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Emission Detected Circular Dichroism from Long-Lived Excited States: Application to Chiral Eu(III) Systems

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Abstract

The measurement of the difference in intensity of luminescence following excitation with left and right circularly polarized light for racemic terdentate Eu(III) complexes with 2,6-pyridine dicarboxylic acids perturbed by the addition of (+)-dimethyltartrate and for tris chiral complexes of Eu(III) with (*R,R*)-*N,N'*-bis(1-phenylethyl)-2,6-pyridine-dicarboxamide are presented. The experimental technique used for these measurements is identical in design to fluorescence detected circular dichroism spectroscopy, but is referred to in this manuscript as emission detected circular dichroism (EDCD) because of the long lifetime of the Eu(III) excited state requiring specialized instrumentation. These measurements required relatively slow modulation of the incident circular polarization, which was accomplished with a liquid crystal polarizer. The results are compared with conventional CD measurements, and additional characteristics and potential applications of EDCD are presented.

Keywords

Eu(III); luminescence; circular dichroism; lanthanide

INTRODUCTION

The measurement of the differential (left minus right) absorption of circularly polarized light, i.e., circular dichroism (CD) by chiral (optically active) molecular systems is an important tool for the study of the ground state structure of chiral molecules, especially chiral biopolymers such as proteins.¹ Commercial instruments for the measurement of CD in the UV/Visible spectral region have been available for more than 40 yr, and modern instrumentation can now provide reliable measurements of CD into the NIR, and more recently instrumentation for the measurement of vibrational CD (VCD) in the infra red region has become available.² The measurement of the circularly polarized component in the luminescence (CPL) of chiral molecules has also developed in the last 30 yr into a useful probe of the excited state structure of chiral molecules.^{3,4} This technique is only possible, of course, for luminescent species, and applications to date have been limited to researchers who have constructed their own specialized instrumentation. A related chiroptical technique for probing the structure of chiral luminescent species is the measurement of the differential luminescence intensity resulting from the differential absorption. In this technique, the total luminescence intensity resulting

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from differential circularly polarized excitation is monitored. This spectroscopic technique is commonly referred to as fluorescence detected circular dichroism (FDCD),⁵⁻⁸ but in this report we will use the more general term of emission detected circular dichroism (EDCD) to accommodate the long-lived excited states of selected luminescent lanthanide (III) ions. For isolated chromophores, CD and EDCD give redundant information. Luminescence methods are generally more sensitive than absorption measurements, allowing for the study of dilute solutions in which CD might not be possible because of availability of material or solubility problems. There are other situations in which the luminophore is populated through radiationless energy transfer from a chiral absorber. In these experiments, unique structural information may be obtained; however, interpretation of the various chiroptical measurements may be more complicated.⁹

EDCD (or FDCD) has long been recognized as a way of probing the chirality of absorption chromophores that lead to luminescence. This approach was originally developed as a way to study "local" chirality of a specific chromophore in a complex system, since overlapping chiral absorption chromophores that do not lead to luminescence will not contribute to the total signal.⁵ For example, conventional CD measurements in the UV/Visible spectral region are commonly used to assess the average structure of a protein in terms of percent alpha helicity, or beta sheet content.^{1,10} This is done by well-developed curve fitting of the resultant CD spectrum.¹⁰ EDCD or CPL of individual chromophores within a large biomolecule do not report on secondary or tertiary structure, but rather reflect local chiral structure or structural changes associated with the local environment surrounding the emitting chromophore.

In this communication, we report on the first measurements of EDCD from chiral lanthanide (III) systems. In particular, we have measured the EDCD of a perturbed chiral equilibrium involving the tris-terdentate complex of Eu(III) with 2,6-pyridine-dicarboxylate (dipicolinate = DPA). A preliminary report of the EDCD, CPL, and CD of this system has already been published.¹¹ This complex is known to form chiral racemic D₃ complexes in aqueous solution which can be made nonracemic through the addition of chiral noncoordinating environment compounds.¹²⁻¹⁵ The perturbed racemic mixture used for the new measurements reported here has been chosen only because it is well characterized, and CPL and conventional CD results have previously been published. We also report the EDCD spectrum of the chiral tris complex of Eu(III) with (*R,R*)-*N,N'*-bis(1-phenylethyl)-2,6-pyridinedicarboxamide.¹⁶ As described later, the EDCD of compounds such as these with long-lived excited states (>0.1 msec.) have not been possible because of the experimental characteristics of the available instrumentation. In this work, the instrumentation constructed for these kinds of measurements is briefly described, and the utility of these types of measurements in the development of chiral structural probes is presented.

