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The Effect of Excited State Energy Transfer on the Circularly Polarized Luminescence from Sol–Gels Containing Racemic Complexes of Eu(III): Theory and Experiment

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Excited state energy transfer between enantiomers in concentrated samples will diminish the differential excited state concentrations of a photoenriched racemic mixture, and this phenomenon will be reflected in a decrease in the observed circularly polarized luminescence as compared to low concentration samples where this energy transfer process can be neglected. Such a decrease is reported here for complexes of Eu(III) with 2,6-pyridine-dicarboxylate and 2,2'-bipyridine-*N,N'*-dioxide = bpyO₂ ligands. This work represents the first experimental observation of this phenomenon for samples prepared in high concentration by incorporation into high-quality strain-free sol–gels. These results are fit to a theoretical model appropriate for randomly oriented and dispersed solute chromophores, and the Förster critical transfer distance is obtained. Limitations of the model and other experimental difficulties are described.

1. Introduction

In many systems of fundamental and practical interest, an understanding of the nonradiative transfer of energy from an excited molecular or ionic donor to an acceptor is essential. Within this broad area of research, energy transfer between identical chromophores has been the subject of numerous theoretical and experimental investigations.^{1–13} This form of excited state energy transfer is sometimes referred to as “energy migration” or “energy hopping”, depending upon the particular circumstances or system. These studies have involved regularly ordered crystal systems, randomly dispersed “impurities” in crystals, or between chromophores dissolved in liquids or polymers. This phenomenon is of obvious interest in investigations of natural and synthetic photochemical antenna systems in which there exists a large number of absorbing chromophores but typically a small number of photoactive centers.

Since excited state energy transfer also has the effect of scrambling an initially photoselected orientational distribution, as measured by diminished linear polarization in the fluorescence from a rigid system (concentration depolarization), this phenomenon has also been used to probe the structure of polymer composites at the molecular level.¹⁴ Excited state energy transfer also may have consequences in the measurement of circular polarization from molecular systems. In a theoretical treatment of circularly polarized luminescence (CPL) from racemic systems, Hilmes and Riehl have described the effect of energy transfer on the magnitude of the degree of circular polarization in experiments in which a nonracemic excited state distribution of chiral molecules is prepared from a racemic ground state by using a circularly polarized excitation beam.¹⁵ In this work, it was assumed that the energy transfer from identical enantiomers occurs at the same rate as that between opposite enantiomers. The effect of energy transfer is therefore to reduce the net enantioenriched concentration prepared by the

circularly polarized excitation beam. The work presented here represents the first experimental observation of this phenomenon and is part of a overall program aimed at a more complete understanding of the effects of excited state energetic, chemical, and structural processes on the stereochemical properties of lanthanide complexes in solution.

The measurement of CPL from racemic solutions of enantiomeric compounds following circularly polarized excitation is one of the most useful applications of CPL spectroscopy.¹⁶ In this technique, an enantioenriched excited state distribution is created through differential absorption of the circularly polarized excitation. This experiment, which will be referred to as CPE/CPL, is successful only if the excited state enantiomeric excess is at least partially maintained during the excited state lifetime. In addition to the effects of energy transfer, the molecular species studied must also be not susceptible to complete chemical racemization during the same time period. As described below, this technique is particularly suited to the study of racemic solutions of chiral lanthanide complexes and has been successfully applied to the study of the excited state dynamics of a number of luminescent lanthanide (III) ions (Tb³⁺, Eu³⁺, Sm³⁺, and Dy³⁺) in eight and nine coordinated lanthanide complexes with multidentate ligands in structures with rather high (*C*₄, *D*₃, *D*₄, and *D*₂) symmetry.^{17–20}

Of particular interest in CPE/CPL studies has been the study of complexes with the terdentate ligands, 2,6-pyridine-dicarboxylate (DPA) and oxydiacetate (ODA).^{17,18} In previous work, it has been shown that tris-terdentate complexes of Eu(III) with DPA, which have approximate *D*₃ symmetry, do not racemize in aqueous solutions on the emission time scale of Eu(III), whereas Eu(III) complexes with ODA in H₂O and D₂O do not exhibit measurable CPL when excited by circularly polarized light. At elevated temperatures, racemization of Eu(DPA)₃^{3–} does affect the CPL signal,²¹ so we have been interested in designing experiments in which racemization can be eliminated, but circular polarization measurements can still be undertaken. Such a situation exists for a class of high quality strain-free sol–gels. Recently, we have reported circularly polarized

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luminescence results for these kinds of complexes in rigid sol-gels in which the racemization process is assumed to be eliminated.²² In this work, circular polarization was measured for $\text{Eu}(\text{ODA})_3^{3-}$, indicating that racemization of this complex had been reduced; however, for both $\text{Eu}(\text{ODA})_3^{3-}$ and $\text{Eu}(\text{DPA})_3^{3-}$ the values obtained were much less than expected. These preliminary results were reproducible and were interpreted in terms of circular depolarization due to excited state energy transfer.

