changes in the properties of complexes of Ln^{3+} with the ligand, but that overall, the behavior of **L(Et)** and the chiral $[\text{Ln}(\text{L(Et)})_n]^{3+}$ complexes it forms with Ln^{3+} ions, e.g., La^{3+} , Eu^{3+} , Gd^{3+} , and Tb^{3+} , in solution is consistent with the behavior of other structurally similar ligands.^[10–13] This is a promising result for the use of this family of ligands as luminescent probes, as studies of other families of ligands have shown that structural changes in the ligands may have larger consequences in the structure and properties of the Ln^{3+} :ligand complexes.^[5,6,9,14]

In particular, the structural change in **L(Et)** results in a change in the stability constants for the formation of $[\text{Eu}(\text{L(Et)})]^{3+}$, $[\text{Eu}(\text{L(Et)})_2]^{3+}$, and $[\text{Eu}(\text{L(Et)})_3]^{3+}$, determined via luminescence titrations of $\text{Eu}^{3+}:\text{L(Et)}$, but using an excess of ligand drove the formation of the desired $[\text{Eu}(\text{L(Et)})_3]^{3+}$ species, where three ligand molecules are coordinated to the Ln^{3+} center. ^1H NMR titrations of $\text{La}^{3+}:\text{L(Et)}$ showed the formation of the $[\text{La}(\text{L(Et)})_3]^{3+}$ complex with D_3 symmetry, and the (Eu^{3+}) $^5\text{D}_0 \leftarrow ^7\text{F}_0$ excitation spectra of the $[\text{Eu}(\text{L(Et)})_3]^{3+}$ species and the long luminescent lifetimes of $[\text{Eu}(\text{L(Et)})_3]^{3+}$ and $[\text{Tb}(\text{L(Et)})_3]^{3+}$ further confirmed that the desired species was formed in solution, excluding solvent molecules from the inner coordination sphere. While changing the ligand results in a change in the quantum yield and luminescence sensitization values of the $[\text{EuL}_3]^{3+}$ complexes, the values are not significantly reduced and the complex can still be indirectly excited via the antenna effect.

Using a single enantiomer of **L(Et)** induces the preferential formation of one chiral $[\text{Ln}(\text{L(Et)})_3]^{3+}$ complex, consistent with the $[\text{LnL}_3]^{3+}$ complexes formed with other ligands in this family.^[10–13] The $[\text{Eu}(\text{L(Et)})_3]^{3+}$ complex with (*R,R*) enantiomer of **L(Et)** exhibits

strong CPL activity, where the magnitude of the g_{lum} is independent of the polarization of the excitation beam, and the sign is independent of whether direct or indirect excitation is used, which indicates that a single diastereomer of the chiral complex is formed in solution.^[6b,23] In addition, the CPL sign patterns of complexes with (*R,R*) enantiomer of **L(Et)** are consistent with the CPL sign pattern of related $[LnL_3]^{3+}$ complexes with the (*R,R*) enantiomer of the respective ligands. The sign pattern of the $[Eu(L(Et))_3]^{3+}$ complex with the (*R,R*) enantiomer of **L(Et)** is (–, –) then (+) for the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions, which is consistent with the results across the ligands studied within this family.^[10–13] Using the (*R,R*) enantiomer of the ligand resulted in preferential formation of the Λ diastereomer of the $[EuL_3]^{3+}$ complexes, and the CPL sign pattern of the $[EuL_3]^{3+}$ complexes is the same as that of the $[Eu(L(Et))_3]^{3+}$ complex – (–, –) then (+) for the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions, respectively. An opposite behavior was observed when the *S,S* enantiomer was used.

This correlation between the chirality of the ligand to the stereochemistry of the metal complex to the CPL sign pattern is significant because it shows that, within this family of ligands, there is a relationship between structure and chiroptical properties. In addition, to preserve the favorable CPL activity, an enhancement of the photophysical properties and a solubility increase in aqueous media can be obtained with varying the substitutions at the *R*₁ position of the 2,6-pyridine dicarboxamide unit.^[21,22] It also leads to a more notable reversal CPL signal for the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} , as evidenced for the $[Eu(L(MeOBu))_3]^{3+}$ complex.^[22] As of yet, there is no simple method for predicting chiral structure using spectroscopy. Further study of this family of ligands and the $[LnL_3]^{3+}$ complexes they form may lead to the development of exciting luminescent chiral probes for use as molecular probes, including for biological applications and sensing.

