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Circularly Polarized Luminescence from Chiral Octadentate Complexes of Yb(III) in the Near-Infrared

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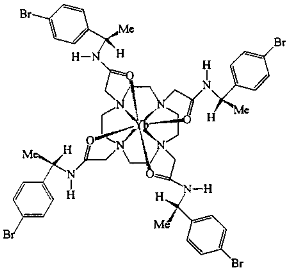
The measurement of circular polarization from chiral luminescent molecular systems (CPL) in the ultraviolet and visible part of the spectrum has been shown to be a useful experimental technique in a wide variety of applications.[1,2] CPL is the emission analogue of circular dichroism (CD) and, as such, reflects the chiral symmetry of the excited state in the same manner that CD probes the chiral ground state. In some applications, CPL provides additional information concerning molecular dynamics and energetics by probing processes that occur between the excitation event and the emission. Recent advances in high-speed digital counting now permit the detection of very small differences in the intensity of left versus right circular polarization and the ability to apply the technique to weakly luminescent systems. One of the more fruitful areas of research for CPL spectroscopy has been the study of chiral or racemic lanthanide complexes. This is because of the large CPL or CD that may be observed from intraconfigurational f ↔ f transitions, particularly those that obey magnetic dipole selection rules ($\Delta J = 0 \pm 1$). CPL from Tb(III), Eu(III), and, to a lesser extent, Dy(III) has been observed from a number of stable chiral complexes or from these ions used as substitutional probes of Ca(II) or Fe(III) sites in proteins.[1] The results from these measurements have provided useful information concerning chiral structure and structural changes that take place on the time scale of the emission. The motivation for the work reported in this paper is the increasing interest in the development of luminescent probes of biological samples in the near-infrared (near-IR) region.[3,4] This region of the spectrum is relatively free of background luminescence, and in addition, in this spectral region, serum and tissue are essentially transparent.[5]

In this paper, we report on the first attempt to extend the measurement of CPL from chiral species in solution to the near-IR spectral region through the study of several chiral Yb(III) complexes. Yb(III) (electron configuration $4f^{13}$) is particularly suited for this application, since there exists only two spin−orbit coupled f electronic states ($J = {}^5/_2$ and ${}^7/_2$) derived from the ^2F term, and the emissive transition between these states ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) at approximately 980 nm satisfies magnetic dipole selection rules. The complexes selected for this initial study are based on ligands derived from 1,4,7,10-tetraazacyclododecane. A number of these types of octadentate ligands are known to bind lanthanide(III) ions quite strongly, resulting in very robust aqueous complexes.[6−8] The specific complexes studied here are depicted below



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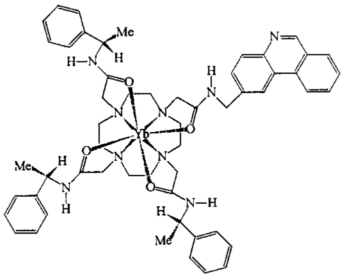

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Complex (1) was prepared in a manner described previously[9] using both enantiomers of the *p*-Br-phenylamine substituent. Other lanthanide analogues of this complex have been characterized by NMR, CD, and CPL, and it has been shown that for each enantiomer only a single C_4 orientation of the macrocyclic ligand around the central lanthanide ion is observed. We, thus, denote the complex prepared with the *S* enantiomer of the amine as Yb-$(\text{pBrS})_4{}^{3+}$. In complex (2), one of the chiral amines has been replaced by the achiral aminomethylphenanthridyl group. It has also been demonstrated from NMR and CPL measurements that the C_4 orientation around the lanthanide ion is fixed by the chirality of the three phenylethylamines, and thus, only one complex is formed.[10] These species will be denoted Yb(phndyl)-$S_3{}^{3+}$ and Yb(phndyl)$R_3{}^{3+}$. It should be noted that the resultant orientation of ligands around the Yb(III) ion (Δ or Λ) has yet to be determined. Solutions for CPL measurements were prepared by dissolving weighed amounts of the trifluoromethanesulfonate salts in D_2O.

Indirect excitation of Yb(III) was accomplished by a 150-W Xe-arc lamp. The excitation wavelength was chosen so as to maximize the luminescence at 980 nm. The luminescence was monitored at 90° relative to the direction of excitation. The optical detection system for measuring circular polarization in the luminescence is based on an instrument described previously for CPL detection in the UV−visible region.[11] The luminescence was directed through a photoelastic quarter-wave modulator (PEM Hinds Int.) operating at 50 kHz, followed by a high quality near-IR linear polarizer, long pass filter, and monochromator (Spex 1681B). The emission was detected by an Electron Tube Ltd. 9684B photomultiplier tube (S1) cooled to −100 °C, operating in photon-counting mode. At this temperature, the dark count rate was measured at less than 100/s. The total count rate for the samples studied here were greater than 10^4 at the peak maximum. A gated photon-counting system, referenced to the 50-kHz polarization modulation, was used to alternately direct TTL pulses into separate high-speed counters corresponding to left and right circularly polarized luminescence.

