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# Characterization of the Electronic Excited-State Energetics and Solution Structure of Lanthanide(III) Complexes with the Polypyridine Ligand 6,6′-Bis[bis(2-pyridylmethyl)aminomethyl]-2,2′-bipyridine

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Absorption, emission, and excitation spectra for solid-state and solution of Tb(III), Dy(III), and Gd(III) complexes with the polypyridine ligand 6,6′-bis[bis(2-pyridylmethyl)-aminomethyl]-2,2′-bipyridine ($C_{36}H_{34}N_8$) are presented. Measurements of excited-state lifetimes and quantum yields in various solvents at room temperature and 77 K are also reported and used to characterize the excited-state energetics of this system. Special attention is given to the characterization of metal-to-ligand energy transfer efficiency and mechanisms. The measurement of circularly polarized luminescence (CPL) from the solution of the Dy(III) complex following circularly polarized excitation confirms the chiral structure of the complexes under study. No CPL is present in the luminescence from the Eu(III) or Tb(III) complex because of efficient racemization. The variation of the magnitude of the CPL as a function of temperature from an aqueous solution of DyL is used for the first time to characterize the solution equilibria between different chiral species.

## 1. Introduction

The preparation and characterization of lanthanide chelates with strong luminescence properties continues to be of great interest because of their potential to be sensitive and selective probes in a wide variety of biological and material-science applications. One important feature in the design of useful lanthanide-based luminescent systems is the inclusion of strongly absorbing chromophores (usually aromatic organic substituents) in the chelate to overcome the low molar absorbance coefficient associated with the intraconfigurational f ↔ f transitions of lanthanide(III) ions. The selection of the organic aromatic chromophore is also important in the effective transfer of the absorbed energy to the metal ion's resonant levels. In the overall light-conversion process, the quantities that contribute to the metal luminescence intensity are the efficiency of the ligand absorption, the ligand-to-metal energy transfer, and the metal luminescence. The design of efficient luminescent lanthanide-based probes for application to biological systems also requires detailed knowledge concerning solution structure and dynamics and the influence that these have on the important photochemical and photophysical properties. It is well known, for example, that the presence of water or alcohol molecules in the first coordination sphere of these complexes results in decreased emission due to radiationless deactivation pathways.[1,2] It has also been shown that subtle twists along the $C_4$ axis of certain chiral macrocyclic chelates have a dramatic effect on the overall chiroptical activity.[3]

By far, the lanthanide(III) ions most widely used as luminescent probes are Eu(III) and Tb(III). The luminescence from these ions is in the visible region and is characterized by large Stokes shifts, narrow-band emissions, and long luminescence lifetimes, making them ideal for applications in hetero- and homogeneous fluoroimmunoassays[4−8] and as labels for proteins and nucleic acids[9] and numerous other types of luminescent probes.[10−13] Luminescence measurements reflect the environment of the excited state, and because the lifetimes of Tb(III) and Eu(III) are of the order of milliseconds, little or no information concerning the shorter time-scale solution dynamics is available from these types of experiments. For example, the racemization of chiral complexes may be occurring much faster than the luminescence, and therefore, experiments designed to probe this feature of complex dynamics would be unsuccessful.[14] Although generally not as luminescent as Tb(III) or Eu(III) in solution, there has been some interest in studying the visible luminescence from complexes containing Dy(III) because the lifetime of this ion is on the order of microseconds, allowing one to probe shorter time scales.[15] For example, it has been shown that circularly polarized luminescence[16−18] (CPL) may be observed from racemic complexes if circularly polarized laser excitation is used to prepare excited-state distributions that are not racemic by preferential absorption. This technique is successful only if the nonracemic excited-state population is maintained during the excited-state lifetime. This will be one of the key aspects of the work presented here.