Experimental Section

Materials and Methods:

Solvents and starting materials were purchased from Acros or Sigma-Aldrich and used without further purification unless otherwise stated. HPLC-grade solvents were dried before use and stored over activated molecular sieves. The Ln(III) content of stock solutions was determined by titrations with a standardized solution of EDTA in the presence of 0.1 M ammonium acetate and aqueous arsenazo(III). All spectroscopic measurements were done in anhydrous acetonitrile solutions.

Optical rotation values were measured from 6.67×10^{-3} M solutions in anhydrous MeCN at 298 K with the help of a Rudolph Autopol III polarimeter (sodium D line). 1H and ^{13}C NMR spectra experiments ($\{^1H-^1H\}$ COSY, $\{^1H-^{13}C\}$ HSQC, and DEPT-135) were performed on a 300 MHz Mercury NMR spectrometer. Chemical shifts are given in ppm with respect to tetramethylsilane. Gas chromatography–mass spectrometry (GC-MS) data were obtained using an Agilent Technologies 6890N GC 5975B MSD instrument. Pneumatically assisted electrospray mass spectrometry (ES-MS) spectra were recorded from anhydrous acetonitrile solutions on an Agilent 6520 Q-TOF mass spectrometer by infusion at 0.5 mL/min. Elemental analyses were conducted at Desert Analytics, Inc. (Tucson, AZ). Electronic spectra in the UV/Visible range were recorded at 298 K with a Varian Cary 50 Bio UV/

Visible spectrophotometer with an attached Cary Single Cell Peltier Accessory for temperature control. Fluorescence at 298 K and above was measured on a Varian Cary Eclipse fluorescence spectrophotometer with an attached Quantum Northwest Temperature Control. Phosphorescence scans (77 K) were taken on a Perkin-Elmer LS50B instrument. During luminescence titrations, a Masterflex L/S compact, variable-speed pump was used with Chem-Duranc Bio and Tygon Chemical 2001 tubing to transfer solutions to a 1.0 cm flow cuvette (Starna Cells, Inc.), and a Masterflex L/S Digital Drive with a Masterflex L/S Easy-Load II pump head for precision tubing was used to automatically dispense $\text{Eu}(\text{NO}_3)_3$ solutions. Luminescence lifetimes at room temperature, 333 K, and 77 K were taken using the Varian Cary Eclipse fluorometer, with the same physical setup as the luminescence scans. Data was measured and recorded through the Cary Eclipse Lifetimes Application. Reported lifetimes values are an average of at least three independent measurements with an uncertainty of 0.01 ms.

The quantum yields (Φ) were measured by the optically dilute relative method by use of the equation (4) where $\int I d\lambda$ is the numerically integrated intensity from the luminescence spectra, I is the luminescent intensity at the excitation wavelength, A is the absorbance at the excitation wavelength, and n is the index of refraction of the solution.^[24] The subscript R denotes reference.

$$\frac{\Phi_{\text{Sample}}}{\Phi_R} = \left(\frac{\int I_{\text{Sample}} d\lambda}{\int I_R d\lambda} \right) \left(\frac{I_{R, \text{exc}}}{I_{\text{Sample}, \text{exc}}} \right) \left(\frac{A_{R, \lambda_{\text{exc}}}}{A_{\text{Sample}, \lambda_{\text{exc}}}} \right) \left(\frac{n_{\text{Sample}}}{n_R} \right)^2 \quad (4)$$

Quantum yields of the ligand-centered emission were measured relative to **L(Me)** ($Q_{\text{abs}} = 21.2\%$).^[13b] Quantum yields of the Ln^{3+} -centered emission were determined at excitation wavelengths at which (i) the Lambert–Beer law is obeyed and (ii) the absorption of the reference closely matches that of the sample. $[\text{Ln}(\text{L}(\text{Me}))_3]^{3+}$ ($\text{Ln}^{3+} = \text{Eu}, \text{Gd}, \text{and Tb}$) complexes were used as standards for the $\text{Eu}(\text{III})$, $\text{Gd}(\text{III})$, and $\text{Tb}(\text{III})$ -containing complexes ($Q_{\text{abs}} = 1.0, 2.2, \text{ and } 8.6\%$).^[13b] The estimated error for quantum yields is $\pm 10\%$.

