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The measurement of circularly polarized luminescence from racemic lanthanide complexes prepared in sol-gels

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Abstract

Circularly polarized luminescence (CPL) has been measured from rigid sol-gels containing racemic D_3 complexes of Eu(III) with 2,6-pyridine-dicarboxylate (DPA) and oxydiacetate (ODA). These complexes occur in solution and sol-gels as racemic mixtures. CPL was generated from the racemic mixture by preparing a non-racemic excited state through circularly polarized excitation. The CPL measured from the sol-gel containing $\mathrm{Eu(DPA)}_3^{3-}$ is significantly less from that measured in solution. This result is interpreted in terms of the effects of concentration depolarization.

Keywords: Circularly polarized luminescence; Racemic lanthanide complexes; Sol-gels

1. Introduction

Circularly polarized luminescence (CPL) spectroscopy has been shown to be a particularly useful technique for studying chiral lanthanide complexes that occur in solution as racemic mixtures, but do not interconvert during the emitting state lifetime [1,2]. In this application of CPL, the excitation beam is circularly polarized, and is used to generate a non-racemic excited state distribution, from a ground state molecular distribution that is racemic, through differential absorption. Although this technique, which we will refer to as CPE/CPL, may in principle be applied to any luminescent racemic mixture, it is practically limited to species in which the absorption and emission transitions have large chiral discrimination for the reasons described below [3]. For this reason, virtually all of the applications of CPE/CPL reported to date have involved chiral luminescent lanthanide complexes.

In CPL spectroscopy it is common to report results in terms of the luminescence dissymmetry ratio at wavelength λ, $g_{\mathrm{lum}}(\lambda)$, which is defined in terms of the intensity of left (I_{L}) and right (I_{R}) circularly polarized emitted light as follows:

$$g_{\mathrm{lum}}(\lambda) = \frac{I_{\mathrm{L}} - I_{\mathrm{R}}}{\frac{1}{2}(I_{\mathrm{L}} + I_{\mathrm{R}})} \tag{1}$$

It has been shown [4] that the magnitude of the CPL signal for a non-interconverting racemic mixture, $g_{\mathrm{lum}}^{\mathrm{rac}}(\lambda)$, can be related to the product of the *absorption* dissymmetry ratio at the excitation wavelength, $g_{\mathrm{abs}}^{R}(\lambda')$, and the *luminescence* dissymmetry ratio at the emission wavelength, $g_{\mathrm{lum}}^{R}(\lambda)$, of the pure R enantiomer:

$$g_{\mathrm{lum}}^{\mathrm{rac}}(\lambda) = \tfrac{1}{2} g_{\mathrm{abs}}^{R}(\lambda') g_{\mathrm{lum}}^{R}(\lambda) \tag{2}$$

From Eq. (2) it can be seen that excitation and emission transitions should be chosen with large intrinsic dissymmetry ratios in order to maximize the measurement of g_{lum}. Transitions of luminescent lanthanide (III) ions that satisfy magnetic-dipole selection rules, i.e. $\Delta J = 0, \pm 1$ (except $0 \leftrightarrow 0$), are often associated with large intrinsic dissymmetry ratios, and are, therefore, particularly suited for CPE/CPL. The ideal situation is one in which both the absorption and emission are magnetic-dipole allowed.

At room temperature, it has been shown that tris-terdentate complexes of Eu(III) with 2,6-pyridinedicarboxylate (DPA), which are known to have approximate D_3 symmetry, do not racemize in aqueous solutions on the emission time scale of Eu(III) (approximately 1 ms), and are therefore suitable for study by CPE/CPL [5]. Complexes of Eu(III) with oxydiacetate (ODA) in water or D_2O do not show measurable CPL when excited with circularly polarized light, however aqueous complexes of $\mathrm{Dy(ODA)}_3^{3-}$ do exhibit CPE/CPL. These results have been explained by assuming that the racemization rate is faster

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than the decay rate of $Eu(ODA)_3^{3-}$, but that complete racemization does not occur on the time scale of Dy(III) emission (approximately 0.01 ms).

