THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2008, *112,* 6789–6793
Published on Web 07/03/2008

A Promising Change in the Selection of the Circular Polarization Excitation Used in the Measurement of Eu(III) Circularly Polarized Luminescence

King Do, Françoise C. Muller,[†] and Gilles Muller*

Department of Chemistry, San José State University, One Washington Square, San José, California 95192-0101

Received: May 20, 2008; Revised Manuscript Received: June 10, 2008

A judicious change in the selected transition used for circular polarization excitation will overcome the low oscillator strength limitation of the currently allowed magnetic-dipole $^5D_1 \leftarrow {}^7F_2$ (Eu(III)) transition chosen for circularly polarized luminescence (CPL) measurement. The proposed allowed magnetic-dipole $^5D_1 \leftarrow {}^7F_0$ (Eu(III)) transition will facilitate the detection of CPL from the Eu(III) systems of interest. CPL on the acetonitrile solution of the chiral tris complex of Eu(III) with (*R*,*R*)-*N*,*N*′-bis(1-phenylethyl)-2,6-pyridinedicarboxamide ($[Eu((R,R)\text{-}\mathbf{1})_3]^{3+}$), recently suggested as an effective and reliable CPL calibrating agent, confirms the feasibility of the proposed experimental procedure. A comparable CPL activity exhibited by the acetonitrile solution of $[Eu((R,R)\text{-}\mathbf{1})_3]^{3+}$ following direct excitation in the spectral range of the $^5D_1 \leftarrow {}^7F_0$ transition and upon indirect excitation through the ligand absorption bands ($\lambda_{exc} = 308$ nm) was observed. This confirms that the recommended magnetic-dipole allowed absorption transition, $^5D_1 \leftarrow {}^7F_0$, is the transition to be considered in the measurement of CPL. This work provides critical direction for the continued instrumental improvements that can be done for developing CPL into a biomolecular structural probe.

1. Introduction

Circularly polarized luminescence (CPL) spectroscopy is the emission analog to circular dichroism (CD). CD allows one to detect the differential absorption of left and right polarized light, whereas CPL measures the difference in the emission intensity of left circularly polarized light versus right circularly polarized light.[1]

The latest CPL review written by Riehl and Muller summarizes the important structural information that can be deduced with the CPL technique.[1] CPL became increasingly useful as a probe of luminescent lanthanide complexes as sensory systems for anion binding in aqueous media and of the existence of chiral lanthanide structures (i.e., predominant isomer in solution or if the solution of a complex containing an achiral ligand is indeed a racemic mixture). It is also an indicator of changes in chiral structure (i.e., importance of the helical wrapping of the ligand strand contribution and, therefore, its influence on the diastereomeric induction). In addition, information concerning metal-ion environments and the associated chiral structures of metal-containing biological systems could be obtained through the measurement of CPL. The considerable increase in the use of CPL spectroscopy most probably originated from the discovery, of Luk and Richardson in 1975, that luminescence from intraconfigurational f ↔ f transitions of the lanthanide(III) ions obeying magnetic-dipole selection rules often showed large circular polarization.[2] Transitions that satisfy the formal selection rules of $\Delta J = 0, \pm 1$ (except $0 \leftrightarrow 0$) are magnetic-dipole allowed, where J stands for the total angular momentum quantum number found in the definition of the term symbol, $^{2S+1}L_J$, describing the electronic states of lanthanides.[3] One would expect that the advantage of using lanthanide(III) ions as chiral probes may be emphasized by the measurement of larger luminescence dissymmetry values (g_{lum}), as high as 0.5 for selected transitions of lanthanide(III) compounds, compared to chiral organic molecules for which the extent of circular polarization is almost always less than 1×10^{-2}. For example, a value of g_{lum} equal to 1×10^{-3} has been measured for chiral triarylamine-based helicenes,[4] whereas Eu(III) complexes with chiral hydroxy-2-isophthalamide-, pyridyldiamide- and 1-hydroxy-2-pyridinone-based ligand derivatives exhibited luminescence dissymmetry values of +0.29, +0.18 and −0.12 in the spectral range of the $^5D_0 \rightarrow {}^7F_1$ (Eu(III)).[5–7]