Luminescence titrations were performed overnight with an automatic titration system where a solution containing $5.0 \times 10^{-5} \text{ M L(Et)}$, as well as $0.1 \text{ M Et}_4\text{NClO}_4$ to maintain ionic strength, was constantly pumped back and forth from a sealed round-bottom flask and through a 10 mm quartz flow cuvette placed in the cell holder of a Varian Cary Eclipse Fluorescence Spectrophotometer set to scan every 15–18 minutes. At consistent time intervals, a solution of $1.0 \times 10^{-3} \text{ M Eu}(\text{NO}_3)_3$ in $0.1 \text{ M Et}_4\text{NClO}_4$ was dispensed into the **L(Et)** solution by an automatic peristaltic pump designed for precision. For each titration, at least 15 minutes were allowed for the solution in the flask to homogenize with that in the cuvette as well as allow for the Eu^{3+} -species to equilibrate. Factor analysis and stability constant determinations were carried out with the program Hyperquad2006.^[25] All data reported are the average of three independent measurements.

Circularly polarized luminescence (CPL) and total luminescence spectra were recorded on an instrumentation described previously.^[13a,23,26] In short, the instrumentation is equipped with a 1000 W xenon arc lamp from a Spex FluoroLog-2 spectrofluorometer, with excitation

and emission monochromators of dispersions 4 nm/mm (SPEX, 1681B). $^5D_0 \leftarrow ^7F_0$ (Eu) laser excitation measurements for the Eu^{3+} -containing complex solutions in anhydrous acetonitrile at 295 K were accomplished by using a Coherent-599 tunable dye laser (0.03 nm resolution) with a Coherent Innova Sabre TMS 15 as a pump source. The laser dye used in the measurements was rhodamine 6G dissolved in ethylene glycol. The calibration of the emission monochromator (and subsequently the dye laser wavelength) was performed by passing scattered light from a low power He-Ne laser through the detection system. The error in the dye-laser wavelength is assumed to correspond to the resolution of the emission monochromator (0.1 nm). The optical detection system consisted of a focusing lens long-pass filter and 0.22 m monochromator. A cooled EMI-9558B photomultiplier tube operating in photon-counting mode detected the emitted light. The standard deviation, σ_d , in the measurement of the luminescence dissymmetry factor, g_{lum} , is defined as $\sigma_d = (2/N)^{1/2}$ where N is the total number of photon-pulses counted. One can see that the determination of accurate g_{lum} values can be done in a short time for transitions associated with large g_{lum} values of highly luminescent compounds, whereas a longer time of collection is required for transitions associated with small g_{lum} values of weakly luminescent systems for achieving the same percent error. As the time required for measuring a CPL spectrum is dependent on the intensity of the luminescence of the system of interest and the “chirality” of the transition analyzed, the photo-pulses are collected for the same amount of time at each wavelength. As a result, the relative error at each of these wavelengths is the same in the CPL spectrum measured. The g_{lum} values are given with a standard deviation, σ_d , of ± 0.01 . It should be noted that a value of 0 for g_{lum} corresponds to no circular polarization, while the absolute maximum value is 2. It is often the case that rigid Ln^{3+} systems exhibit large g_{lum} values, while racemic or other types of mixtures give g_{lum} values in the range of ca. 10^{-2} – 10^{-3} .^[4,6b,27] All measurements were performed in a quartz cuvette with a path length of 1.0 cm. $^5D_0 \leftarrow ^7F_0$ (Eu³⁺) laser excitation spectra were analyzed using the deconvolution software Jandel Peak Fit. As in previous work,^[26a,28] the $^5D_0 \leftarrow ^7F_0$ (Eu) laser excitation spectra plotted in Figure 1 were fitted to a sum of two or three Lorentzian peaks as appropriate. All peaks were assumed to be pure Lorentzian in shape, so only the peak position and Lorentzian width were varied. For the case where there are two Eu(III) species (α and β) in equilibrium, the equilibrium constant, K_{eq} , may be expressed as depicted below. Therefore, the total concentration of each species will be related to the area, A , of the peak associated with the transition, where k is a proportionality factor. It must be noted that it is assumed that the proportionality constant, k , are independent of pressure (or temperature).^[26a,28] A similar procedure was used when three Eu(III) species were in equilibrium instead of two.