EDCD MEASUREMENTS

Although the first report of FDCD appeared more than 30 yr ago,⁶ applications of FDCD have been limited. This is due to a large part to the fact that this technique is applicable only to chiral luminescent systems, but one also must address complications associated with data analysis and various experimental problems. For strongly absorbing or concentrated solutions, the output differential fluorescence intensities must be corrected for differential absorption of the incident light as it passes from the front to back of the sample cell. This is particularly difficult in system containing multiple chiral absorbers with only one, perhaps, being luminescent. The chiral species at the front surface of the cuvet sees equal amounts of left and right circularly polarized excitation; however, at the rear surface the excitation polarizations are not equal, so a correction term must be applied. This correction can be minimized by the use of dilute or weakly absorbing solutions, but the net signal is reduced accordingly. Since for most chiral

organic chromophores, the difference in absorption intensity for left versus right circularly polarized light is generally less than 1%, working in dilute solutions is not often practical.

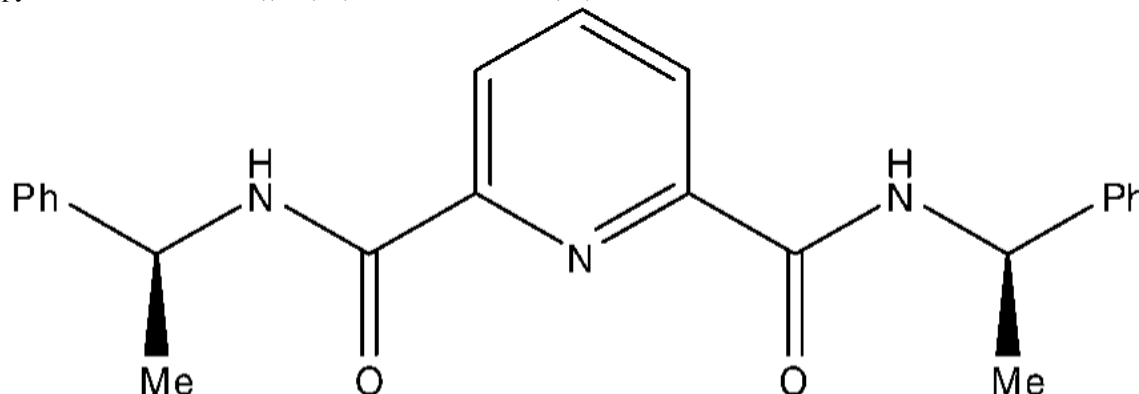
More problematic to FDCD measurements are intrinsic polarization artifacts because of the non-isotropic orientational distribution of emitting molecules because of photo-selection effects. Since almost all fluorescence experiments are performed in a 90° geometry, assuming for discussion that the emission and absorption dipole moments are parallel, the number of emitting species oriented perpendicular to the direction of the incident absorption beam will be greater than those oriented parallel to this beam. This situation will be true until the orientational distribution becomes randomized at times far from the excitation event. Of course, in the limit of large molecular systems in viscous media the non-isotropic distribution will be maintained for a long time. If the incident circular polarizations were pure 100% left or right, there would be no consequences to this photoselection. However, the real problem is the fact that even with high quality optics, the generation of circular polarization results in a small amount of linear polarization in the excitation beam. This linear polarization results in a real difference in orientational distribution that is generated in phase with the circular polarization modulation. Differences in total intensity will reflect the presence of this photoselected distribution and will not be entirely due to differential absorption of left minus right circularly polarized excitation. The various problems of this type have been the focus of several studies, and various experimental techniques have been proposed and used to deal with these experimental constraints.^{17,18}

For a number of years, we have been interested in applying the EDCD technique to complexes containing long-lived luminescent lanthanide (III) ions. The absorption of these species are formally forbidden intraconfigurational $f \leftrightarrow f$ transitions, and as such are extraordinarily weak. These complexes are normally prepared in solutions in concentrations less than 0.05 M, and in this case no correction due to differential absorption is necessary. Furthermore, Eu(III) and Tb(III) have luminescent lifetimes on the order of msec, so for the relatively small chiral molecular complexes in solution of interest to our research groups, there should be no complications due to photoselection. This is because of the presumed complete relaxation of the initial excited state orientational distribution. An experimental consequence of the long excited state lifetime is that the conventional way of generating circularly polarized exciting light using high frequency (e.g., 50 kHz) photoelastic modulators may not be used since this is insufficient time (20 μ sec) for the excited molecules to relax to the ground state. Therefore, the luminescence collected during the time window corresponding to a particular circular polarization will not measure the absorption during this window. To overcome this problem, as described later, we employ a liquid crystal quarter-wave polarizer (LCP) with a variable cycle time which may be calibrated for the absorption wavelength selected.