Although most of the CPL measurements published in the literature have been performed with custom-made instruments,[1,8–10] the detection of CPL can now be done with a high degree of sensitivity (~1 part in 10^4-10^5) and reliability using modern instrumentation.[11] However, the future of this technique will probably depend on the continued instrumental improvements that can be done for developing CPL into a biomolecular structural probe. The current strategies elaborated to improve the measurement of weak CPL signals are mainly oriented toward the design of Ln(III)-based systems with improved stability, efficiency and, in particular, selectivity by choosing selected (i) sensitizing and (ii) discriminating moieties into the ligand molecules.[12] The concepts are to bind to the Ln(III) ion a selected chromophoric group that can improve the absorption and luminescence efficiency ("antenna effect") and to attach selected substituents that may lead to larger enantiomeric/diastereomeric excesses or, in the case of a chiral group, the possibility of a complete resolution of the racemic solution. Although these strategies have led to successful applications

---

* To whom correspondence should be addressed. Phone: +1 408-924-4973. Fax: +1 408-924-4945. E-mail: gilles.muller@sjsu.edu.

[†] Currently at Spectra-Physics, Division of Newport Corp., 1335 Terra Bella Av., Mountain View, CA 94043.

10.1021/jp804463e CCC: $40.75

of CPL spectroscopy in the study of the chiral structures and solution dynamics of luminescent lanthanide(III) complexes,[1] only a few attempts have been made to improve the CPL instrumentation itself (see below). Knowing that most of the organic ligands that have been designed require excessive synthetic efforts and that various energy conversion processes occurring in the Ln(III)-based systems may not be optimum (i.e., incomplete intersystem crossing transfer, weak efficiency of the luminescence sensitization by the ligand, efficient nonradiative deactivation processes, poor efficiency of the $^3\pi\pi^*$-to-Ln energy transfer,...),[13–16] a considerable improvement in the CPL instrumentation would facilitate the detection of weak signals and result in a very important and more selective tool for probing specific chiral structural changes. On the other hand, it is also well established that photochemical changes that may easily alter biological molecules or the organic parts of lanthanide(III) complexes[17] may occur when indirect sensitizations through the ligand absorption bands are used in the measurement of CPL. One way to minimize these potential photochemical degradations upon long UV-light exposure would be to excite directly (and selectively) the lanthanide(III) ion. From this standpoint, we hypothesize that the selection of appropriate absorption and emission transitions will lead to larger intrinsic g_{lum} values than those currently observed.

In the present study, we report on a judicious change in the selected transition used for circular polarization excitation that would overcome the limitation of the low intensity of the currently allowed magnetic-dipole $^7F_2 \rightarrow {}^5D_1$ (Eu(III)) transition chosen for the measurement of CPL. The potential of this proposed way of measuring CPL would facilitate its detection. It should be mentioned that this work will be limited to the study of Eu(III) systems, due to the fact that (i) the Eu(III) spectroscopy is probably the most useful tool for probing the speciation, solvation numbers, excited-state energetics, or solution dynamics of luminescent lanthanide complexes and of metal-containing biomolecular systems such as Ca(II)-binding proteins,[18–20] (ii) Eu(III) possesses several absorption transitions and also one emission transition that meet the appropriate selection rules,[1,3] and (iii) the limited choice of magnetic-dipole allowed absorptions of the luminescent lanthanide(III) ions for which CPL have been reported (see Tables S1 and S2).[1,14,21–23] For instance, Tb(III), one of the most luminescent lanthanide ions along with Eu(III), does not have such allowed absorption transitions. Indeed, Tb(III) only possesses an emissive $^5D_4 \rightarrow {}^7F_5$ transition that does obey these selection rules.