In this work, we report the results of CPL from complexes of $\text{Eu}(\text{DPA})_3^{3-}$ and $\text{Eu}(2,2'\text{-bipyridine-}N,N'\text{-dioxide})_4^{3+}$ prepared in sol-gels as a function of concentration. Incorporation of lanthanide complexes in sol-gels has become an established technique for studying the spectroscopy and structure of these species.^{23–26} The results described here are also compared to a theoretical calculation of the effect of energy transfer on CPL based on a theoretical development of orientationally averaged excitation transport by Gochanour and Fayer (GF) using a simple dipole-dipole energy transfer mechanism.¹ Although from previous studies the use of this energy transfer mechanism for Eu-Eu energy transfer may be called into question,^{7,10,11} application of the GF theory which has been parametrized for randomly dispersed solute chromophores represents a good starting point for analysis for the polarization measurements presented here. It is shown that the variation of CPL with concentration can be fit to the theoretical result, and a value for the critical transfer distance, which is a measure of the energy transfer rate, may be obtained.

2. Experimental Section

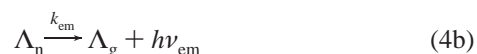
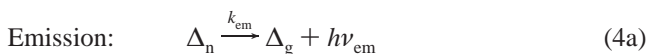
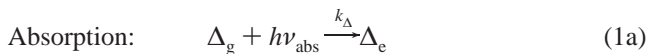
A stock solution of 0.35 M dipicolinic acid (DPA, Aldrich) in H_2O was prepared, and the pH was adjusted to 8. The sol-gel samples were synthesized by the acid-catalyzed hydrolysis and condensation of tetraethoxysilane (TEOS) with deionized water. After homogenization, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) and sufficient volumes of DPA solution were introduced to the stirred sol so that the ligand:Eu ratio was 3.5:1. The pH of the solutions were adjusted with NH_4OH . For every pH value, two samples of different Eu^{3+} molar (0.0877 and 0.00438) concentration were prepared. The gelation occurred in one or several days, depending on the final pH. The samples were then aged for one month at room temperature. Three samples of different Eu^{3+} molar concentrations (0.082, 0.0084, 0.00083) of $\text{Eu}(\text{bpyO}_2)_4^{3+}$ were prepared in the same manner. The pH of the sol was approximately 6. $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) and 2,2'-bipyridine- N,N' -dioxide (Aldrich) were used as the substrates. Transparent monolithic solid samples were obtained both for $\text{Eu}(\text{DPA})_3^{3-}$ and $\text{Eu}(\text{bpyO}_2)_4^{3+}$.

CPL spectra were recorded using 0.22 m monochromator equipped with a cooled EMI 9558 photomultiplier tube used in photon counting mode, using an instrument described previously.²⁷ The excitation source was either an argon laser (Coherent CR6) operating in the visible region (472.7 nm) or a CW tunable dye laser (Coherent CR599). The excitation was converted to circular polarization by using a high quality quarter-wave plate. The polarization of the excitation was varied from left to right polarization by rotation of the quarter wave plate to ensure that the opposite sign CPL result was obtained. The circular analyzer was a photoelastic modulator (PEM, Hinds Int.) operating at 50 kHz for $\lambda/4$ retardation and a Glan-Thompson linear polarizer (Karl Lambrecht). The high-resolution emission spectra of complexes under study in aqueous solutions and doped silica sol gels were measured using a Spectra Pro 0.75 m monochromator equipped with an Oxford

1024 continuous flow helium cryostat. Luminescence decay times were measured using a Jobin-Yvon THR 1000 monochromator and Lambda-Physik 105 excimer laser.

3. Theory

CPL from a Racemic Mixture. A complete theoretical treatment of the measurement of CPL from racemic mixtures including the effects of energy transfer and chemical racemization has been presented by Hilmes and Riehl,¹⁵ and therefore, only a very brief summary appropriate for rigid systems which cannot racemize on the luminescence time scale will be presented here. We consider a racemic mixture composed of an equal mixture of luminescent Δ and Λ enantiomers, in which we allow for the following kinetic processes:



where e denotes an intermediate excited state and n denotes the emitting state. It is important to note that, although we have explicitly listed the processes for both enantiomers in eqs 2–4, the rate constants for the enantiomeric processes are identical. We have only allowed for a enantiomeric differences in the absorption process. In fact, k_Λ and k_Δ will only be different if the excitation beam is circularly polarized.

From the equations given above, we may write the following expressions for the time-dependent populations of the emitting state, n:

$$\frac{dN_{\Lambda_n}}{dt} = -k_{\text{em}}N_{\Lambda_n} - k_{\text{et}}N_{\Lambda_n}N_{\Delta_g} + k_{\text{et}}N_{\Lambda_g}N_{\Delta_n} \quad (5a)$$

$$\frac{dN_{\Delta_n}}{dt} = -k_{\text{em}}N_{\Delta_n} - k_{\text{et}}N_{\Delta_n}N_{\Lambda_g} + k_{\text{et}}N_{\Delta_g}N_{\Lambda_n} \quad (5b)$$