$$\begin{aligned} \text{Eu}(\alpha) &\rightleftharpoons \text{Eu}(\beta) \\ C_\alpha &= k_\alpha A_\alpha \text{ and } C_\beta = k_\beta A_\beta \\ K_{\text{eq}} &= \frac{C_\beta}{C_\alpha} = \frac{k_\beta A_\beta}{k_\alpha A_\alpha} \end{aligned}$$

The luminescence sensitization (η_{sens}) value was determined for the Eu^{3+} complex using the following equation:

$$Q_{\text{tot}}^{\text{Eu}} = \eta_{\text{sc}} \cdot \eta_{\text{FT}} \cdot Q^{\text{Eu}} = \eta_{\text{sens}} \cdot Q^{\text{Eu}}$$

where $Q_{\text{tot}}^{\text{Eu}}$ is the Eu^{3+} -centered luminescence quantum yield obtained upon ligand excitation, Q^{Eu} the intrinsic luminescence quantum yield of the $\text{Eu}(\text{III})$ ion, η_{sens} the efficiency of the luminescence sensitization by the ligand, η_{sc} the efficiency of the intersystem crossing process from the ligand singlet to triplet state, and η_{ET} the efficiency of the ligand-to- Eu^{3+} energy transfer.^[18] The intrinsic quantum yield Q^{Eu} is defined as the ratio between the observed and radiative lifetimes of the $\text{Eu}({}^5\text{D}_0)$ level:

$$Q^{\text{Eu}} = \tau_{\text{obs}} / \tau_{\text{R}}$$

where the radiative lifetime τ_{R} can be estimated from:

$$\tau_{\text{R}} = \frac{1}{A_{\text{MD},0} \cdot n^3} \cdot \left(\frac{I_{\text{MD}}}{I_{\text{tot}}} \right)$$

$A_{\text{MD},0}$ is the spontaneous emission probability of the $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$ transition (14.65 s^{-1}), n is the refractive index (1.354 for the anhydrous acetonitrile solution) and $I_{\text{MD}}/I_{\text{tot}}$ is the intensity ratio of the $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$ transition to the total emission of the ${}^5\text{D}_0$ level.

Computational chemistry calculations were performed on a Windows 7 64-bit PC with an Intel Centrino, Core i5 processor. The WebMO computational chemistry interface was used to run jobs, and the web server software used was Apache HTTP Server by The Apache Software Foundation. The Firefly Quantum Chemistry Package (Firefly QC), formerly known as PC Gamess, was used to perform geometric optimization of the ligand structures. Firefly QC is partially based on the GAMESS source code.^[15c,15d] The modeling method chosen for the geometry optimization was self-consistent field (SCF) density functional theory (DFT) using B3LYP and the 6-31G(d) basis set.^[13b,29] Final output was confirmed to have reached the stationary point, where the SCF converged and there were no imaginary vibration modes.^[15a,15b] The bond angles and bond lengths were calculated from the optimized structures and the molecular visualization of the results were rendered using Gabedit.^[15e]

Synthesis and Characterization:

The (*R,R*) and (*S,S*) enantiomers of *N,N'*-bis(1-phenylpropyl)-2,6-pyridinedicarboxamide, **L(Et)**, were synthesized via previously published methods.^[13a]

(*R,R*)-**L(Et)**:

A solution of 3.97 g (29.4 mmol) of *R*(+)-(α)-ethylbenzylamine (99+% optical purity) was added to a stirring mixture of 140 mL of CH_2Cl_2 and 140 mL 5 % sodium bicarbonate. Pyridine-2,6-dicarbonyl dichloride (2.85 g, 14.0 mmol) was added to the mixture in portions over a five minute period and vigorous stirring was continued overnight. The organic layer was separated, washed with $2 \times 20 \text{ mL}$ 5 % sodium bicarbonate followed by 20 mL water,