The photophysical and structural characteristics that are important in the design of useful luminescent probes containing lanthanide(III) ions have become increasingly understood.[19−27] It has been demonstrated, for example, that complexes containing the bipyridine (bpy) unit within an organic ligand are often

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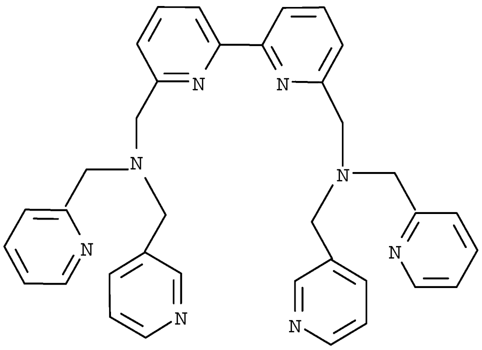

**(L)**

6,6'-bis[bis(2-pyridylmethyl)aminomethyl]-2,2'-bipyridine

**Figure 1.** Structural formula of the ligand.

useful as the absorbing chromophore and as a constituent of an effective complexing agent.[19,28] One approach to obtaining highly emissive complexes is to employ flexible macrocyclic ligands capable of forming a suitable cavity for lanthanide ions and effectively eliminating solvent molecules from the first coordination sphere.[29] Lanthanide complexes with podand-type ligands that incorporate the bpy unit are of special interest because they fulfill the requirements related to complex stability and luminescence efficiency. Recently, the preparation, crystal structure, photophysical properties, and dynamics of the excited states for the europium podate, $[EuC_{36}H_{34}N_8Cl_2]\cdot5H_2O$, have been reported.[30,31] Working along these lines, we have synthesized the Tb(III), Dy(III), and Gd(III) complexes with the same podand ($C_{36}H_{34}N_8$). This work describes a series of experiments aimed at providing important information concerning this ligand with continued emphasis on the relationship between solution structure and dynamics and luminescence properties.

## 2. Experimental Section

The 6,6′-bis[bis(2-pyridylmethyl)aminomethyl]-2,2′-bipyridine ligand (L) (Figure 1) was synthesized according to methods published previously.[32] The Tb(III) and Dy(III) complexes with L were prepared as described elsewhere.[31] Results of elementary analysis show the following composition of the complexes: $[DyL]Cl_3\cdot5H_2O$ and $[TbL]Cl_3\cdot5H_2O$. Electronic absorption spectra of the Tb(III) complex in different solvents ($CH_3CN$, $CD_3OD$, $CH_3OH$, $D_2O$, and $H_2O$) and in a solid were recorded using a Cary-Varian 500 spectrophotometer at room temperature in the 250−500 nm spectral region. Emission and excitation spectra were performed at 293 and 77 K using a SLM Aminco SPF500 spectrofluorometer equipped with a 300 W Xe arc lamp and a liquid-$N_2$-cooled cryostat.

Luminescence decay times were measured on a Jobin-Yvon THR1000 system using a Lambda-Physik 105 excimer laser. The luminescence quantum yield for TbL ($\lambda = 318.0$ nm) was determined by the method described by Haas and Stein[33] using fluorescein in 0.1 M NaOH as a standard ($\Phi = 0.90$) at 293 K.[34] Circularly polarized luminescence spectra were recorded using an instrument described previously.[35] The excitation source was a CW tunable dye laser (Coherent CR 599) with rhodamine 6G dissolved in ethylene glycol pumped with an argon laser (Coherent Innova-70). The laser excitation beam was oriented at 90° to the direction of the emission detection. Circularly polarized excitation was accomplished by passing the largely linear polarized laser excitation through a high-quality linear polarizer and quarter-wave plate was varied by rotating the device 45° to generate linear polarization and then rotation by 90° to create the opposite circular polarization. For temperature-dependent experiments, the temperature of the sample was controlled by placing a 1.0-cm cuvette inside an anodized aluminum cell jacket that was connected to a NESLAB RTE-101 circulating temperature bath, and monitored by placing the temperature probe (Fisher calibrated to 0.1 °C) in the sample compartment before and after each measurement. The circulation fluid was water. The connections from the circulator to the aluminum cuvette jacket were insulated to help maintain consistent temperatures.