EXPERIMENTAL DETAILS

Eu(DPA)₃³⁻ solutions were prepared from stock solutions of Eu(III) (EuCl₃, Aldrich) and 2,6-pyridine dicarboxylic acid (Aldrich). The pH of the final solutions was adjusted to be ~5. The Eu(III) concentration was 0.02 M. The ratio of Eu(III) to ligand was 1:3.5 to ensure complete formation of the tris complex. (+)-dimethyl-L-tartrate, (+)DMT, was added to the solutions prepared above and stirred until clear. The ratio of Eu(III) to (+)-DMT in the solutions examined in this work was 1:275. This system has been studied previously, and it has been determined that the large excess of (+)-DMT perturbs the racemic equilibrium between the Λ and Δ enantiomers of the D₃ solution complexes of this species without measurable effects on the solution structure.^{13,14}

Eu((*R,R*)-1)₃³⁺ complex solutions were prepared in situ from stock solutions of Eu(III), Eu(Otf)₃ (Otf = trifluoromethanesulfonate) and (*R,R*)-*N,N'*-bis(1-phenylethyl)-2,6-pyridinedicarboxamide ((*R,R*)-1) in MeCN. The Eu(III) concentration was 6.67×10^{-3} M



and the Eu:1 ratio was 1:5 to ensure complete formation of the tris complex. (*R,R*)-1, an analog of the *N,N'*-dibenzylpyridine-2,6-dicarboxamide ligand where the dibenzyl substituents have been replaced by chiral phenylethyl groups,^{16,19} was synthesized from 2,6-pyridinedicarboxylic acid chloride (Acros) with a slight excess of (*R*)-(+)-(α)-methylbenzylamine (Acros) in a one-step procedure using modified Schotten–Baumann conditions.^{16,20}

EDCD measurements were made possible by a straight-forward modification of our custom-made CPL spectrometer. A schematic diagram is given in Figure 1. A more detailed description of the EDCD instrumentation will be given in a forthcoming publication. In the EDCD experiment, the output of a Coherent CR-599 tunable dye laser was directed through a liquid crystal quarter-wave polarizer (LCP) (Meadowlark Optics, LVR-100-VIS-IL) oriented at 90° to the direction of emission detection. The polarization of the incident laser beam was modulated through a D/A converter from a central computer workstation. On a cycle time normally greater than 1 sec, set by the measurement software, a signal was sent to the liquid crystal controller (Meadowlark Optics, B1020) switching the polarization state from left to right. A small dead time was allowed for the liquid crystal to realign following the change in applied voltage. The time windows for left and right circularly polarized excitation were set to be equal. The voltages applied to the liquid crystal device to generate left and right circular polarization were determined by prior wavelength calibration. The total emission intensity was measured in phase with the incident polarization modulation, averaged over the half modulation cycle, and used to calculate the EDCD signal. At each wavelength the same number of measurement cycles were taken and averaged to obtain comparative signal to noise ratios. In EDCD, the absorption is related to the total emission intensity and may be simply expressed as

$$g_{\text{EDCD}} = \frac{E_L - E_R}{1/2(E_L + E_R)} \quad (1)$$

where E_L and E_R denote the intensity of the emission detected in phase with left (L) or right (R) incident circular polarization.

An approximate energy level diagram for Eu(III) is given in Figure 2. The energy states are described by their $^{2S+1}L_J$ terms. It is well known that for $f \leftrightarrow f$ transitions of lanthanides, the largest dissymmetry values are associated with transitions that obey magnetic dipole selection rules ($\Delta J = 0, \pm 1$, except $0 \leftrightarrow 0$). These are illustrated in this figure. The splitting of the ground state 7F term is such that there is a significant population of the excited 7F_1 state ($\sim 13\%$) and 7F_2 state ($\sim 1\%$) at room temperature. Emission originates from the 5D_0 state to the manifold

of ground states with the most intense transition normally being the so-called hypersensitive transition $^5D_0 \rightarrow ^7F_2$ at ~ 615 nm as shown.

For the measurements reported here, excitation of Eu(III) was accomplished with either a Coherent Innova-70 or Coherent Sabre TSM 15, and the dyes used were rhodamine 6G for excitation from the thermally excited 7F_1 state to the 5D_0 state (584–600 nm), or coumarin 6 for excitation from the 7F_0 ground state to the 5D_1 state (525–529 nm). The resolution of the dye laser is 0.03 nm. The total emission intensity of the $^5D_0 \rightarrow ^7F_2$ transition of Eu(III) was monitored at 615 nm with a bandpass of 10 nm while the dye laser was stepped through the absorption region in 0.1 nm increments. No correction has been made for the variation in incident laser power intensity; however, over this narrow wavelength range the change in laser power spectrum of rhodamine 6G is quite small.