As a first step toward this goal, we report on the first measurement of CPL for the $^5D_0 \rightarrow {}^7F_1$ transition of a chiral tris complex of Eu(III) with (*R,R*)-*N,N*′-bis(1-phenylethyl)-2,6-pyridinedicarboxamide following direct excitation in the spectral range of the $^5D_1 \leftarrow {}^7F_0$ transition. This chiral Eu(III) complex used for the new measurement reported here has been chosen because (i) Bonsall et al. have recently shown that the optical isomers of *N,N*′-bis(1-phenylethyl)-2,6-pyridinedicarboxamide (**1**) coordinated to europium(III) ions in a Eu:**1** ratio of 1:3 are reliable CPL calibrating agents, and (ii) their CPL spectra are known.[11]

2. Experimental Section

$[\mathrm{Eu}((R,R)\text{-}\mathbf{1})_3]^{3+}$ 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 acetonitrile. 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.[11]

Circularly polarized luminescence and total luminescence spectra were recorded on an instrument previously described.[11] It is common to report the degree of CPL in terms of the luminescence dissymmetry factor, $g_{\mathrm{lum}}(\lambda)$, which is defined as follows:

$$g_{\mathrm{lum}} = \frac{\Delta I}{\frac{1}{2}I} = \frac{I_L - I_R}{\frac{1}{2}(I_L + I_R)}$$

where I_L and I_R refer respectively to the intensity of left and right circularly polarized emissions. The standard deviation, σ_d, in the measurement of the luminescence dissymmetry factor, g_{lum}, is defined as follows:

$$\sigma_d = \sqrt{\frac{2}{N}}$$

where N is the total number of photon pulses counted. The light source for indirect excitation was a 450 W xenon arc lamp from a Spex FluoroLog-2 spectrofluorometer, equipped with excitation and emission monochromators with dispersions of 4 nm/mm (SPEX, 1681B). Selective 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. Calibration of the emission monochromator (and subsequently the dye laser wavelength) was accomplished by passing scattered light from a low power He−Ne laser through the detection system. The error in the dye-laser wavelength is assumed to equal the resolution of the emission monochromator (0.1 nm). The optical detection system consisted of a focusing lens, long pass filter, and 0.22 m monochromator. The emitted light was detected by a cooled EMI-9558B photomultiplier tube operating in photon-counting mode. All measurements were performed with quartz cuvettes with a path length of 0.4 or 1.0 cm.

3. Results and Discussion

CPL measurements have limited sensitivity due to the low absorption of the luminescent lanthanide(III) complexes because f ↔ f transitions are forbidden by the Laporte rule. Thus, a powerful excitation source has to be used such as a CW dye laser pumped by a CW argon-ion laser, an argon-ion laser without the dye laser (direct excitation), or a CW 450 W xenon arc lamp (indirect excitation) for performing CPL experiments. One particular limitation to overcome is the low oscillator strength of the actual $^5D_1 \leftarrow {}^7F_2$ transition used for circularly polarized excitation (CPE), which complicates the detection of CPL from Eu(III) complexes. This is even more problematic when the system of interest exhibits a weak emission signal. As mentioned earlier, the uncertainty in the measurement of g_{lum} values is $N^{-1/2}$, whereas the difficulty of obtaining reliable and useful results will depend on the sensitivity of the selected transitions. One should consider absorption and emission transitions that will exhibit large intrinsic g_{lum} values. It has been shown that such transitions are often those that obey the magnetic-dipole selection rules ($\Delta J = 0, \pm 1$, except $0 \leftrightarrow 0$).[3]

Several attempts have been made to improve the measurement of weak CPL signals. First, the absorption transitions that have been used for CPE/CPL studies are $^5D_1 \leftarrow {}^7F_2$ and $^5D_0 \leftarrow {}^7F_1$ centered respectively at about 557 and 595 nm (Figure 1).[1,24,25] Even though the initial states are only 1% and 15% populated,