The experimental measurement of CPL is directly proportional to the difference in excited state population of the enantiomers

$$\frac{d\Delta N_n(t)}{dt} = \frac{d(N_{\Lambda_n} - N_{\Delta_n})}{dt} \quad (6)$$

substituting from above, we obtain

$$\frac{d\Delta N_n(t)}{dt} = -k_{\text{em}}\Delta N_n - 2k_{\text{et}}N_{\Delta_n}N_{\Lambda_g} + 2k_{\text{et}}N_{\Delta_g}N_{\Lambda_n} \quad (7)$$

In our applications, the number of molecules that are promoted to the excited state is small compared to the total number present; thus, we assume that

$$N_{\Delta_g} = N_{\Lambda_g} = N/2 \quad (8)$$

where N is the total number of molecules present in the illuminated sample volume. Substituting this result into eq 7, we obtain

$$\frac{d\Delta N_n(t)}{dt} = -[k_{em} + Nk_{et}(t)]\Delta N_n \quad (9)$$

where we have now noted the explicit time dependence of the bimolecular energy transfer rate constant. The formal solution of eq 9 is

$$\Delta N_n(t) = \Delta N_n(0)e^{-k_{em}t}e^{A(t)} \quad (10)$$

where

$$A(t) = -\int_0^t Nk_{et}(t) dt \quad (11)$$

and $e^{A(t)}$ is the probability that an initial excitation of an Λ (or Δ) molecule remains on an Λ (or Δ) molecule at time t .

In CPL spectroscopy, it is common to report results in terms of the so-called luminescence dissymmetry factor, $g_{lum}(\lambda)$. For a particular enantiomer, Δ , measured at wavelength λ this is defined as follows:

$$g_{lum}(\Delta, \lambda) = \frac{I_{left}(\Delta, \lambda) - I_{right}(\Delta, \lambda)}{\frac{1}{2}(I_{left}(\Delta, \lambda) + I_{right}(\Delta, \lambda))} = \frac{\Delta I(\Delta, \lambda)}{\frac{1}{2}I(\Delta, \lambda)} \quad (12)$$

where I_{left} and I_{right} refer, respectively, to the measured intensity of left and right circularly polarized emitted light. The factor of $1/2$ in this equation is added so that this definition is consistent with the related quantity in CD, namely, the absorption dissymmetry factor $g_{abs}(\Delta, \lambda')$

$$g_{abs}(\Delta, \lambda') = \frac{\epsilon_{left}(\Delta, \lambda') - \epsilon_{right}(\Delta, \lambda')}{\frac{1}{2}(\epsilon_{left}(\Delta, \lambda') + \epsilon_{right}(\Delta, \lambda'))} = \frac{\Delta\epsilon(\Delta, \lambda')}{\frac{1}{2}\epsilon(\Delta, \lambda')} \quad (13)$$

where $\epsilon_{left}(\Delta, \lambda')$ denotes the extinction coefficient for left circularly polarized light of enantiomer Δ at wavelength λ' . By symmetry, the absorption of right circularly polarized light by the Δ enantiomer is exactly equal to the absorption of left circularly polarized light by the Λ enantiomer. Thus, eq 13 may be rewritten as follows:

$$g_{abs}(\Delta, \lambda') = \frac{\epsilon_{left}(\Delta, \lambda') - \epsilon_{left}(\Lambda, \lambda')}{\frac{1}{2}[\epsilon_{left}(\Delta, \lambda') + \epsilon_{left}(\Lambda, \lambda')]} = \frac{\Delta\epsilon(\Delta, \lambda')}{\frac{1}{2}\epsilon(\Delta, \lambda')} \quad (14)$$

For a racemic mixture, the number of molecules of each enantiomer, $N_{left}(\Delta)$ and $N_{left}(\Lambda)$, that are excited with incident left circularly polarized light at wavelength λ' , is proportional to the individual extinction coefficients, and thus, we may derive the following expression:

$$g_{abs}(\Delta, \lambda') = \frac{N_{left}(\Delta) - N_{left}(\Lambda)}{\frac{1}{2}[N_{left}(\Delta) + N_{left}(\Lambda)]} \quad (15)$$

The difference in excited state population divided by the total excited state population is equal to the excited state enantiomeric excess, η , created at the time of excitation which we define as $t = 0$. Thus

$$g_{abs}(\Delta, \lambda') = 2\eta_{left}(0) \quad (16)$$

and using the result given in eq 10, we can express the steady state enantiomeric excess as follows:

$$\eta_{left} = \eta_{left}(0) \left[\frac{\int_0^\infty e^{-k_{em}t} e^{A(t)} dt}{\int_0^\infty e^{-k_{em}t} dt} \right] = \frac{\eta_{left}(0)}{\tau} \int_0^\infty e^{-k_{em}t} e^{A(t)} dt \quad (17)$$

where τ is the emission lifetime.

For measurement of CPL at wavelength λ from a solution containing a mixture of enantiomers, the dissymmetry factor will be directly proportional to the enantiomeric excess in the emitting state. Thus, we may write

$$g_{lum}^L(\lambda) = \eta_{left} g_{lum}(\Delta, \lambda) = \frac{1}{2} g_{abs}(\Delta, \lambda') g_{lum}(\Delta, \lambda) \int_0^\infty e^{-k_{em}t} e^{A(t)} dt = \frac{1}{2} g_{abs}(\Delta, \lambda') g_{lum}(\Delta, \lambda) B/\tau \quad (18)$$

where the superscript L denotes incident left circularly polarized excitation. The term B/τ , which is defined by eq 18, is a measure of the reduction of g_{lum} due to energy transfer.