The measured value for $g_{lum}^{rac}(\lambda)$ will be reduced if the complex is racemizing during the emission lifetime, and will be 0 if the sample is completely racemized. In some cases the racemization rate may be determined from a measurement of the time [6] or temperature [7] dependence of g_{lum}. In this work we report the first attempt at measuring CPL from racemic complexes that have been prepared in rigid sol-gels to prevent racemization. Results are presented for tris-terdentate complexes of Eu(III) with 2,6-pyridinedicarboxylate (dipicolinate, DPA), and preliminary results are presented for complexes with oxydiacetate (ODA). Comparison is made with similar measurements on these same complexes prepared in aqueous solutions.

2. Experimental

The sol-gels doped with Eu(III) complexes were prepared using the method described in Refs. [8,9]. Silica gels are usually obtained by hydrolysis of silica alcoholates using inorganic acids or bases (for example, NH_4OH) as a catalyst. The sol-gel process can be described by the following three reactions [10]:

Hydrolysis:

$$Si(OR)_4 + nH_2O \rightarrow Si(OR)_{4-n}(OH)_n + ROH$$

Condensation:

$$(RO)_3Si–OR + HO–Si(OR)_3 \rightarrow (RO)_3Si–O–Si(OR)_3 + ROH$$

$$(RO)_3Si–OH + HO–Si(OR)_3 \rightarrow (RO)_3Si–O–Si(OR)_3 + H_2O$$

where R is an alkyl group, C_xH_{2x+1}. The H_2O to Si molar ratio can range from 1 to 50. The concentration of the catalyst may be varied from 0.01 to 7 M depending on the specific nature of the final product. The appropriate quantities of tetraethylo-orthosilicate $Si(OC_2H_5)_4$ (TEOS), distilled water and small amounts of hydrochloric acids were mixed until the solution was homogeneous. The $Eu(DPA)_3^{3-}$ and $Eu(ODA)_3^{3-}$ complexes were then incorporated into the sol; the required pH value was obtained via addition of ammonia. The sols were left for gelation at room temperature.

A schematic diagram of the instrumentation used to measure CPE/CPL is presented in Fig. 1. Excitation of