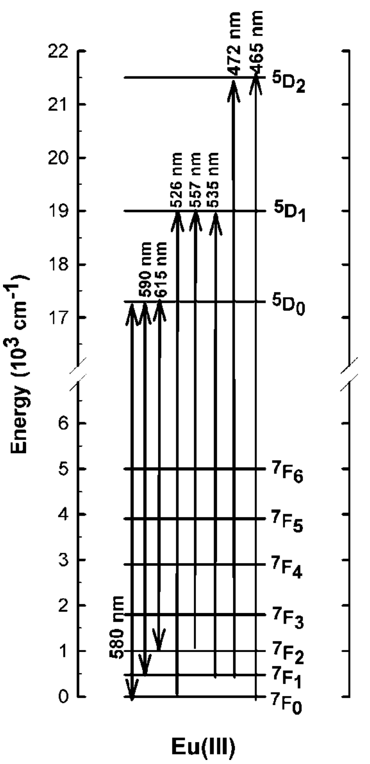

Figure 1. Approximate partial energy level diagram for Eu(III).

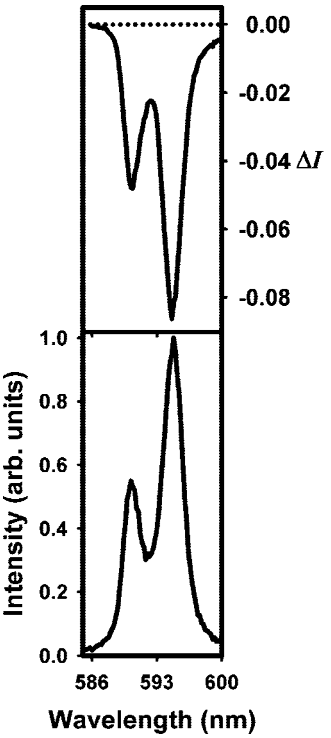

Figure 2. Circularly polarized luminescence (upper curves) and total luminescence (lower curves) spectra for the $^5D_0 \rightarrow {}^7F_1$ transition of $[Eu((R,R)\text{-}\mathbf{1})_3]^{3+}$ in 6.67×10^{-3} M MeCN at 295 K, following excitation in the spectral range of the $^5D_1 \leftarrow {}^7F_0$ transition.

these transitions satisfy the selection rules given above and may lead to a chiral discrimination. However, the weak population of these thermally populated excited states generates an important problem in maximizing emission intensity that cannot be easily overcome. A second inconvenience of selecting the $^5D_0 \leftarrow {}^7F_1$ absorption transition is that the emissive transition does not obey the selection rules (i.e., the strong emissive $^5D_0 \rightarrow {}^7F_2$ transition is centered at about 615 nm). Indeed, the only emission transition for Eu(III) is the $^5D_0 \rightarrow {}^7F_1$ transition. An additional complication is the small gap between the two transitions and therefore would require the use of very sharp and accurate optical filters. However, the cutoff filters available have a bandwith range that will also cut the light emitted by the sample, thus tampering with the results. Not having such filters would allow the detection of scattered light from the laser absorption in the emission. As a consequence, the experimental CPL signal detected would result from the circular polarization light, but mainly from the laser's linear polarized light. Therefore, the outcome of this choice would not be better in our attempt to improve the measurement of CPL. The use of the other emission transitions of Eu(III), i.e. $^5D_0 \rightarrow {}^7F_3$ or $^5D_0 \rightarrow {}^7F_4$, would not improve the detection of CPL as these transitions are weaker than $^5D_0 \rightarrow {}^7F_2$ and do not satisfy the selection rules, even if their wavelength (about 650 or 690 nm versus 615 nm) is farther from the laser wavelength absorption. Another possibility is the use of the species-selective $^5D_0 \leftarrow {}^7F_0$ excitation transition and either the $^5D_0 \rightarrow {}^7F_1$ or $^5D_0 \rightarrow {}^7F_2$ emission transition. These different sets of transition were not conclusive for the same reasons given above and also because the $^5D_0 \leftarrow {}^7F_0$ transition does not meet the requirement of the Laporte selection rules.