RESULTS

In Figure 3, we show the excitation spectrum (lower curve) and EDCD spectrum (upper curve) of a 0.02 M aqueous solution of $\text{Eu}(\text{DPA})_3^{3-}$ in which a large excess of (+)-DMT has been added. For this measurement, the incident circular polarization alternated between left and right circular polarization every 0.5 sec, and 20 cycles were averaged for each wavelength. It should be noted that this absorption originates from the 7F_1 excited electronic state, which as stated previously is located $\sim 370 \text{ cm}^{-1}$ above the ground 7F_0 state as shown in Figure 4A. This complex has almost perfect D_3 symmetry and in D_3 the $J = 1$ state is split into two crystal field states. The two peaks shown in Figure 3 are the result of this crystal field splitting which is measured to be 90 cm^{-1} . A complication with making this particular measurement is that the peak of the emissive transition used to monitor the absorption is only 20 nm separated from the absorption peak. To ensure the integrity of the differential measurement, care must be taken to filter the emission beam and employ other means to avoid scattering of the incident laser beam into the emission monochromator.

It is interesting to compare the results presented in Figure 3 with previous reports of the CD and CPL from this identical system. These spectra for the same transition displayed in Figure 3 are reproduced in Figure 5. The measurement of the CD from this system is quite difficult since the extinction coefficient is so small. Çoruh et al.¹⁴ were able to make this measurement by employing a CD cell with an 8-cm path length. These authors also reported the CPL spectrum which we have remeasured and is given on the right in this figure. Note that the differences in the intensity of the two crystal field peaks in the luminescence spectrum as compared with the absorption spectra is due to the fact that this transition originates from the nondegenerate 5D_0 excited state.

The accuracy of the EDCD measurements may be checked by comparison with the CD and CPL results previously reported. In CD, it is common to report results in terms of the absorption dissymmetry factor, g_{abs} , and in CPL, one determines the luminescence dissymmetry factor, g_{lum} . The definitions of these two quantities are given below.

$$g_{\text{CD}} = \frac{A_L - A_R}{1/2 (A_L + A_R)} = \frac{\varepsilon_L - \varepsilon_R}{1/2 (\varepsilon_L + \varepsilon_R)} \quad (2)$$

$$g_{\text{lum}} = \frac{I_L - I_R}{1/2 (I_L + I_R)} \quad (3)$$

A_L and A_R denote, respectively, the absorbance of left (L) and right (R) circularly polarized light; ε_L and ε_R are the extinction coefficients of left and right circularly polarized light; and in CPL, I_L and I_R refer, respectively, to the intensity of right and left circularly polarized emitted light. Since the three measurements displayed in Figures 3 and 5 all involve the same transition,

the dissymmetry values should be the same. Dissymmetry factor results for the two crystal field transitions measured at the peak wavelengths are summarized in Table 1.

To eliminate certain experimental difficulties with excitation so close to the emissive transition, and to increase the net signal, we have undertaken exciting the accessible magnetic dipole transition originating from the ground electronic state, namely, the $^5D_1 \leftarrow ^7F_0$ transition centered at ~ 527 nm as depicted in Figure 4B. In Figure 6, we show the excitation spectrum and EDCD spectrum for a solution of $\text{Eu}[(R,R) - 1]_3^{3+}$ in acetonitrile. Data was collected with a cycle time of 0.5 sec with 10 cycles per wavelength. Excitations corresponding to transitions from the 7F_0 and 7F_1 states to the 5D_1 excited state are shown, but only the EDCD for the magnetic dipole transition was measured. The two peaks observed in this case are due to crystal field splitting of the excited 5D_1 state. This was determined to be 50 cm^{-1} . No correction for laser power spectrum variations has been applied to the results given in this figure. Dissymmetry values measured at the peak of the two transitions are also given in Table 1.

SUMMARY AND CONCLUSION

The results presented earlier for the perturbed equilibrium of $\text{Eu}(\text{DPA})_3^{3-}$ by (+)-DMT show that for the one transition studied, virtually identical results for the CD and CPL dissymmetry values can be obtained by the EDCD technique using the LCP in quarter-wave mode. Of course, the dissymmetry factor for this transition, $^5D_0 \leftarrow ^7F_1$ was known to be quite large making the measurement relatively easy. It is our experience that the determination of g_{EDCD} values on the order of 0.01 are readily accessible using our existing instrumentation. As will be described in a forthcoming publication, the polarization of the incident circularly polarized beam was determined to be more than 98% circularly polarized. This was determined by passing a small portion of the circularly polarized excitation beam through the detection system of our CPL spectrometer. No measurable effects were observed because of laser heating of the liquid crystal, and the fact that we were able to control the precise but relatively long cycle time for the polarization modulation eliminated any effects associated with the finite time to reorient the liquid crystals at the time window boundaries.

Of course, EDCD (or FDCD) measurements provide no new information over conventional CD measurements for isolated chromophores, if the CD measurement is easily measurable. The detection of differential absorption by the measurement of luminescence does have the advantage of the inherently more sensitive detection schemes for luminescence over absorbance. One is therefore able to work with significantly lower concentrations than might be required in CD measurements. Again, for isolated chromophores, EDCD and CPL provide redundant information concerning chiral structure, if there is no structural change upon electronic excitation. For $\text{Eu}(\text{III})$ and the other luminescent lanthanides, no structural change is expected to be seen upon excitation of these relatively isolated f electrons that are not significantly involved in covalent bonding.