dried with sodium sulfate and filtered. Solvent was removed by rotary evaporation and then at high vacuum for 45 minutes in a warm water bath. Recrystallization was performed by dissolving the solids in a warm mixture of 120 mL hexane and 28 mL chloroform. The mixture was then cooled to -20°C overnight and collected on a pre-cooled medium glass frit. The white needles were washed with cold pentane ($3 \times 25\text{ mL}$) and dried under vacuum for an hour to reach constant weight (3.80 g, 68 %). Mp. $156.5\text{--}157.5^{\circ}\text{C}$. $^1\text{H-NMR}$ in CDCl_3 : δ 0.92 (t, 6H, $J = 7.4\text{ Hz}$), 1.85–2.05 (m, 4H), 5.07 (q, 2H, $J = 7.4\text{ Hz}$), 7.3–7.4 (m, 10H), 7.97 (d, 2H, $J = 7.7\text{ Hz}$), 8.00 (t, 1H, $J = 7.7\text{ Hz}$), 8.32 (d, 2H, $J = 7.7\text{ Hz}$). $^{13}\text{C NMR}$ in CDCl_3 : δ 10.5, 29.3, 55.1, 125.0, 126.5, 127.6, 128.8, 139.1, 141.7, 148.7, 162.6. DEPT-135: CH_3 (10.5); CH_2 (29.3) and CH (55.1, 125.0, 126.5, 127.6, 128.8, 139.1). IR $\nu(\text{cm}^{-1}, \text{nujol})$: $\tilde{\nu} = 3364, 3321, 3269, 1680, 1640, 1534$. EI-MS (CH_2Cl_2): m/z 401 ($[\text{M}]^+$). Optical rotation $[\alpha]_D^{20}$ (20 mM, CH_3CN): -191.4° . $\text{C}_{25}\text{H}_{27}\text{N}_3\text{O}_2$: calcd. C 74.8, H 6.8, N 10.5; found C 74.6, H 6.9, N 10.6.

(S,S)-L(Et):

Preparation was by the same method as for (*R,R*)-L(Et). 61 % yield. Mp. $157.5\text{--}158.3^{\circ}\text{C}$. $^1\text{H-NMR}$ in CDCl_3 : δ 0.93 (t, 6H, $J = 7.5\text{ Hz}$), 1.85–2.05 (m, 4H), 5.07 (q, 2H, $J = 8.3\text{ Hz}$), 7.3–7.4 (m, 10H), 7.93 (d, 2H, $J = 8.0\text{ Hz}$), 8.01 (t, 1H, $J = 8.0\text{ Hz}$), 8.33 (d, 2H, $J = 7.7\text{ Hz}$). $^{13}\text{C NMR}$ in CDCl_3 : δ 10.5, 29.3, 55.1, 125.0, 126.5, 127.6, 128.8, 139.1, 141.7, 148.7, 162.6. IR $\nu(\text{cm}^{-1}, \text{nujol})$: $\tilde{\nu} = 3365, 3321, 3269, 1680, 1640, 1523$. EI-MS (CH_2Cl_2): m/z 401 ($[\text{M}]^+$). Optical rotation $[\alpha]_D^{20}$ (20 mM, CH_3CN): -191.3° . $\text{C}_{25}\text{H}_{27}\text{N}_3\text{O}_2$: calcd. C 74.8, H 6.8, N 10.5; found C 74.6, H 6.9, N 10.5.

Supplementary Material

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Acknowledgments

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Figure 1. $5D_0 \leftarrow 7F_0$ excitation spectra of solutions containing various ratios $\text{Eu}^{3+}:\text{L}(\text{Et})$ of 1:0.5 (red), 1:1 (orange), 1:2 (yellow), 1:3 (green), 1:5 (blue), and 1:10 (black) in anhydrous acetonitrile at room temperature and upon monitoring the Eu^{3+} luminescence at 615.0 nm.

Figure 2. Normalized time-resolved (top) and steady-state (bottom) luminescence spectra of **L(Et)** (solid line), $[\text{Gd}(\text{L}(\text{Et}))_3]^{3+}$ (dotted line), $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ (solid red line), and $[\text{Tb}(\text{L}(\text{Et}))_3]^{3+}$ (solid green line) in the solid state at 77 K (frozen anhydrous acetonitrile solution) and recorded with time delays of 0.1 and 0.0 ms, respectively.

Figure 3.

CPL (top curves) and luminescence (bottom curves) spectra of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (top left), $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (top right), and $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (bottom) transitions of $[\text{Eu}(\text{L}(\text{Et}))_3]^{3+}$ (top) and $[\text{Tb}(\text{L}(\text{Et}))_3]^{3+}$ (bottom) in anhydrous acetonitrile at room temperature, following excitation at 310 nm. (*R,R*)-**L(Et)** (Blue) and (*S,S*)-**L(Et)** (black).