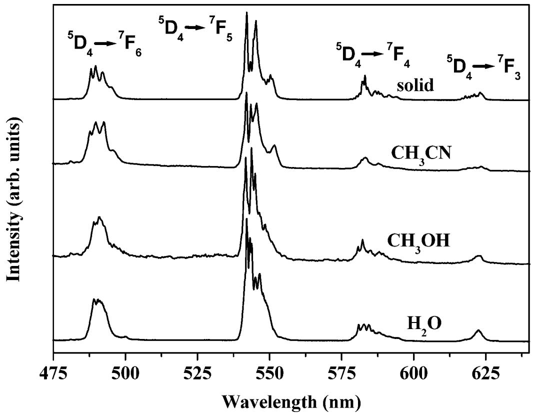

**Figure 2.** Emission spectra at 77 K of TbL in the solid state and dissolved in various solvents.

## 3. Results and Discussion

As shown in Figure 2, complexes of Tb(III) with the 6,6′-bis[bis(2-pyridylmethyl)amino-methyl]-2,2′-bipyridine complex (TbL) show strong luminescence upon excitation into the ligand absorption band at room temperature and at 77 K in both the solid state and in solution. The bands that are observed and displayed in this figure correspond with the well-known transitions $^5D_4 \rightarrow {}^7F_J$ (Figure 2). The luminescence spectrum of TbL in $CH_3CN$ resembles the spectrum obtained from a solid-state sample in the region of the $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ transitions, which suggests a very similar metal ion coordination in both acetonitrile solution and in a solid. This conclusion is confirmed by earlier spectroscopic investigations of EuL in which for the nondegenerate $^5D_0 \rightarrow {}^7F_0$ transition, a singlet was observed for the solid and $CH_3CN$ solution samples and a doublet was observed for aqueous and alcoholic solutions. The presence of the doublet is indicative of two forms of the Eu(III) complex, which have been interpreted in terms of solvent penetration into the first coordination sphere: $[EuLCl_2]^+$ and $[EuLClR]^{2+}$ (R = solvent molecule).[30]

Absorption spectra for TbL and for the free ligand in alcoholic solutions and the excitation spectra of TbL and EuL in $CH_3OH$ at room temperature are plotted in Figure 3. The absorption spectrum of DyL in methanol is identical. As seen by comparing the free-ligand and complex absorption spectrum, the $\pi\pi^*$ bipyridine band is shifted by 32 nm toward lower energy. This shift in energy is indicative of a stronger interaction of the bipyridine chromophore with the metal ion as compared to the pyridine units. Ligand bands corresponding to the $\pi \rightarrow \pi^*$ bipyridine absorption with a maximum at 320 nm and pyridine absorption with a maximum at 260 nm are the only transitions visible in the absorption and excitation spectra of the TbL solution dissolved in both methanol ($c = 1.5 \times 10^{-5}$ M) and water. The ligand-to-metal ion energy transfer is so efficient in these systems that the much weaker f → f transitions are not observable in the excitation spectrum. The excitation spectra

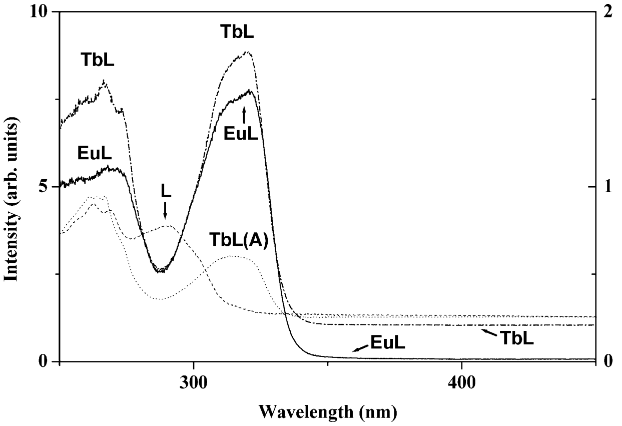

**Figure 3.** Excitation spectra of TbL and EuL and absorption spectra of TbL (A) (···) and free ligand (L) (- - -) in $CH_3OH$ at 293 K.