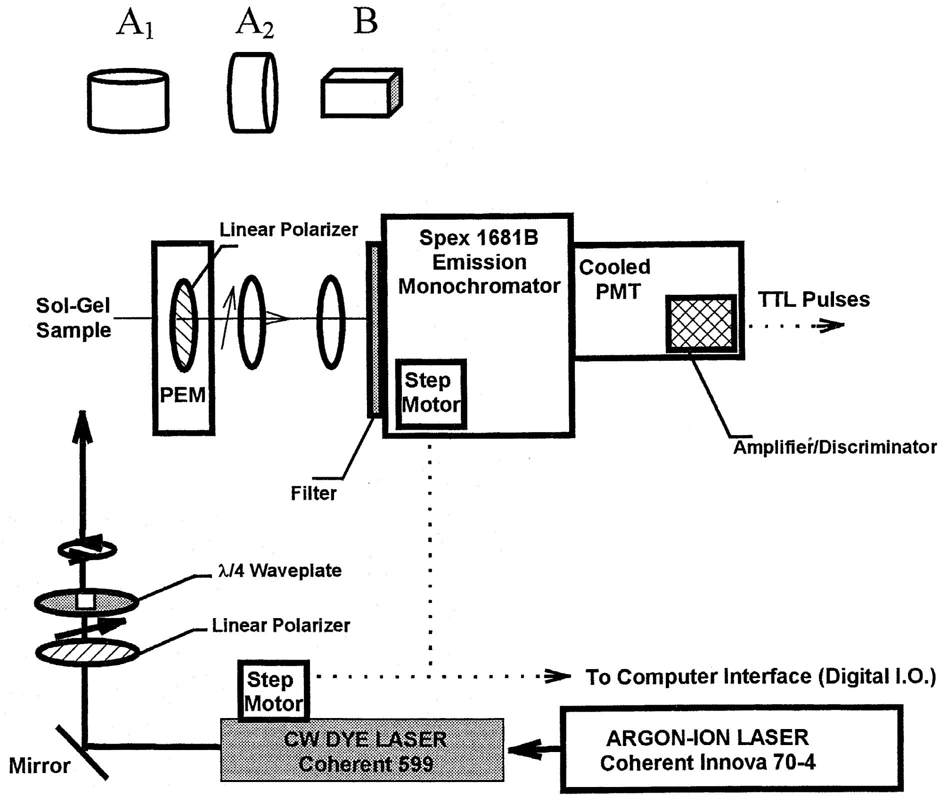

Fig. 1. Schematic diagram of the instrumentation used to measure CPE/CPL (see text) operating in photon-counting mode. The luminescence passes through a photoelastic modulator (PEM) and linear polarizer which together act as a circular analyzer. Sol-gels were studied in various orientations as shown.

Eu(III) (550–585 nm) was accomplished by using a Coherent-599 tunable dye laser and an argon-ion laser (472.7 nm). The laser dye used in all measurements was rhodamine 110 dissolved in ethylene glycol. 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. The orientation of the quarter-wave plate was verified by rotating the device 45° to generate linear polarization, and then rotation by 90° to create the opposite circular polarization.

In weakly luminescent samples or other samples contaminated with significant baseline scattering, it is often necessary to apply a numerical correction to the measured dissymmetry ratio. This was necessary for some of the measurements presented here. If the measured intensity of left and right circularly polarized emission is contaminated with unpolarized background signal, I_{back}, then the measured luminescence dissymmetry ratio (see Eq. (1)) is given by

$$g_{\mathrm{lum}}^{\mathrm{meas}}(\lambda) = \frac{I_{\mathrm{L}} + I_{\mathrm{back}} - I_{\mathrm{R}} - I_{\mathrm{back}}}{\frac{1}{2}(I_{\mathrm{L}} + I_{\mathrm{back}} + I_{\mathrm{R}} + I_{\mathrm{back}})} = \frac{\Delta I}{\frac{1}{2}(I_{\mathrm{L}} + I_{\mathrm{R}}) + I_{\mathrm{back}}} \qquad (3)$$

where the significant point is that the background signal does *not* contribute to the differential emission intensity, ΔI. To calculate $g_{\mathrm{lum}}(\lambda)$ from the measured value, one needs to calculate ΔI from the *measured* I and g_{lum}; determine I_{back} from the total emission spectrum and subtract it from the measured intensity to obtain I; and recalculate $g_{\mathrm{lum}}(\lambda)$ from ΔI and I.

3. Results

In Fig. 2 we plot the total luminescence (lower curve) and circularly polarized luminescence, ΔI (upper curve), for an aqueous solution of $\mathrm{Eu(DPA)}_3^{3-}$ and a sample of $\mathrm{Eu(DPA)}_3^{3-}$ which is contained in a rigid sol-gel prepared as described above. The spectral region displayed corresponds to the ${}^5D_0 \rightarrow {}^7F_1$ transition of Eu(III). Similar data are presented in Fig. 3 for the ${}^5D_0 \rightarrow {}^7F_2$ transition. The excitation used for these results was left circularly polarized 558.5 nm light from a tunable dye laser. This excitation wavelength corresponds to a maximum in the ${}^7F_2 \rightarrow {}^5D_1$ excitation spectrum as presented in Fig. 4. Although the ${}^7F_2$ is only approximately 1% populated at room temperature, it is a useful transition for excitation of racemic mixtures because it satisfies magnetic-dipole selection rules [3]. In all cases the polarization of the excitation was varied from left to right polarization by rotation of the quarter-wave plate placed in the excitation beam (see Fig. 1) to ensure that the opposite signed result for g_{lum} was obtained.