Excited State Energy Transfer. Using a diagrammatic Greens function approach, Gochanour and Fayer¹ have examined the effect of excitation transfer for isotropic molecular systems in which the mechanism for energy transfer is assumed to be dipole–dipole and have shown that the probability that an initially excited molecule remains excited at time t , $G_s(t)$, may be calculated from the inverse Laplace transform of $G_s(\epsilon)$, which is given by the following equation

$$\hat{G}_s(\epsilon) = \frac{\tau \left\{ \left(\frac{\pi^2 \gamma^2 C^2}{4} \right) \left[1 - \left(\frac{32}{\pi^2 \gamma^2 C^2} \right) (\epsilon\tau - 0.1887\gamma^2 C^2) \right]^{1/2} + 4(\epsilon\tau - 0.1887\gamma^2 C^2) \right\}}{4(\epsilon\tau - 0.1887\gamma^2 C^2)} \quad (19)$$

where γ is an orientation factor and is equal to 0.846 corresponding to random orientations¹ and C is a reduced concentration

$$C = (4/3)\pi R_0^3 \rho \quad (20)$$

R_0 is the so-called critical transfer distance, i.e., the molecular separation in which the energy transfer rate is equal to the sum of the rates of all other radiative and nonradiative processes, and ρ is the number density. If we make the reasonable approximation that in the racemic mixture $\Lambda \leftrightarrow \Lambda$ and $\Lambda \leftrightarrow \Delta$ energy transfer occur at the same rate, then the probability that an excitation which was initially located on a Δ molecule remains on a Δ molecule at time t , $G_\Delta^\Delta(t)$, is

$$G_\Delta^\Delta(t) = G_s(t) + \frac{1}{2}[1 - G_s(t)] \quad (21)$$

and the probability that an initial excitation of a Δ molecule is now located on a Λ molecule is given by the following equation:

$$G_\Delta^\Lambda(t) = \frac{1}{2}[1 - G_s(t)] \quad (22)$$

So that

$$N_{left}(\Delta, t) = N_{left}(\Delta, 0)G_\Delta^\Delta(t) + N_{left}(\Lambda, 0)G_\Delta^\Lambda(t) \quad (23)$$

and

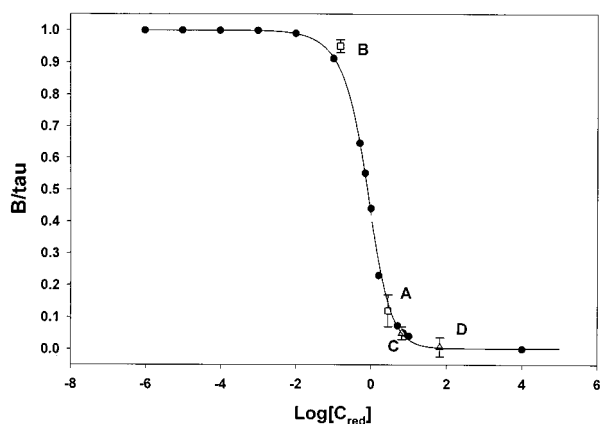


Figure 1. Calculated values of B/τ vs log of the reduced concentration obtained from numerical inversion of eq 19 (filled circles). The solid line represents numerical smoothing of the results. Open squares are results for $\text{Eu}(\text{DPA})_3^{3-}$, and open triangles are results for $\text{Eu}(\text{bpyO}_2)_4^{3+}$. The point labels are defined in Table 3.

$$N_{\text{left}}(\Lambda, t) = N_{\text{left}}(\Lambda, 0)G_{\Lambda}^{\Lambda}(t) + N_{\text{left}}(\Lambda, 0)G_{\Lambda}^{\Lambda}(t) \quad (24)$$

and it is easily shown that

$$\Delta N_{\text{left}}(t) = \Delta N_{\text{left}}(0)G_s(t) \quad (25)$$

From the discussion above and eq 10, it then follows that

$$G_s(t) = e^{A(t)} \quad (26)$$

The Laplace transform of eq 19 can thus be used to calculate the time dependence of g_{lum} due to excited state energy transfer.

In Figure 1, we plot the results for the quantity B/τ as a function of reduced concentration. This result was obtained by performing a numerical inverse Laplace transform of eq 19, and then performing the time integral given in eq 18. The solid line in this figure is a curve fit to the points that were calculated. As can be seen in this figure, at low concentrations where energy transfer is very unlikely, there is no decrease in g_{lum} as measured by a value of 1 for B/τ , whereas at high reduced concentrations,

there is almost complete racemization as evidenced by the limiting value of 0.