In summary, the current "ideal" situation is the one involving the $^5D_1 \leftarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ absorption and emission transitions, respectively. Besides the weak population of the $^7F_2$ initial state estimated at about 1%, the main disadvantage of considering this set of transitions is the interpretation of CPL measurements in terms of structural changes. This is even amplified in the situation where the system of interest possesses a low symmetry as there could be as many as fifteen individual crystal field transitions, $(2J + 1)(2J + 1)$, within the absorption band.

The most promising direction for this attempt of improving the detection of CPL is to consider a completely different absorption transition of Eu(III) which obeys the selection rules and also possesses a limited number of individual crystal field levels. This latter requirement is important for Eu(III) compounds with low symmetries if one wants to interpret the specific structural changes. Working along these lines, we propose to use the $^5D_1 \leftarrow {}^7F_0$ transition (525−529 nm) in absorption and the $^5D_0 \rightarrow {}^7F_1$ transition in emission, as both of them are magnetic-dipole allowed transitions.

The CPL spectra for the $^5D_0 \rightarrow {}^7F_1$ transition of a 6.67×10^{-3} M acetonitrile solution of $[Eu((R,R)\text{-}\mathbf{1})_3]^{3+}$ following excitation in the spectral range of the $^5D_1 \leftarrow {}^7F_0$ transition (λ_{exc} = 526.5 or 527.3 nm) are plotted in Figure 2. The selected excitation wavelengths were determined from the $^5D_1 \leftarrow {}^7F_0$ high-resolution excitation spectrum of $[Eu((R,R)\text{-}\mathbf{1})_3]^{3+}$ in acetonitrile (Figure 3). It is interesting to note that the strong CPL activity exhibited by this Eu(III) complex is comparable when either a direct excitation of the Eu(III) ion in the spectral range of the $^5D_0 \rightarrow {}^7F_1$ transition (Figure 2) or an indirect excitation through the ligand absorption bands ($\lambda_{exc} = 308$ nm)[11] is used. The g_{lum} values amounted to −0.18(1) and −0.17(1) versus −0.19(1) and −0.18(1) at the two peaks of the $^5D_0 \rightarrow {}^7F_1$ transition (~590 and 595 nm), respectively. Observation of similar CPL spectra following direct and indirect excitations indicates that the same species in solution is responsible for the CPL activity detected. A useful experiment to determine whether or not the solution contains a mixture of species is to excite directly the Eu(III) ion with circularly polarized light.

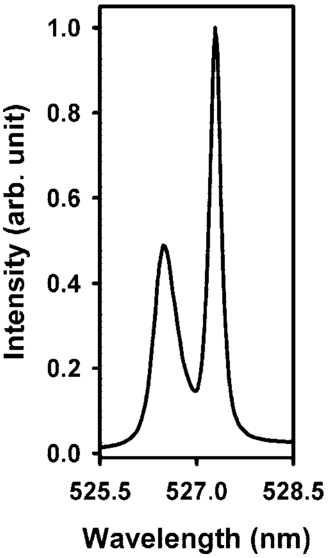

Figure 3. $^5D_1 \leftarrow {}^7F_0$ transition excitation spectrum of $[Eu((R,R)\text{-}\mathbf{1})_3]^{3+}$ in 6.67×10^{-3} M MeCN at 295 K. The luminescence was monitored at about 615 nm.

These experiments have shown that the g_{lum} values obtained for $[Eu((R,R)\text{-}\mathbf{1})_3]^{3+}$ solutions were independent of the polarization of the excitation beam (i.e., right-, left-, or plane-polarized light). This is consistent with the presence of only one species in solution.[1,17,24,26] Should the solution have contained a mixture of diastereomers or enantiomers, the CPL should have been dependent on the excitation polarization, as previously observed for 1:3 Eu:L complexes with the chiral ligands 2,6-bis[(1-methylbenzimidazol-2-yl)]-pyridine-4-carboxylate or 3-[2,6-bis(diethylcarbamoy)pyridine-4-yl]-*N*-(tert-butoxycarbonyl)alanine ester.[27,28]

4. Concluding Remarks

Although the use of the proposed $^5D_1 \leftarrow {}^7F_0$ transition for the study of the dynamics of the racemic equilibrium of $[Eu(2,6\text{-pyridinedicarboxylate} = DPA)_3]^{3-}$ through the measurement of time-resolved CPL has been reported once in the literature,[29] no one has considered this excitation transition as the future of the continued experimental development of CPL as a biomolecular structural probe.