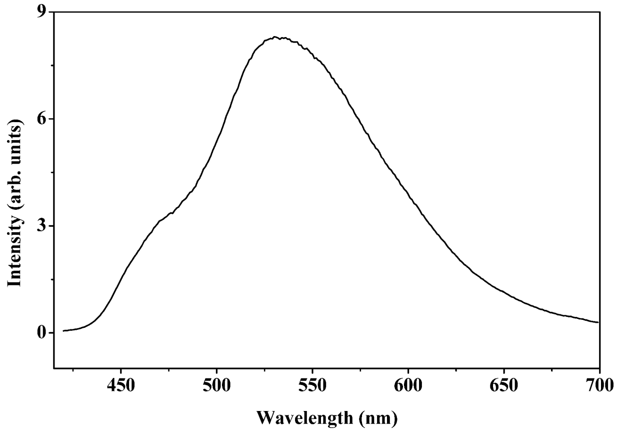

**Figure 4.** Phosphorescence spectrum of GdL at 77 K.

differ from the absorption spectra in the relative intensities of the observed bands. The $\pi \rightarrow \pi^*$ bipyridine band is more intense than that of pyridine, which implies a more efficient sensitization of Tb(III) ion emission as a result of bipyridine absorption. This is presumably due to better overlap with the excited energy levels of Tb(III). It is worth noting that the relative intensity of the absorption bands are different for TbL and EuL complexes, which may be indicative of a somewhat different relative contribution of the absorption chromophores or a difference in energy-transfer mechanisms. According to the results discussed in refs 25 and 27, selection rules state that in the case of Tb(III) the multipolar mechanism dominates, whereas in the case of Eu(III), the exchange mechanism is the dominant one, which is a result of the quantum number ($J$) change.

**TABLE 1: Luminescence Decay Results for TbL in the Solid State and in Various Solutions at 293 and 77 K**

| | 293 K | | 77 K | | | | | |
|---|---|---|---|---|---|---|---|---|
| TbL | $\tau_H$ (ms) | $\tau_D$ (ms) | $\tau_H$ (ms) | $\tau_D$ (ms) | $k_r$[a] ($s^{-1}$) | $k_{nr}(T)$[b] ($s^{-1}$) | $k_{nr}(OH)$[c] ($s^{-1}$) | $n$[d] |
| in $CH_3OH$ | 1.5 | 1.67 | 1.8 | 2.93 | 341 | 257 | 68 | 0.56 |
| in $H_2O$ | 1.53 | 1.76 | | | | | 86 | 0.36 |
| in $CH_3CN$ | 1.4 | | 1.35 | | | | | |
| solid | 1.4 | | 1.78 | | | | | |

[a] Defined as $[\tau(MOD)_{77K}]^{-1}$. [b] Defined as $[\tau(MOD)_{300K}]^{-1} - [\tau(MOD)_{77K}]^{-1}$. [c] Defined as $[\tau(MOH)_{300K}]^{-1} - [\tau(MOD)_{300K}]^{-1}$. [d] Number of bound solvent molecules as calculated from $k([\tau(MOH)_{300K}]^{-1} - [\tau(MOD)_{300K}]^{-1})$, where $k = 4.2$ for $H_2O$ and 8.4 for $CH_3OH$.

In Figure 4, we plot the phosphorescence spectrum of methanolic solutions of the GdL complex at 77 K. From these data, we can estimate the position of the bipyridine triplet state to be 21 929 $cm^{-1}$. The energy difference between the Tb(III)-emissive level ($^5D_4$) and the ligand triplet state is calculated to be 1438 $cm^{-1}$. This comfortably meets the condition of phonon-assisted resonance, and allows for the presence of back energy transfer, as described earlier for other Tb(III) complexes, both in solutions and in the solid state.[20,21,24,30] The $^5D_4$ level luminescence decay times confirm the presence of a temperature-dependent process in the system under investigation. The luminescence decay times for aqueous, methanol, and acetonitrile solutions and the solid-state results are presented in Table 1. The radiative and nonradiative decay rates are also given in this table. From these data, one can conclude that the contribution of multiphonon relaxation process promoted by high-energy vibrations of $OH^-$ groups of methanol is slight. The number of solvent molecules was calculated using Horrocks' equation and was determined to be 0.56 for $CH_3OH$ and 0.36 for water.[37,38] It should be noted that the luminescence decay observed in aqueous solutions at low temperatures (e.g., 77 K) was clearly nonexponential, hindering the determination of the contribution of temperature-dependent nonradiative emission quenching processes. At room temperature, two different forms of the TbL complex can exist as a result of dissociation as seen for EuL. Evidently, conversion from one form to the other is too fast a process to manifest itself as additional components in the luminescence decay times at 293 K. The $^5D_4$ Tb(III)-level emission decay times at 293 K are the same for a solid and solution in $CH_3CN$. Differences are present at 77 K, where the emission decay time is longer for the solid state.