If a complex system has many absorbers, but only a small number of emitting chromophores, EDCD may have important applications. In the simplest case, the final spectrum is simplified because of the small number of chromophores contributing to the measured spectrum. There also are cases in which time discrimination can eliminate background fluorescence. In these more complex cases, the role of energy migration is important in determining whether or not the EDCD reflects the chirality of the emitting chromophore or the collection of absorption chromophores.

There are situations in which the EDCD measurements are easier to perform than CPL studies. This will be the case when the available emissive transition might not be a magnetic dipole transition, and thus have a relatively low luminescence dissymmetry value, but an accessible

absorption transition might be magnetic dipole allowed. For example, the transition used for EDCD measurements for Eu(III) will most likely always be the so-called hypersensitive transition $^5D_0 \rightarrow ^7F_2$ since it often has the largest luminescence intensity. This transition normally has a very small g_{lum} compared with the magnetic dipole allowed $^5D_0 \rightarrow ^7F_1$ transition which may be much less intense.

The results presented in Figure 6 illustrate the experimental advantage that may be obtained in chiral Eu(III) systems by being able to scan in the spectral region corresponding to the $^7F_0 \rightarrow ^5D_1$ absorption. This transition is far removed from the emissive transition, and as mentioned earlier, the initial state is the ground state not a thermally populated excited state. This transition was also utilized by Metcalf et al.²¹ in a study of the dynamics of the racemic equilibrium of $Eu(DPA)_3^{3-}$ through the measurement of time-resolved CPL, but these authors employed a circularly polarized pulsed laser system. Direct excitation of Eu(III) complexes in solution via the 5D_1 excited state is not common, and similar to that observed for excitation of the 5D_0 state, the overlap of these f-electronic states with excited states of donor/acceptor aromatic ligands in close proximity may influence the quantum yield for these kinds of measurements. This is a research area of current interest.

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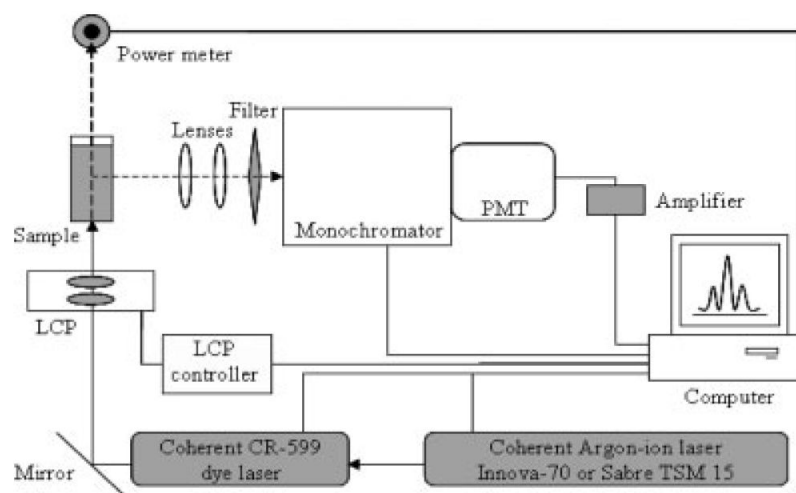


Fig. 1. Schematic diagram for instrumentation used to measure emission detected circular dichroism.