Scheme 1.

Schematic of the 2,6-pyridinedicarboxamide moiety, DPA, L(4p), L(hh1), L(hh2), L(1yl), L(2yl), L(Me), and L(Et) from top left to bottom right.

Scheme 2. Schematic of **L'(1yl)** and **L(MeOrBu)** from left to right.

Table 1.

Summary of photophysical data from **L** and **[LnL]₃]³⁺ (**Ln**³⁺ = La, Gd, or Lu).**

Species	$E(^1\Pi^* - ^3\Pi^*)$ [cm ⁻¹]	I/I^0	IST ($S^* \rightarrow T^0$) [%]	Φ^0 [%]
L(Et)	8,250	4.3×10^{-3}	0.55	22.0
L(Me) ^[a]	4,190	4.0×10^{-3}	-	21.0
[Gd(L(Et))₃]³⁺	6,402	4.0×10^{-2}	3.2	2.8
[Gd(L(Me))₃]³⁺ ^[a]	5,070	4.7×10^{-2}	-	2.2
[La(L(4p))₃]³⁺ ^[b]	6,800	8.0×10^{-3}	-	5.5×10^{-2}
[Lu(L(4p))₃]³⁺ ^[b]	7,545	4.7×10^{-3}	-	6.5×10^{-2}

^[a] Taken from ref. [13b].

^[b] Taken from ref. [9].

Table 2.

Summary of luminescence sensitization and quantum yield data from **L** and $[\text{LnL}_3]^{3+}$ ($\text{Ln}^{3+} = \text{Eu}$ and Tb).

Ligand L	η_{sens}	$\eta_{\text{sens}}[\%]$	$\Phi^{\text{F}} [\text{EuL}_3]^{3+}[\%]$	$\Phi^{\text{F}} [\text{TbL}_3]^{3+}[\%]$
L(Et)	4.1×10^{-5}	4.1×10^{-3}	1.4	8.3
L(Me) ^[a]	4.0×10^{-5}	4.0×10^{-3}	1.0	8.6
L(4p) ^[b]	-	-	2.2×10^{-1}	1.2
L(1yl) ^[c]	4.9×10^{-2}	4.9	7.3	-
L(2yl) ^[d]	1.2×10^{-1}	12.0	1.9	-
L(hh2) ^[e]	7.3×10^{-2}	7.3	2.1	-

^[a] Taken from ref.[13b].

^[b] Taken from ref.[9].

^[c] Taken from refs.[12].

^[d] Taken from ref.[12a].

^[e] Taken from ref.[11].

Table 3.Summary of CPL data from $[\text{Eu}((R,R)\text{-L})_3]^{3+}$.

Ligand L	$^5\text{D}_0 \rightarrow ^7\text{F}_1$	$^5\text{D}_0 \rightarrow ^7\text{F}_2$	
	$g_{\text{lum}} (\lambda \text{ nm})$	$g_{\text{lum}} (\lambda \text{ nm})$	$g_{\text{lum}} (\lambda \text{ nm})$
L(Et)	−0.16 (590.8 nm)	−0.14 (595.8 nm)	+0.10 (614.6 nm)
L(Me) ^[a]	−0.19 (590.5 nm)	−0.18 (595.3 nm)	+0.21 (615.6 nm)
L(4p) ^[b]	−0.02 (591.0 nm)	-	-
L(1yl) ^[c]	−0.24 (589.9 nm)	−0.05 (593.6 nm)	+0.25 (614.1 nm)
L(2yl) ^[d]	-	−0.16 (595.6 nm)	+0.17 (619.0 nm)
L(hh1) ^[e]	-	−0.15 (600.0 nm)	+0.06 (619.0 nm)
L(hh2) ^[f]	−0.15 (589.0 nm)	−0.17 (592.0 nm)	+0.10 (614.0 nm)
L'(1yl) ^[g]	−0.18 (589.0 nm)	-	+0.13 (615.0 nm)
L(MeOrBu) ^[h]	−0.16 (590.2 nm)	−0.26 (595.0 nm)	+0.11 (615.7 nm)

^[a] Taken from ref.[13a].^[b] Taken from ref.[9].^[c] Taken from refs.[12].^[d] Taken from ref.[12a].^[e] Taken from ref.[10].^[f] Taken from ref.[11].^[g] Taken from ref.[21].^[h] Taken from ref.[22].