The TbL emission quantum yield (Φ) at 293 K under 318 nm excitation is approximately 17.7% in $D_2O$, and 13.7% in $CD_3OD$. Also, the emission decay times are longer in $D_2O$ than in $CD_3OD$. The relatively modest emission quantum yields are probably due to back energy transfer from the $^5D_4$ Tb(III) level to the excited ligand triplet state. One can estimate the efficiency of the ligand-to-metal energy transfer, $\eta_{et}$, following excitation into the ligand singlet state through the following equation[19] using the assumption that the decay process at 77 K in deuterated solvent is purely radiative

$$\eta_{et} = \frac{\Phi}{\eta_M} \tag{1}$$

where $\eta_M$ is the emission efficiency upon metal excitation

$$\eta_M = \frac{\tau_{MeOH}(293\ K)}{\tau_{MeOD}(77\ K)} \tag{2}$$

The value of $\eta_M$ was determined to be 0.51, and using the value for the quantum yield for the $CD_3OD$ solution given above (0.137), we obtain a result of $\eta_{et} = 0.27$. This value is a bit lower than expected, perhaps due to the presence of some nondeuterated solvent molecules in the sample that was measured. This may be part of the explanation of the modest experimental quantum yield in comparison to the small fraction of nonradiative temperature-dependent and non-temperature-dependent processes. However, a major factor influencing the quantum yield value is the position of the lowest triplet state level.[21,26]

The quantum yield for EuL in $D_2O$ is 8.9% and the decay rates are $k_{nr}(OH) = 270\ s^{-1}$, $k_{nr}(T) = 136\ s^{-1}$, and $k_{nr}(OH) = 501\ s^{-1}$ for aqueous and alcoholic solutions, respectively.[31] As mentioned above, a comparison of the excitation spectra of EuL and TbL in solutions shows differences in the relative band intensities. This may indicate a participation of a ligand-to-metal charge transfer (LMCT) state in the ligand-to-metal energy

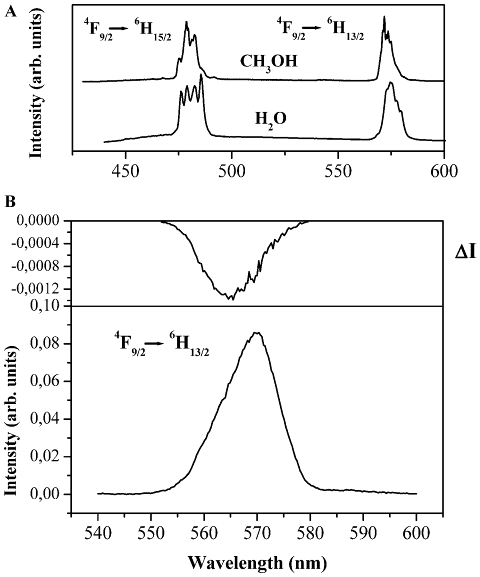

**Figure 5.** Total luminescence spectra of DyL in $H_2O$ and $CH_3OH$ at 77 K (A). Total luminescence (lower curve) and circularly polarized luminescence ($\Delta I$, upper curve) for an aqueous solution of DyL at 293 K. The solution was excited at 457.9 nm.

transfer process leading to Eu(III) ion emission. The obtained emission quantum yield is smaller than one would expect for the comparatively low temperature-dependent and non-temperature-dependent decay rates. As demonstrated in earlier theoretical calculations, the presence of charge-transfer (C-T) states always leads to a reduction of emission quantum yield. This can account for the lower quantum yields for Eu(III) complexes in which C-T states may participate in the energy-transfer process. This effect is not expected to be operative for Tb(III) in the spectral region between 200 and 350 nm. Recent theoretical studies on LMCT states (the position of which cannot be determined by way of experimental measurements) have led to a better understanding of the effect of these states on emission quenching processes and associated quantum yields.[25,39] These theoretical calculations show, for example, that the quantum yield for a Eu(III) cryptate depends on the LMCT state energy with respect to the ligand singlet and triplet state, being the lowest for a LMCT-state energy close to the triplet state.