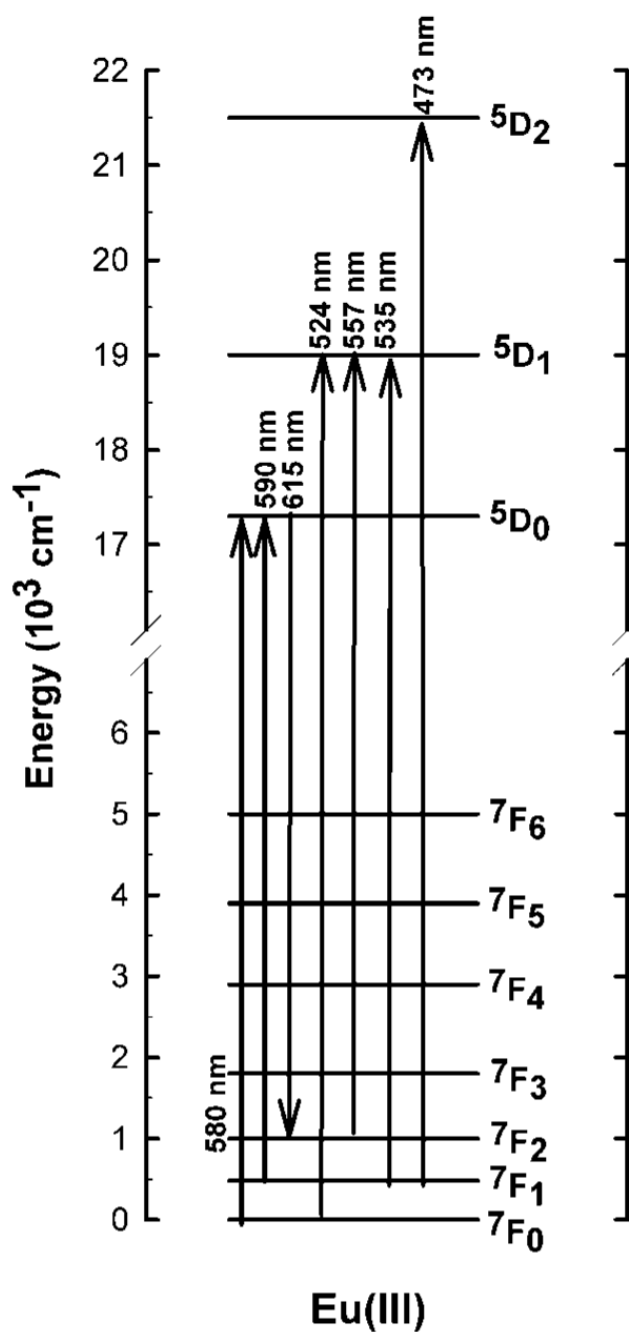


Fig. 2.
Approximate partial energy level diagram for Eu(III).

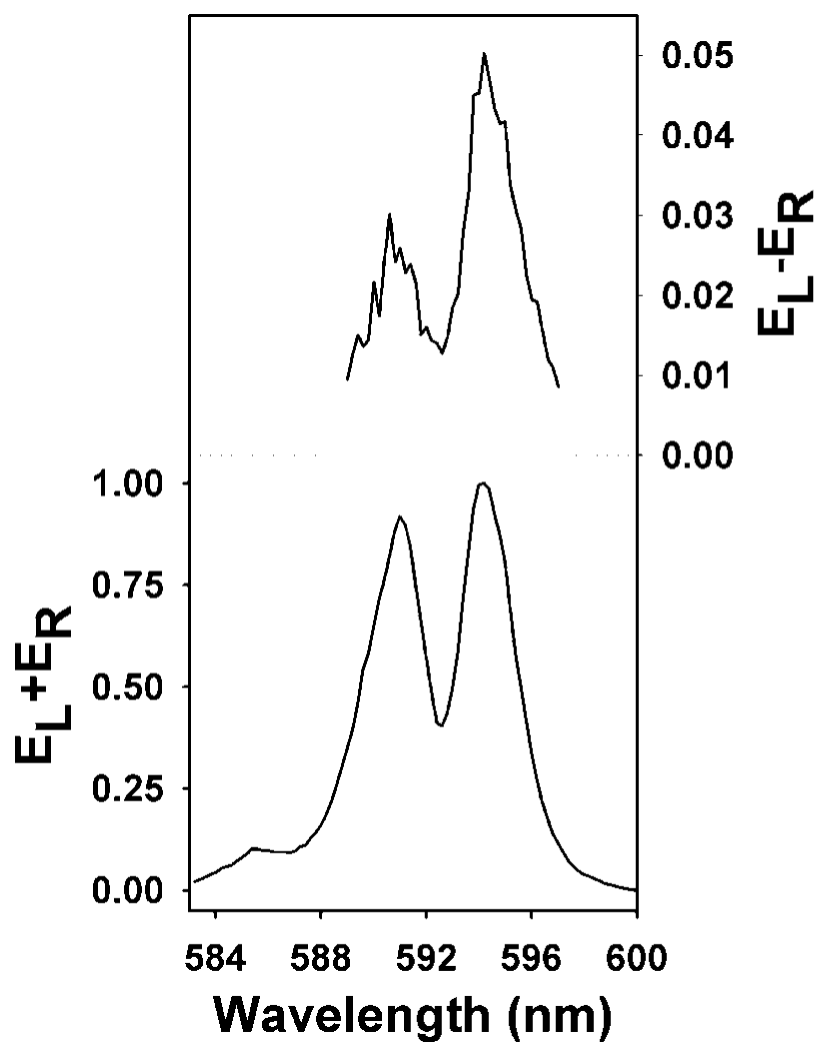
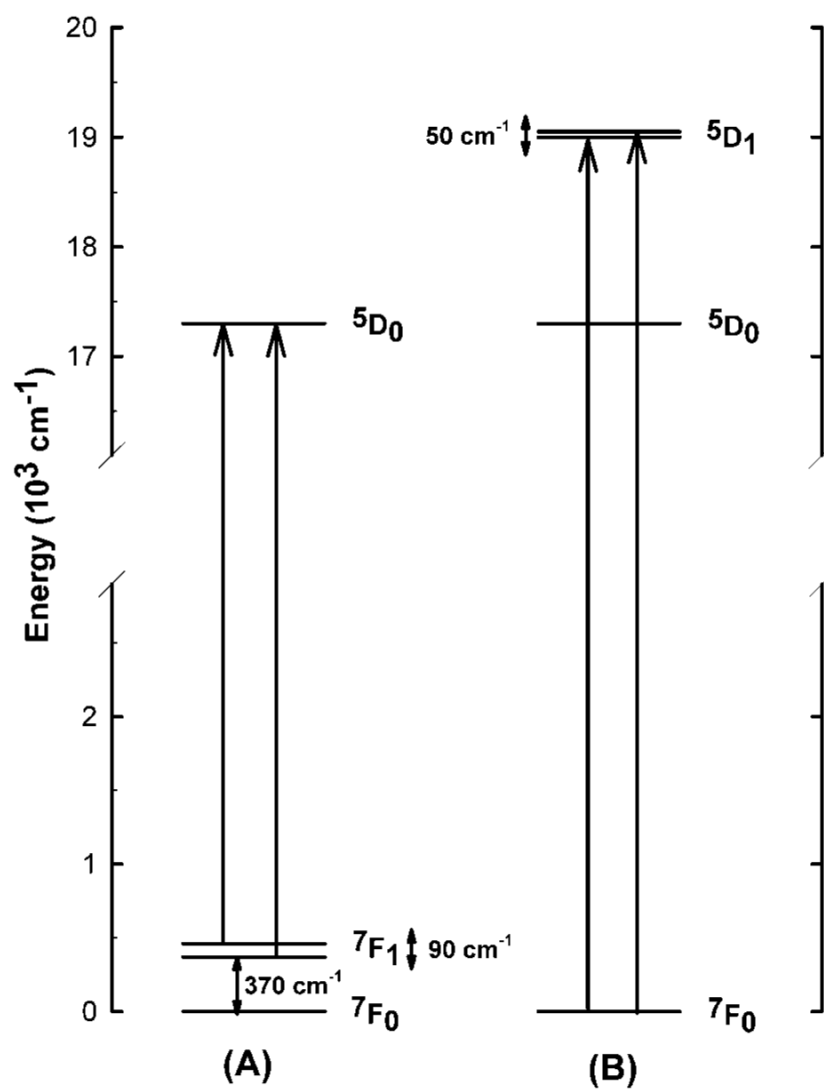