In Figure 1 we plot the total luminescence (I) and circularly polarized luminescence (ΔI) measured for solutions of Yb-

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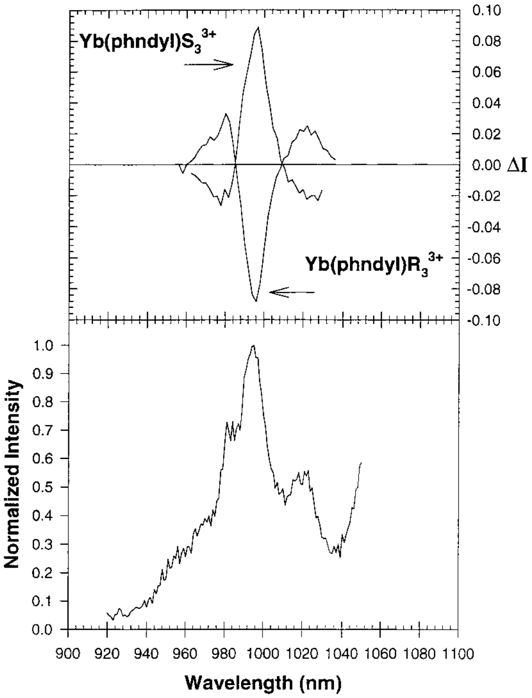

Figure 1. Total luminescence spectrum (A) and the circularly polarized luminescence spectrum (B) for the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb(III) in 1 mM aqueous solutions of Yb(phndyl)S$_3^{3+}$ and Yb(phndyl)R$_3^{3+}$. λ_{exc} = 380 nm.

(phndyl)S$_3^{3+}$ and Yb(phndyl)R$_3^{3+}$ in D_2O. A drop of trifluoroacetic acid was added to each sample, due to the fact that these complexes are significantly more emissive if the phenanthridyl group is protonated. The excitation wavelength, chosen to maximize the emission intensity, for these samples was 380 nm with a band-pass of 20 nm. Recent time-resolved transient absorption measurements involving the triplet state of the phenanthridine group, in conjunction with time-resolved detection of the Yb(III) emission, has established that intramolecular energy transfer is mediated by the aryl triplet state.[12] The precise mechanism for indirect excitation of Yb(III) in other complexes has been an area of recent interest.[13,14]

At least four resolvable peaks can be seen in the spectra corresponding to different crystal field transitions within C_4 symmetry. In the C_4 double group, three possible crystal field states are possible for the $J = {}^5/_2$ emitting state, and four states are possible for the $J = {}^7/_2$ ground state. As can be seen in Figure 1, as required by symmetry, almost exactly opposite CPL spectra are observed for the two enantiomers. The circular polarization in the luminescence observed for this transition is quite large and easily measurable under the conditions of these experiments. In CPL spectroscopy it is common to report results in terms of the luminescence dissymmetry ratio, g_{lum} which is defined as follows

$$g_{lum}(\lambda) = \frac{\Delta I(\lambda)}{I(\lambda)/2} = \frac{I_L(\lambda) - I_R(\lambda)}{[I_L(\lambda) + I_R(\lambda)]/2} \qquad (1)$$

For the spectra shown, g_{lum} at each wavelength was calculated from the ratio of the difference in photon counts $I_L - I_R$, divided by the average count $(I_L + I_R)/2$. The values obtained for $|g_{lum}|$ for the three main peaks in this spectrum are all greater than 0.1. These values are comparable to those observed for magnetic dipole allowed transitions for similar complexes involving Eu(III) and Tb(III). The sharp increase in intensity at long wavelength is due to the onset of long wavelength ligand emission from the phenanthridyl group (>530 nm) which is beyond the filter cutoff and is being detected in second order.

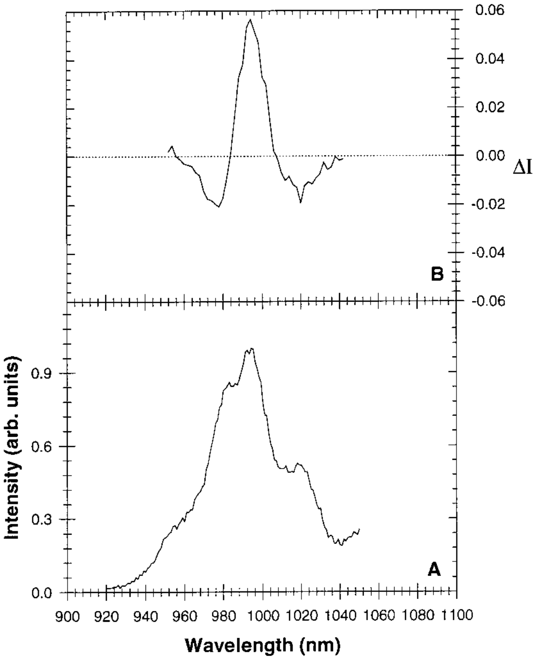

Figure 2. Total luminesence spectrum (A) and the circularly polarized luminescence spectrum (B) for the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb(III) in a 0.5 mM aqueous solution of Yb(pBrS)$_4^{3+}$. λ_{exc} = 296 nm.

In Figure 2 we show total luminescence and CPL results for an aqueous solution of Yb(pBrS)$_4^{3+}$. Although the absolute values of g_{lum} obtained from this complex are somewhat smaller than that observed in Figure 1, it is important to note that the sign pattern is identical to that seen for Yb(phndyl)S$_3^{3+}$. This is further evidence that the C_4 twist around the central metal ion is not changed in replacing one of the chiral amines by the achiral phenanthridyl group.

The results presented in Figures 1 and 2 represent the first report of CPL in the near-IR from luminescent optically active complexes in solution. The only other report of measurements of this type is by Herren and Morita who recently published circularly polarized emission from Er(III) doped into chiral crystals of $Gd_2(MnO_4)_3$ at very low temperature.[15] These results were obtained by mechanically rotating a quarter-wave plate instead of employing a photoelastic polarization modulator and are only qualitative. Results for enantiomeric crystals were not given. The data presented in this work and described above show the potential of using Yb(III) complexes as chiral luminescence probes in the near-infrared. A more detailed description of the instrumentation is in preparation.[16] Extensions of this work to other chiral luminescent Yb(III) complexes and studies aimed at exploring the behavior of these complexes in the presence of chiral biomolecules, are underway.

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