Examination of the crystal structure of GdL shows that the metal cation is in a chiral environment. Circularly polarized luminescence (CPL) measurements were undertaken to investigate this aspect of molecular structure. Because the overall solution structure of these complexes is racemic, CPL can be generated only if circularly polarized excitation is used to prepare an enantio-enriched emitting state and any nonracemic population is stable on the emission time scale. All of the attempts at observing CPL from aqueous or methanol solutions containing EuL or TbL were unsuccessful. These experiments could be interpreted as either the solution structure is not chiral or that the solution dynamics is such that any photoenriched sample has racemized during the relatively long excited-state lifetimes of these species.

As shown in Figure 5, CPL was observed for an aqueous solution of DyL in the spectral region corresponding to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. In Figure 5B we plot the observed CPL spectrum, and in Figure 5A we show the luminescence spectra at 77 K. The CPL was measured with the use of the 457.9 nm line of an Ar ion laser. This line overlaps with the $^6H_{15/2} \rightarrow {}^4F_{15/2}$ absorption of Dy(III). In this experiment, both the excitation and emission transitions obey magnetic dipole selection rules that are known to yield the largest discrimination between enantiomers.[40] Excitation via the $^6H_{15/2} \rightarrow {}^4F_{9/2}$ transition using 476.5-nm radiation yields a large emission intensity but no measurable CPL. The CPL signal confirmed the chiral character of the complex resulting from a structure in which the two cations, each one coordinated by seven nitrogen atoms of ligand and two chlorine atoms, are almost related by a glide plane at $y = 0$, and the orientation of the noncoordinated pyridine group differs by 180°.[41]

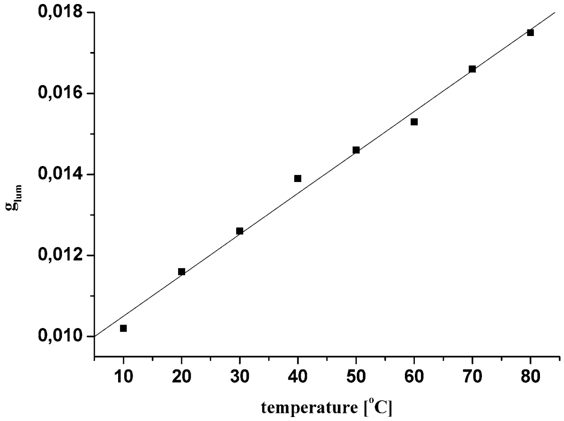

**Figure 6.** A plot of the measured luminescence dissymmetry factor, $g_{\text{lum}}$, measured at 570 nm versus temperature for a solution of DyL in water.

**TABLE 2: Excited State Lifetime Results for DyL in the Solid State and Dissolved in various solvents**

| DyL | $\tau$(293 K) ($\mu$s) | $\tau$(77 K) ($\mu$s) |
|---|---|---|
| in $CH_3OH$ | 9 | 23 |
| in $CD_3OD$ | 11 | 25 |
| in $H_2O$ | 10 | 22 |
| in $CH_3CN$ | 12 | 24 |
| solid | 7.8 | 21 |

The reason that we are able to observe CPL from DyL but not from TbL or EuL must be due to the fact that the emission lifetime of Dy(III) is much shorter than that for Tb(III) or Eu(III), so there is not enough time for the chiral excited-state distribution to completely racemize. In Table 2, we present the measured excited-state lifetime data for DyL at room temperature and 77 K in the solid state and various solutions. Note that the lifetimes are approximately 100 times shorter than those for TbL. These results and conclusions are consistent with other observations on this system[30] as well as NMR measurements on solutions of LaL in water and methanol.[42] To investigate this further, we measured the observed CPL from aqueous solutions of DyL under conditions of variable temperature. These results are given in Figure 6. In this plot, $g_{\text{lum}}$ is the so-called luminescence dissymmetry factor and is defined as follows

$$g_{\text{lum}} = \frac{I_{\text{left}} - I_{\text{right}}}{\frac{1}{2}(I_{\text{left}} + I_{\text{right}})} \tag{3}$$

where $I_{\text{left}}$ and $I_{\text{right}}$ refer to the intensity of left and right circularly polarized emitted light, respectively. A $g_{\text{lum}}$ value of zero means that the excited state is not chiral, so the interesting result is that as temperature increases the net circular polarization increases. In a number of other systems, we have observed a decrease in $g_{\text{lum}}$ at elevated temperatures, indicating incresed racemization, but this is clearly not the case here.