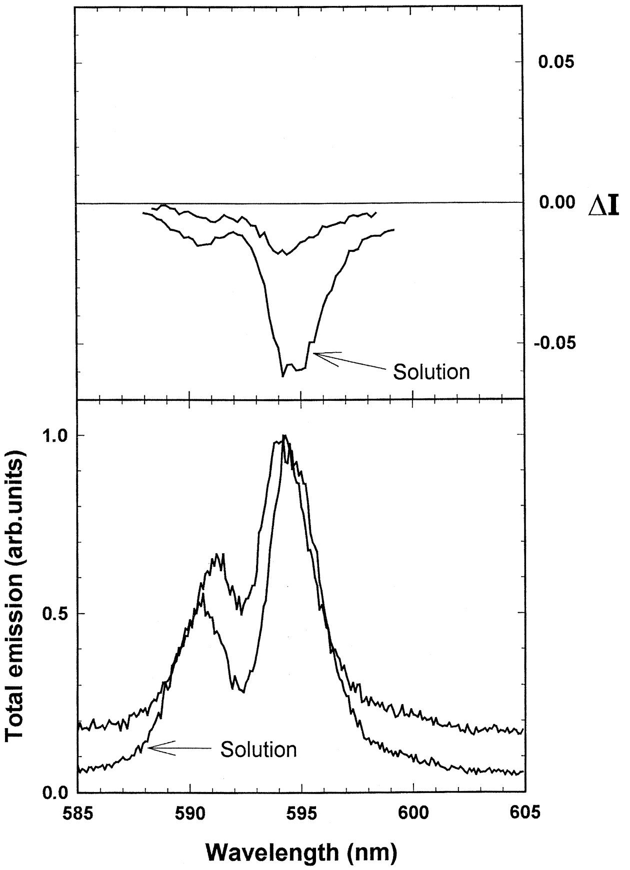

Fig. 2. Circularly polarized emission (upper curve) and total luminescence (lower curve) for an aqueous solution of $\mathrm{Eu(DPA)}_3^{3-}$, and a sample of this complex prepared in a sol-gel and measured with orientation A_1. The spectral region displayed corresponds to the ${}^5D_0 \rightarrow {}^7F_1$ transition of Eu(III). $\lambda_{\mathrm{exc}} = 558.5$ nm.

The data presented in Figs. 2–4 were obtained using a cylindrical sol-gel sample which was placed in orientation A_1 (see Fig. 1). However, the same sol-gel with orientation A_2 or a different sol-gel with rectangular shape, B, gave similar results. The numerical values for the luminescence dissymmetry ratios under a variety of experimental conditions are presented in Table 1. These values have been corrected for background scattering when necessary.

In Fig. 5 we plot the total luminescence for $\mathrm{Eu(ODA)}_3^{3-}$ which was prepared in a rigid sol-gel. As can be seen, the background scattering was quite large compared to the emission, and a complete CPL spectrum was not obtained. The uncorrected luminescence dissymmetry ratio for left (L) and right (R) circularly polarized excitation at one excitation wavelength is also given in this figure.

4. Summary and conclusion

The data presented in Figs. 2–4 represent the first

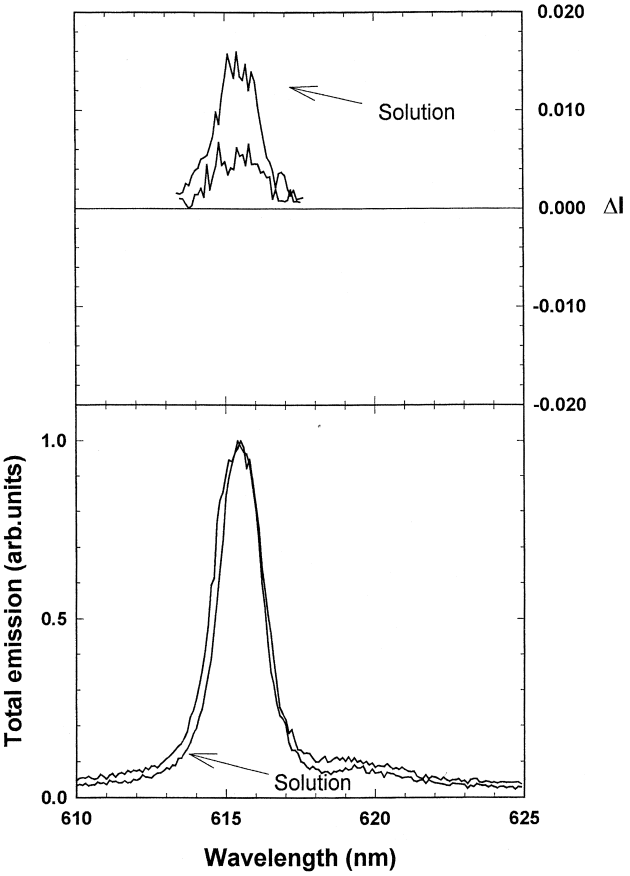

Fig. 3. Circularly polarized emission (upper curve) and total luminescence (lower curve) for an aqueous solution of $\mathrm{Eu(DPA)}_3^{3-}$, and a sample of this complex prepared in a sol-gel and measured with orientation A_1. The spectral region displayed corresponds to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu(III). $\lambda_{\mathrm{exc}} = 558.5$ nm.