4. Spectroscopic Results

In Figures 2 and 3, we plot the high-resolution luminescence spectra of $\text{Eu}(\text{DPA})_3^{3-}$ and $\text{Eu}(\text{bpyO}_2)_4^{3+}$, respectively, in an aqueous solution and incorporated into a silica sol–gel at 293 and 77 K. As can be seen in Figure 2, the emission spectra of $\text{Eu}(\text{DPA})_3^{3-}$ exhibits only one peak in the spectral range (578–582 nm) corresponding to the observed $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition in solution consistent with the existence of only one species. Examination of other regions of the spectra associated with the series of $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions also shows that the structures of the complexes do not change significantly in the two different media. The results for the $\text{Eu}(\text{bpyO}_2)_4^{3+}$ complex plotted in Figure 3 at 77 K, however, shows the appearance of two components at 579.5 and 580.3 nm in the sol–gel. This result is consistent with the known lability of this species, and the effect of multiple species on the results obtained here will be discussed below. We also note that a decrease of temperature does lead to a small increase in the relative intensities of certain transitions, due to depopulation of the $^7\text{F}_2$ and $^7\text{F}_1$ energy levels of Eu(III) at 77 K. The luminescence lifetimes of these species are listed in Table 1. Note that the lifetime of $\text{Eu}(\text{DPA})_3^{3-}$ is relatively constant under all conditions but that the lifetime of $\text{Eu}(\text{bpyO}_2)_4^{3+}$ varies somewhat between aqueous solution and in the sol–gels. Of special note is the fact that the lifetime varies as a function of concentration in the sol–gel. $\text{Eu}(\text{DPA})_3^{3-}$ is known to be a very stable compact complex, whereas $\text{Eu}(\text{bpyO}_2)_4^{3+}$ shows considerably more lability and flexibility. This structural variability is reflected in the variation observed in the lifetime measurements.

In Figure 4, we plot the total luminescence and circularly polarized luminescence, ΔI , from $\text{Eu}(\text{DPA})_3^{3-}$ for aqueous solutions and sol–gels following circularly polarized excitation. The spectral region displayed corresponds to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions of Eu(III). In accordance with eq 18, to maximize the value of g_{lum} for CPE/CPL studies, one should select transitions for which the absorption and luminescence

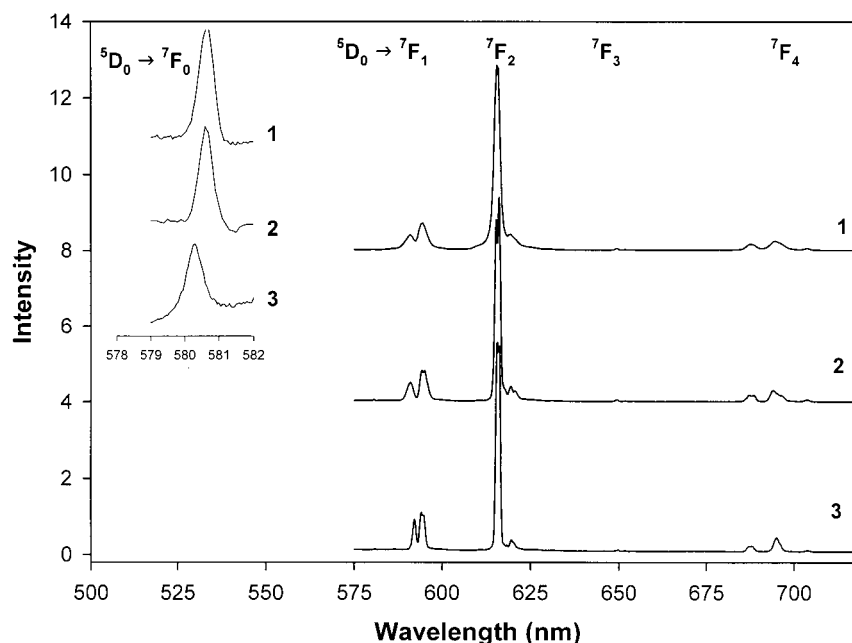


Figure 2. Total luminescence spectra for $\text{Eu}(\text{DPA})_3^{3-}$. Plots 1 and 2 correspond to doped silica sol–gels, and 3 shows results obtained in an aqueous solution. The insert is a magnification of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ spectral region.