It should be noted that the connection between the temperature-dependent $g_{\text{lum}}$ and the thermodynamic parameters or equilibrium constant is not straightforward in this measurement. For the measurement of CPL from two species, α and $\beta$, we can write down the following expression

$$g_{\mathrm{lum}} = \frac{I_{\mathrm{left}}(\alpha) - I_{\mathrm{right}}(\alpha) + I_{\mathrm{left}}(\beta) - I_{\mathrm{right}}(\beta)}{\frac{1}{2}(I_{\mathrm{left}}(\alpha) + I_{\mathrm{right}}(\alpha) + I_{\mathrm{left}}(\beta) + I_{\mathrm{right}}(\beta))} = \frac{\Delta I(\alpha) + \Delta I(\beta)}{\frac{1}{2}(I_{\mathrm{left}}(\alpha) + I_{\mathrm{right}}(\alpha) + I_{\mathrm{left}}(\beta) + I_{\mathrm{right}}(\beta))} \quad (4)$$

where we have explicitly labeled the measured polarization intensities in terms of the individual emitting species. If α and $\beta$ were enantiomers, then the form of eq 4 would simplify. However, in the case where α and $\beta$ are complexes of different molecular and electronic structures, then the form of eq 4 is such that the *measured* $g_{\mathrm{lum}}$ for a mixture may not be directly related to the intrinisic $g_{\mathrm{lum}}$ values for the α and $\beta$ species unless additional molecular information is available.

If the effect of increased temperature was to promote racemization, as seen previously,[43] then the measured value for $|g_{\mathrm{lum}}|$ would decrease because the single or multiple chiral species would yield lower $g_{\mathrm{lum}}$ values for the individual racemic mixtures. Because we know from previous studies that in aqueous solution two species exist it must be the case that increasing the temperature results in an equilibrium shift toward a species that is more chiral. This result is entirely consistent with the results obtained previously for EuL in which excitation spectroscopy was used to determine thermodynamic parameters for the equilibrium between the two species.[30] Therefore, it must be the case that racemization of DyL is not occurring at a rate sufficient to racemize the chiral complexes even at the elevated temperatures used in this study. The temperature changes are sufficient to effect the equilibrium distribution of species as seen previously.

## 4. Summary

The results presented and discussed in this work for lanthanide(III) complexes with the 6,6′-bis[bis(2-pyridylmethyl)-aminomethyl]-2,2′-bipyridine ligand illustrate the quality and quantity of information on the energetics, solution structure, and photophysics that is now available for the characterization of luminescent lanthanide complexes. This type of study is important particularly for researchers interested in the design of complexes containing lanthanide(III) ions for potential use as luminescent probes of biological structure or the use of related species for therapeutic or diagnostic applications.

It has been demonstrated that for TbL, there exists very efficient ligand-to-metal energy transfer. For EuL, the participation of LMCT in the quenching of the emission is predicted based on the excitation spectra, quantum yields, and measured decay rate constants.

Spectroscopic studies of GdL allow one to determine the position of the ligand triplet state, which allows one to compute the energy gap between the ligand and metal states and then an estimate of the efficiency of phonon-assisted energy transfer.

The results presented in Figure 6 for the temperature dependence of the luminescence dissymmetry factor represent the first time that variations in CPL have been used to investigate the temperature dependence of nonracemic equilibria. Although an unambiguous interpretation of these results is not possible, the data are consistent with a equilibrium between a solvent-penetrated first coordination sphere and a dissociated structure. It makes sense that at increased temperature formation of the dissociated species is increased, although no structural evidence for this identification is possible.

The results presented in this work are part of an overall effort to develop specific sensitive luminescent sensors using lanthanide(III) ions. Of special interest is the exploitation of chiral discrimination in this research area, as detected by differences in the magnitude of the circularly polarized luminescence. As indicated by the results here and previously, we believe that encapsulation of luminescent lanthanide ions in chiral podands that are designed to interact with target functional groups, and that contain properly selected absorption chromophores, show great potential to produce useful systems.

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