successful attempt at measuring CPL from a rigid isotropic medium. Previously, Meskers et al. reported linear polarization in the luminescence from $\mathrm{Eu(DPA)}_3^{3-}$ in a 1:2 water/glycol mixture at 157 K [11]. This temperature was chosen so as to minimize depolarization due to strain birefringence, but eliminate rotational brownian motion. The linear polarization in the luminescence from this highly viscous sample was significant when excited with linearly polarized excitation. Measurement of CPL is problematic when linear polarization is present in the luminescence due to the small inherent birefringence in the photoelastic modulator [12], so one concern in the experimental results reported above is the question as to whether or not linear polarization is present in the luminescence. If linear polarization is present, one would expect that the effect would be large, and more or less independent of whether or not the excitation was left or right circularly polarized. This was certainly not the case, since rotation of the incident quarter-wave plate produced the expected oppositely signed result. Further verification that the results presented here are reliable is the fact that, although the g_{lum} values reported above for the $\mathrm{Eu(DPA)}_3^{3-}$ sol-gel samples are smaller than the solution values (see Table 1), the different transitions are in the same ratio, and the reduction in expected polarization is approximately the same for each transition.

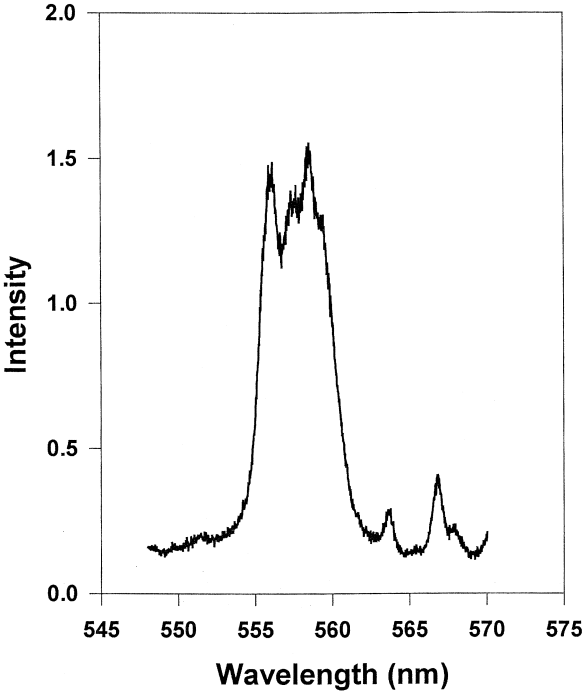

Fig. 4. Excitation spectrum of a sol-gel containing $\mathrm{Eu(DPA)}_3^{3-}$. The spectral region displayed corresponds to the $^7F_2 \rightarrow {}^5D_1$ transition of Eu(III). The emission was monitored at 615 nm.

Two characteristics of this experiment might explain the lack of linearly polarized luminescence. First, the use of plane or circularly polarized excitation reduces the linear polarization in the luminescence as compared to the use of excitation that is linearly polarized, although it does not eliminate it [13]. Secondly, the excitation transitions used in this study are not into isolated crystal field transitions, and therefore of well-defined linear polarization, but rather are in regions of overlapping transitions. The combination of these effects, and the presence of some depolarization due to strain birefringence, may result in the decrease in CPL as compared to the solution values.