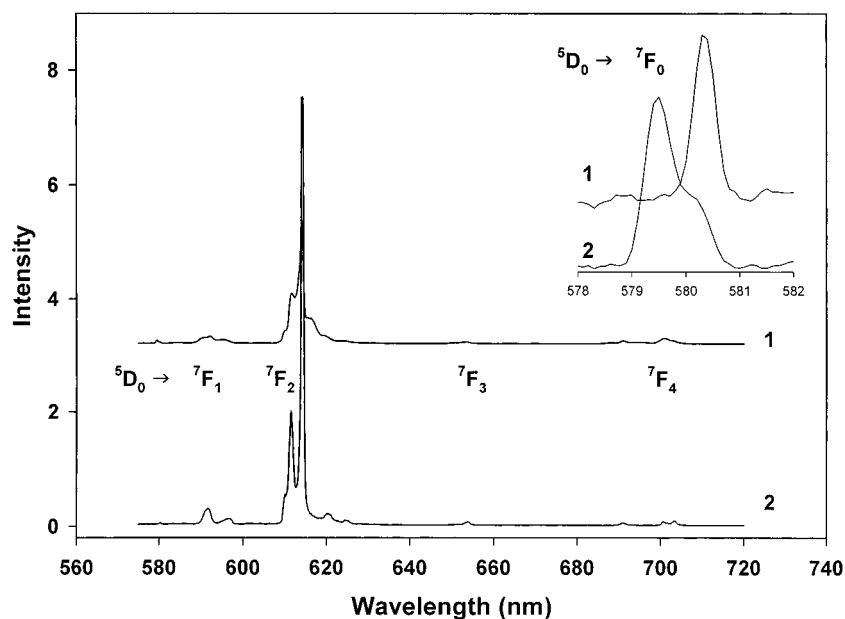


Figure 3. Total luminescence spectra for $\text{Eu}(\text{bpyO}_2)_4^{3+}$. Plot 1 is for a sample doped in a silica sol-gel, and 2 is results for an aqueous solution. The insert is a magnification of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ spectral region.

TABLE 1: Measured Luminescence Decay Times for Eu(III) Complexes under Various Conditions^a

sample	temperature [K]	concentration (M)	decay time [ms]
$\text{Eu}(\text{DPA})_3^{3-}$ (aqueous solution)	293	0.01	1.43
$\text{Eu}(\text{DPA})_3^{3-}$ (sol-gel)	293	0.08770	1.47
$\text{Eu}(\text{DPA})_3^{3-}$ (sol-gel)	293	0.00438	1.57
$\text{Eu}(\text{DPA})_3^{3-}$ (sol-gel)	77	0.08770	1.47
$\text{Eu}(\text{DPA})_3^{3-}$ (sol-gel)	77	0.00438	1.57
$\text{Eu}(\text{bpyO}_2)_4^{3+}$ (aqueous solution)	293	0.01	0.06
$\text{Eu}(\text{bpyO}_2)_4^{3+}$ (sol-gel)	293	0.08200	0.46
$\text{Eu}(\text{bpyO}_2)_4^{3+}$ (sol-gel)	293	0.00840	0.29
$\text{Eu}(\text{bpyO}_2)_4^{3+}$ (sol-gel)	293	0.00083	0.14
$\text{Eu}(\text{bpyO}_2)_4^{3+}$ (sol-gel)	77	0.08200	0.51
$\text{Eu}(\text{bpyO}_2)_4^{3+}$ (sol-gel)	77	0.00840	0.34
$\text{Eu}(\text{bpyO}_2)_4^{3+}$ (sol-gel)	77	0.00083	0.18

^a $\lambda_{\text{exc}} = 308$ nm.

dissymmetry ratios are large. It is known that for chiral lanthanide complexes, transitions that obey magnetic dipole selection rules, i.e., $\Delta J = 0, \pm 1$, are associated with large dissymmetry ratios,²⁸ and these are the transitions of choice for these kinds of studies. For the results presented in Figure 3, we have chosen to use the 472.7 nm line of the Ar-ion laser. This overlaps with the $^7\text{F}_0 \rightarrow ^5\text{D}_1$ absorption transition of Eu(III). In Figure 5, we plot the total luminescence and circularly polarized luminescence, ΔI , for selected transitions of $\text{Eu}(\text{bpyO}_2)_4^{3+}$. In this case, the excitation wavelength corresponds to the maximum in the $^7\text{F}_2 \rightarrow ^5\text{D}_1$ excitation band. Although the $^7\text{F}_2$ level is only approximately 1% populated at room temperature, it is a useful transition for excitation of racemic mixtures, because it satisfies the desired magnetic-dipole selection rules. The selection of excitation wavelength depends on the variable total luminescence intensity measured under the specific conditions of each system.

In Table 2, we show the values for luminescence dissymmetry ratios, g_{lum} , measured for selected transitions of Eu(III) for racemic mixtures of the two complexes under study in this work. These results are for left circularly polarized excitation. Results are presented for different concentrations and, in the case of