Fig. 3. Emission detected circular dichroism (upper curve) and excitation (lower curve) spectra for the $^5D_0 \leftarrow ^7F_1$ transition of 0.02 M $\text{Eu}(\text{DPA})_3^{3-}$ containing 5.5 M (+)-DMT. The emission was monitored at 615 nm.

**Fig. 4.**

A portion of the approximate Eu(III) energy level diagram for $\text{Eu}(\text{DPA})_3^{3-}$ (**A**) and $\text{Eu}[(R,R) - 1]_3^{3+}$ (**B**).

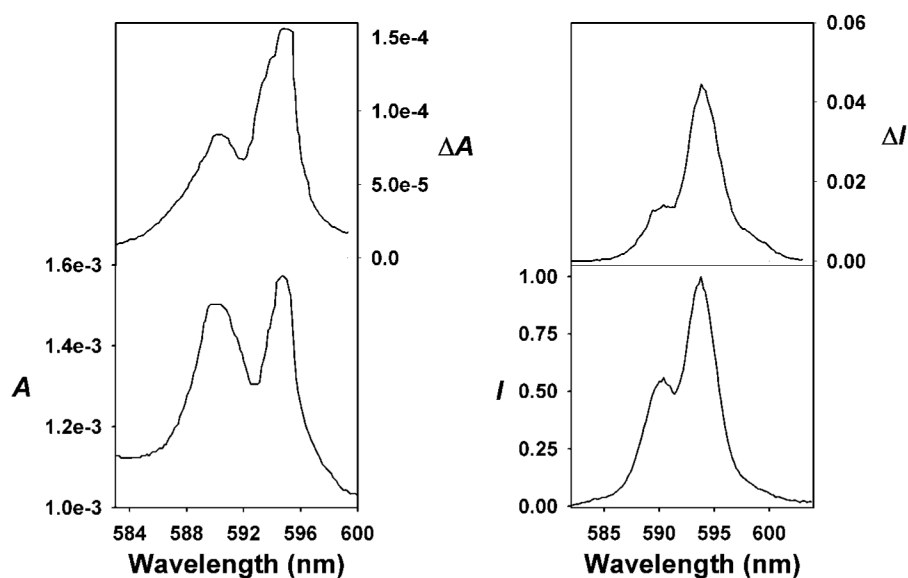


Fig. 5. Circular dichroism (upper curve) and absorption (lower curve) spectra (left) for the $^5D_0 \leftarrow ^7F_1$ transition of an aqueous solution of 275:1 (+) - DMT:Eu(DPA) $_3^{3-}$.¹⁴ Circularly polarized luminescence (upper curve) and total luminescence (lower curve) spectra (right) for the $^5D_0 \rightarrow ^7F_1$ transition of an aqueous solution of 275:1 (+) - DMT:Eu(DPA) $_3^{3-}$.