In the present study, we have carried out the first CPL measurement of an acetonitrile solution of the chiral CPL calibrating agent, $[Eu((R,R)\text{-}\mathbf{1})_3]^{3+}$, following direct excitation in the spectral range of the $^5D_1 \leftarrow {}^7F_0$ transition (Figure 2). This CPL spectrum, which we expected to be comparable to the one recorded upon indirect excitation,[11] confirms that the proposed magnetic-dipole allowed absorption transition, $^5D_1 \leftarrow {}^7F_0$, is the transition to be considered in the measurement of CPL. The additional feature in the proposed way of measuring CPL will contribute to a consequent increase in maximizing emission intensity that could be reached and also would enhance considerably the structural information gained of the selected systems. These would be possible by the choice of two allowed magnetic-dipole transitions and also because the $^5D_1 \leftarrow {}^7F_0$ absorption transition will only have a maximum of three individual crystal field levels versus fifteen for the $^5D_1 \leftarrow {}^7F_2$ transition. This will result in a very important tool for studying specific chiral structural changes and also to be more selective and precise in the selection of a circular polarized excitation wavelength. We believe that this modification of the CPL measurement will have an important impact in the development of this still underemployed technique for probing chiral structural changes.

Advances in bioinorganic chemistry have been driven by the development of various spectroscopic tools including NMR, UV−vis, or CD aimed at understanding the relationships between the structures of proteins and their ability to bind metal ions. Ln(III) ion luminescence may provide useful information concerning the structure of metal-containing biological systems in aqueous media. Of special importance, local information concerning metal-ion environments and the associated chiral structures of these systems can be obtained through the measurement of CPL. This information will complement the one obtained using CD spectroscopy, a much less sensitive chiroptical absorption technique. The latter is mainly used for determining macromolecular information about protein's secondary and tertiary structures.

Another advantage of directly exciting the Eu(III) ion would be to minimize the photochemical changes that may easily alter biological molecules upon long UV-light exposure. It could also be one of the reasons leading to different conclusions as in some of the pioneering studies the CPL spectra have been measured following UV excitation.[1] The study of enantiomeric recognition of biologically substrates is an ongoing active research because it can provide valuable information concerning molecular recognition mechanisms in biological materials. Research in these directions is currently underway.

Acknowledgment. We thank the National Institute of Health Minority Biomedical Research Support (2 S06 GM008192-24A1), Research Corporation Cottrell Science Award (CC6624), San José State University, and the San José State University Research Foundation for the financial support of this research.

Supporting Information Available: Tables of selected magnetic-dipole allowed absorptions and emissive transitions of the lanthanide(III) ions. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Riehl, J. P.; Muller, G. Circularly Polarized Luminescence Spectroscopy from Lanthanide Systems. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Bünzli, J-C. G., Pecharsky, V. K. , Eds.; North-Holland Publishing Company: Amsterdam, 2005; Vol. 34, pp 289−357, and references therein.

(2) Luk, C. K.; Richardson, F. S. *J. Am. Chem. Soc.* **1975**, *97*, 6666.

(3) Richardson, F. S. *Inorg. Chem.* **1980**, *19*, 2806.

(4) Field, J. E.; Muller, G.; Riehl, J. P.; Venkataraman, D. *J. Am. Chem. Soc.* **2003**, *125*, 11808.

(5) Petoud, S.; Muller, G.; Moore, E. G.; Xu, J.; Sokolnicki, J.; Riehl, J. P.; Le, U. N.; Cohen, S. M.; Raymond, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 77.

(6) Leonard, J. P.; Jensen, P.; McCabe, T.; O'Brien, J. E.; Peacock, R. D.; Kruger, P. E.; Gunnlaugsson, T. *J. Am. Chem. Soc.* **2007**, *129*, 10986.