An alternate interpretation of these results may explain both the lack of linear polarization, and the reduction in the expected circular polarization. Hilmes and Riehl [4] presented a theory of circularly polarized luminescence from racemic mixtures in which the effect of racemization and energy transfer on g_{lum} have been included. Resonance energy transfer between identical enantiomers has no effect on the measured CPL signal, but, obviously, transfer between opposite enantiomers will result in a net decrease in g_{lum}. It is also the case that energy transfer will effectively scramble the orientational distribution created by the absorption beam, resulting in decreased linear polarization. The effect on linear polarization is commonly

Table 1
Corrected luminescence dissymmetry ratios for selected transitions of $Eu(DPA)_3^{3-}$ in sol-gels and aqueous solution

λ_{exc} (nm)	g_{lum} (corrected)							
	$^5D_0 \rightarrow {}^7F_1$						$^5D_0 \rightarrow {}^7F_2$	
	594.2 nm				591.0 nm		615.5 nm	
	Sol-gels			Solution	Sol-gel A_1	Solution	Sol-gel A_1	Solution
	A_1	A_2	B					
$^7F_2 \rightarrow {}^5D_1$								
558.5	−0.0409	−0.0365	−0.0465	−0.1288	−0.0263	−0.0609	+0.0139	+0.0311
557.1	+0.0560	+0.0521	+0.0841	+0.1705	+0.0383	+0.0665	−0.0138	−0.0450
$^7F_0 \rightarrow {}^5D_1$								
472.7	−0.0160	−0.0142	−0.0221	−0.0525	–	−0.0315	–	+0.0140

referred to as concentration depolarization, and is well studied [14]. To date no observations of this phenomena as related to circular polarization have been reported. However, it appears to us that this is the most likely explanation of the results presented here. Energy transfer does not occur in this system at the concentrations possible in solution, however the local concentration of Eu(III) complexes in the sol-gel are at least 10 times the concentration prior to gel formation, and might be considerably more depending upon the nature of the cavities formed within the silicate framework. This energy transfer effect between like and opposite enantiomers is an area of active current interest to our research groups. Additional studies in which the concentration of lanthanide complexes is varied are underway.

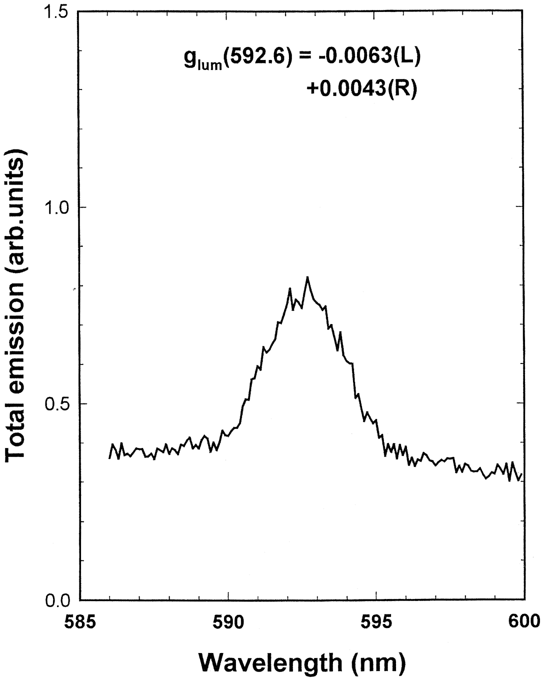

Fig. 5. Total luminescence for $Eu(ODA)_3^{3-}$ in a rigid sol-gel. The spectral region displayed corresponds to the $^5D_0 \rightarrow {}^7F_1$ transition of Eu(III). Also given is g_{lum}(592.6 nm) following left (L) and right (R) circularly polarized excitation.

Although some depolarization of the circularly polarized emission does occur from the rigid sol-gels used in this work, we have demonstrated that the measured CPL is reproducible and the technique should be useful as a structural probe of complexes that undergo racemization in solution in situations where the luminescence dissymmetry ratio is expected to be relatively large. Preliminary results show very weak CPL from a sol-gel containing $Eu(ODA)_3^{3-}$. This result is consistent with previous conclusions based upon the observation of CPL from $Dy(ODA)_3^{3-}$ [5], the extremely low intensity of the $^7F_0 \rightarrow {}^5D_0$ absorption, and the published crystal structure of $Na_3[Eu(ODA)_3] \cdot 2NaClO_4 \cdot 6H_2O$ [15].

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