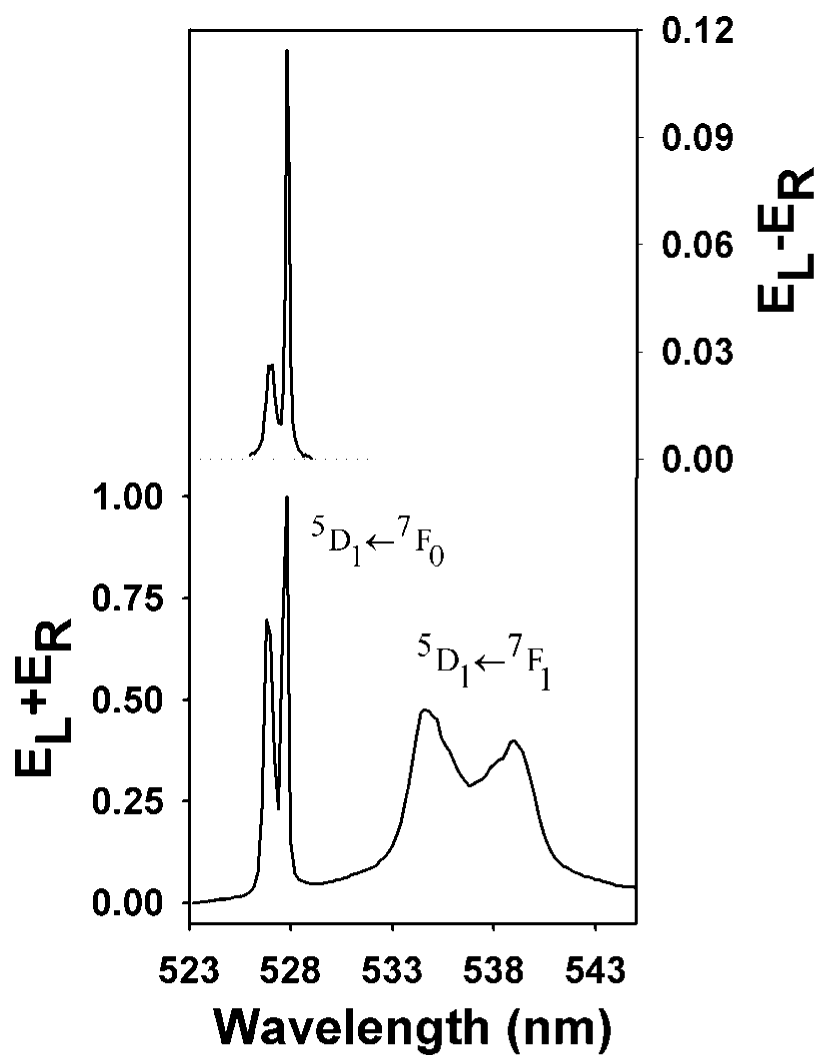


Fig. 6. Emission detected circular dichroism (upper curve) and excitation (lower curve) spectra for the $^5D_0 \leftarrow ^7F_0$ transition of $\text{Eu}[(R,R)-1]_3^{3+}$ in solution at a metal to ligand ratio of 1:5. The Eu(III) concentration was $6.67 \times 10^{-3} \text{ M}$ and the luminescence was monitored at about 615 nm.

TABLE 1

Absorption and luminescence dissymmetry values for the $^5D_0 \leftrightarrow ^7F_1$ transition of $0.02\text{ M Eu(DPA)}_3^{3-}$ containing 5.5 M (+)-DMT and for the $^5D_1 \leftarrow ^7F_0$ and $^5D_0 \rightarrow ^7F_1$ transitions of $6.67 \times 10^{-3}\text{ M Eu[(R,R) - 1]}_3^{3+}$ solution at a ratio of 1:5

$275:1, (+) - \text{DMT} : \text{Eu(DPA)}_3^{3-}$			$1:5, \text{Eu}[(R, R) - 1]_3^{3+}$			
$^5D_0 \leftrightarrow ^7F_1$			$^5D_0 \rightarrow ^7F_1^a$		$^5D_1 \leftarrow ^7F_0$	
591 nm	594 nm	590.5 nm	595.3 nm	527 nm	527 nm	527.8 nm
CPL +0.056	+0.096	-0.19	-0.18	—	—	—
EDCD +0.058	+0.096	—	—	+0.025	—	+0.11
CD ^b +0.065	+0.103	—	—	—	—	—

^aValues from Ref. 16.

^bCalculated from the digitized spectrum given in Figure 5 (left) from Ref. 12. Slight differences in wavelength have been ignored.