(7) Seitz, M.; Moore, E. G.; Ingram, A. J.; Muller, G.; Raymond, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 15468.

(8) Brittain, H. G. *Appl. Spectrosc. Rev.* **2000**, *35*, 175.

(9) Riehl, J. P.; Richardson, F. S. *Chem. Rev.* **1986**, *86*, 1.

(10) Schippers, P. H. PhD. Dissertation, University of Leiden, The Netherlands, 1982.

(11) Bonsall, S. D.; Houcheime, M.; Straus, D. A.; Muller, G. *Chem. Commun.* **2007**, *35*, 3676.

(12) Brunet, E.; Juanes, O.; Rodriguez-Ubis, J. C. *Curr. Chem. Bio.* **2007**, *1*, 11, and references therein.

(13) Bünzli, J-C. G *Acc. Chem. Res.* **2006**, 53, and references therein.

(14) Bünzli, J-C. G.; Piguet, C *Chem. Soc. Rev.* **2005**, *34*, 1048, and references therein.

(15) Parker, D *Coord. Chem. Rev.* **2000**, *205*, 109, and references therein.

(16) Bünzli, J-C. G. Rare Earth Luminescent Centers in Organic and Biochemical Compounds. In *Spectroscopic Properties of Rare Earths in Optical Materials*; Liu, G., Jacquier, B. , Eds.; Springer: Berlin, 2005; Vol. 83, pp 462−499. (see also references therein).

(17) Cantuel, M.; Bernardinelli, G.; Muller, G.; Riehl, J. P.; Piguet, C *Inorg. Chem.* **2004**, *43*, 1840.

(18) Supkowski, R. M.; Horrocks, W. DeW., Jr. *Inorg. Chim. Acta* **2002**, *340*, 44, and references therein.

(19) Lessmann, J. J.; Horrocks, W. DeW., Jr. *Inorg. Chem.* **2000**, *39*, 3114, and references therein.

(20) Feig, A. L.; Panek, M.; Horrocks, W. DeW., Jr.; Uhlenbeck, O. C *Chem. Biol.* **1999**, *6*, 801, and references therein.

(21) Nwe, K.; Richard, J. P.; Morrow, J. R. *Dalton Trans.* **2007**, *44*, 5171.

(22) Bünzli, J-C. G. Metal Ions in Biological Systems. In *Metal Complexes in Tumor Diagnosis and as Anticancer Agents*; Sigel, A., Sigel, H., Eds.; Marcel Dekker Inc.: New York, 2004; Vol. 42, pp 39−75.

(23) Turro, C.; Fu, P. K.-L.; Bradley, P. M. Lanthanide Ions as Luminescent Probes of Proteins and Nucleic Acids. In *Metal Ions in Biological Systems*; Marcel Dekker, Inc., 2003; Vol. 40 (Lanthanides and Their Interrelations with Biosystems), pp 323−353.

(24) Muller, G.; Bünzli, J.-C. G.; Riehl, J. P.; Suhr, D.; von Zelewsky, A.; Mürner, H. *J. Chem. Soc., Chem. Commun.* **2002**, 1522.

(25) Huskowska, E.; Riehl, J. P. *J. Luminesc.* **2000**, *86*, 137.

(26) Parker, D.; Dickins, R. S.; Puschmann, H.; Crossland, C.; Howard, J. A. K. *Chem. Rev.* **2002**, *102*, 1977.

(27) Muller, G.; Riehl, J. P.; Schenk, K. J.; Hopfgartner, G.; Piguet, C.; Bünzli, J-C. G. *Eur. J. Inorg. Chem.* **2002**, 3101.

(28) Muller, G.; Schmidt, B.; Jiricek, J.; Hopfgartner, G.; Riehl, J. P.; Bünzli, J.-C. G.; Piguet, C. *J. Chem. Soc., Dalton Trans.* **2001**, 2655.

(29) Metcalf, D. H.; Snyder, S. W.; Demas, J. N.; Richardson, F. S. *J. Am. Chem. Soc.* **1990**, *112*, 469.

JP804463E