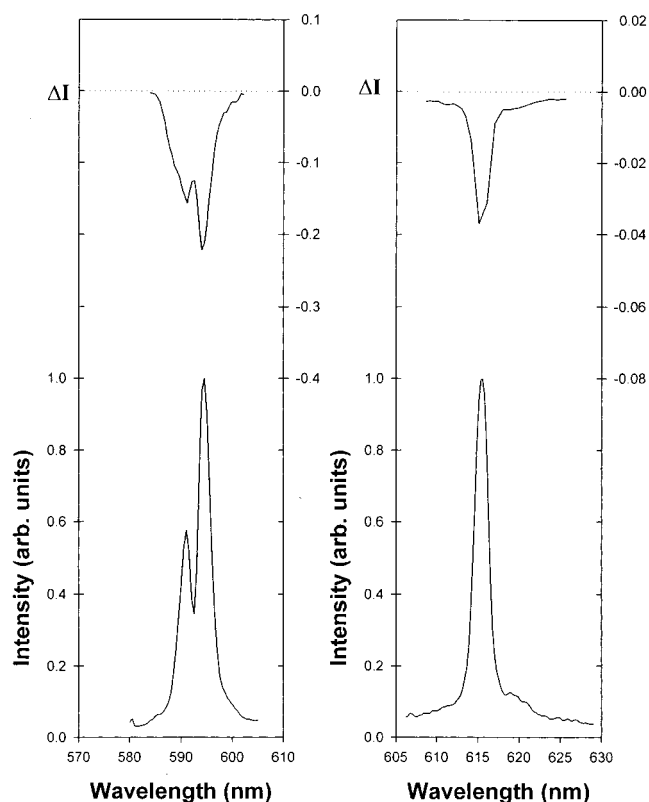


Figure 4. Total luminescence spectra (lower curves) and CPL (upper curves) for two transitions of $\text{Eu}(\text{DPA})_3^{3-}$ doped in a silica sol-gel. The concentration of $\text{Eu}(\text{DPA})_3^{3-}$ is 0.00438 M. $\lambda_{\text{exc}} = 472.7$ nm.

$\text{Eu}(\text{DPA})_3^{3-}$, at different pH conditions. We first note that variation of pH in the range 5–7 has no obvious effect on the measurement of g_{lum} . The variation seen in the results in this table reflect the approximate accuracy of these measurements as indicated by repeated sol-gel preparations. Although the sol-gels prepared for these studies are excellent for these types of polarization measurements, some errors due to sample alignment, orientation etc. are impossible to eliminate completely. Of special importance is the observed variation of g_{lum} with concentration of the complexes. The results collected in

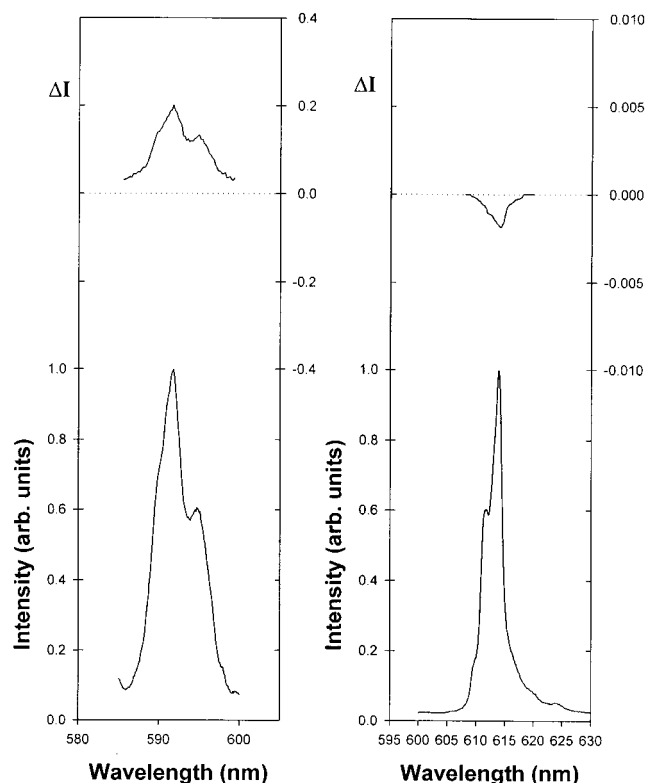


Figure 5. Total luminescence (lower curves) and CPL (upper curves) for two transitions of $\text{Eu}(\text{bpyO}_2)_4^{3+}$ doped in a silica sol–gel. The concentration of $\text{Eu}(\text{bpyO}_2)_4^{3+}$ is 0.00083 M. $\lambda_{\text{exc}} = 552$ nm.

TABLE 2: Measured Luminescence Dissymmetry Values (g_{lum}) for Selected Transitions of $\text{Eu}(\text{DPA})_3^{3-}$ and $\text{Eu}(\text{bpyO}_2)_4^{3+}$ Doped Silica Sol–Gels under Various Experimental Conditions

pH	molar concentration	$^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition	$^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition
$\text{Eu}(\text{DPA})_3^{3-}$ ($\lambda_{\text{exc}} = 472.7$ nm)			
5	0.0877	−0.00579	−0.00489
	0.00438	—	—
6	0.0877	−0.00658	−0.00441
	0.00438	−0.05490	−0.04450
7	0.0877	−0.00550	−0.00392
	0.00438	−0.04520	−0.03740
$\text{Eu}(\text{bpyO}_2)_4^{3+}$ ($\lambda_{\text{exc}} = 552$ nm)			
6	0.082	0.0004	−0.00035
6	0.0084	0.0035	−0.00290
6	0.00083	0.0680	−0.04400

this table are entirely consistent with our earlier preliminary report,²² and the observation that g_{lum} decreases with decreasing concentration confirms the interpretation that the effect is due to excitation transfer.

To model the observations presented above using the results from the theoretical model that is plotted in Figure 1, we have calculated the reduction in g_{lum} due to the presumed energy transfer. For $\text{Eu}(\text{DPA})_3^{3-}$, the values shown correspond to the average for samples at different pH. These results are presented in Table 3. In the case of $\text{Eu}(\text{DPA})_3^{3-}$, we have assumed that the value for g_{lum} obtained in solution at the same excitation wavelength corresponds to the maximum value, whereas for $\text{Eu}(\text{bpyO}_2)_4^{3+}$, it is assumed that at the lowest concentration, energy transfer can be neglected. This latter procedure was used because, as discussed below, the $\text{Eu}(\text{bpyO}_2)_4^{3+}$ complex in aqueous solution exists as a distribution of species.²⁹ Under the assumption that the decrease in g_{lum} for $\text{Eu}(\text{DPA})_3^{3-}$ is accurately described by the results given in Figure 1, we have

TABLE 3: Results for Calculation and Determination of B/τ , C_{red} , and R_0 from Measured Luminescence Dissymmetry Values (See Text)

complex ^c	g_{lum} (594 nm)	g_{lum} (no ET)	B/τ	C_{red}	R_0
$\text{Eu}(\text{DPA})_3^{3-}$					
(A) 0.0877 M	−0.0059	−0.0525	0.11	2.8 ^a	24 Å
(B) 0.00438 M	−0.0501	−0.0525	0.95	0.15 ^b	
$\text{Eu}(\text{bpyO}_2)_4^{3+}$					
(C) 0.0084 M	+0.035	+0.0680	0.05	6.6 ^a	69 Å
(D) 0.082 M	+0.0004	+0.0680	0.006	66.1 ^b	

^a Determined graphically from Figure 1. ^b Calculated from R_0 .

^c Labels correspond to results plotted in Figure 1.

calculated the reduced concentration corresponding to the value of B/τ , and used this result to calculate R_0 using eq 20. The results are given in Table 3. We obtain a value of 24 Å for the critical transfer distance for $\text{Eu}(\text{DPA})_3^{3-}$. This result has then been used to calculate the reduced concentration for the more dilute sample, and the final result is plotted in Figure 1. A similar procedure was used to analyze the results for $\text{Eu}(\text{bpyO}_2)_4^{3+}$. For this complex, the middle concentration was used as the reference value, and a critical transfer distance of 69 Å was obtained. Again, this value was used to determine the reduced concentrations for the other sample, and the final result is plotted in Figure 1. For the purpose of this analysis, the difference in excited state lifetimes observed for the different concentrations was ignored.

5. Discussion

The variation in g_{lum} as a function of concentration observed for the $\text{Eu}(\text{DPA})_3^{3-}$ samples is reproducible, and although it is impossible to completely eliminate depolarization effects due to sample imperfections, experimental optics, etc., it does appear that the decrease in g_{lum} is due to a reduction in the enantioenrichment of the excited state of this complex due to energy transfer. Although the data can be modeled by the theoretical treatment (GF) presented above, the resultant value for the critical transfer distance (24 Å) is larger than one would expect on the basis of previous estimates of this parameter for energy transfer involving lanthanide (III) ions. For example, Selvin and Hearst³⁰ report a value of 65 Å between Tb(III) and a chelate containing the organic dye tetramethyl-rhodamine, and Mathis³¹ has calculated a critical transfer distance of 90 Å for a system involving a Eu(III) cryptate with allophycocyanin. There are other similar reports involving lanthanide ions with organic dyes in which critical transfer distances in the range 50–70 Å have been obtained.³² Although these are all larger than the value, we have estimated from the fit to the GF theory, these systems involve very strong dipole transitions in the acceptor dye molecule, and as a consequence, one would expect to see much smaller values for Eu–Eu transfer involving forbidden f–f transitions.

It is difficult to test the key assumptions in this model, namely, that the sample is randomly distributed and isotropic, that the mechanism of energy transfer is Forster dipole–dipole, and that the energy transfer rate is independent of the chirality of donor and acceptor. In a sol–gel system such as used in this study, the possibility exists that there might be preferential interactions involving opposite enantiomers versus identical enantiomers, or that there might be preferential orientational distributions.³³ For this system, there do not appear to be any experimental indications that would suggest that these two simplifying assumptions are unreasonable. There have been a number of studies involving energy transfer between identical

lanthanide (III) ions in which the primary focus has been the mechanism of energy transfer or energy migration.^{6–11} Most of the experimental measurements have been carried out either in pure or doped crystals. The energy transfer mechanism has been variously described as being due to exchange interactions, or various high order multipole-multipole interactions. Clearly, the results presented here do not lend themselves at this time to a interpretation in terms of a specific operative energy transfer mechanism.

The results presented in Figure 1 for $\text{Eu}(\text{bpyO}_2)_4^{3+}$ may also be fit to the GF theory; in this case, however, there is some experimental evidence that the structure of the complex may be affected by its incorporation into the sol–gel. The primary indication of this is the observation that the lifetime varies as a function of concentration, as illustrated in Table 1. The value of 69 Å for R_0 is much higher than one would expect, and this might indicate that some of the changes observed in g_{lum} as a function of concentration might be due to another effect. We have also some other preliminary spectroscopic evidence that suggests that there may be multiple Eu(III) species or sites in the sol–gel. This will be the topic of a forthcoming publication.²⁹

The application of CPL spectroscopy to lanthanide complexes prepared in sol–gels does allow one to study chiral systems in which the effect of structural racemization can be neutralized. At high concentrations, however, the effect of excited state racemization due to energy transfer cannot be neglected. This area of research has the potential to provide unique information concerning differences in diastereomeric energy transfer rates. Such work is underway in our laboratories.

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