Inorg. Chem. **2006**, *45*, 1739–1744

Modified Dipicolinic Acid Ligands for Sensitization of Europium(III) Luminescence

Michael R. George,[†] Christopher A. Golden,[†] Martin C. Grossel,*[,†] and Richard J. Curry*[,‡]

School of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ U.K., and Advanced Technology Institute, School of Electronics and Physical Sciences, University of Surrey, Guildford, GU2 7XH U.K.

Received August 26, 2005

The effect of substitution at the 4 and 3,5 positions in the pyridine ring of europium(III) pyridine-2,6-dicarboxylate complexes has been investigated with particular emphasis on sensitization of the Eu^{3+} ion. Sensitization of the Eu^{3+} 615-nm emission was achieved through excitation of the ligands in which the 4 substituent was –H, –OH, and –Cl and the 3,5 position was –H. In these cases, the ligand-to-Eu^{3+} ratio was confirmed as being 3:1. The sensitization was found to increase following substitution of the 4 position in the order Cl > H > OH. This is attributed to energy transfer occurring from the ligands into different Eu^{3+} intra-atomic energy levels, with spin selection rules governing the efficiency of this process. The Eu^{3+} luminescence lifetime was measured and found to vary from 1.16 to 2.90 ms depending on the excitation energy, ligand, and solvent. For the case of the 3,5-dibromo-4-hydroxy derivative, no sensitization was observed and a ligand-to-Eu^{3+} ratio of 1:1 was found. The solubility of these complexes in water and their long emission lifetime make them attractive for use as probes in biological systems.

Introduction

Since the demonstration by Weissman[1] of ligand-sensitized emission from lanthanide ions (Ln^{3+}), extensive studies have been carried out on such systems. The spectrally narrow and unique emission obtained from Ln^{3+} is suited to a wide variety of applications including displays,[2] luminescence probes and markers,[3,4] and telecommunications.[5,6]

The emission originates from 4f−4f intra-atomic electronic and magnetic dipole transitions that are parity-forbidden. As such, the absorption cross sections for directly exciting Ln^{3+} are small and the use of ligands to excite Ln^{3+} through an energy-transfer process is, in general, therefore much more effective.[7] The focus of much research into organolanthanide complexes has been based on the understanding and improvement of the excitation and energy-transfer mechanisms. In the majority of systems studied, the excited singlet state of the ligand undergoes fast intersystem crossing (ISC) to the triplet state enhanced by the increased spin−orbit (LS) coupling induced by the heavy lanthanide ion. It is widely believed that it is from this triplet state that energy transfer occurs to the Ln^{3+} ion through either a Dexter ($|\Delta J| = 0, 1$; $J = J' = 0$ excluded) or a Förster ($|\Delta J| = 2, 4, 6$) mechanism.[8] There are, however, a number of reports in which energy transfer to Ln^{3+} occurs from the excited singlet state of the ligand.[9] However, in the case of Yb^{3+}, the exact nature of the energy-transfer process is still unclear.[5]

As well as considering the above-mentioned processes, the study of competing nonradiative mechanisms that lead to the quenching of emission is important. A number of studies have focused on minimizing the nonradiative relaxation of the Ln^{3+} ion (through coupling with O−H and C−H oscillations) by deuteration and halogenation.[10,11] A further

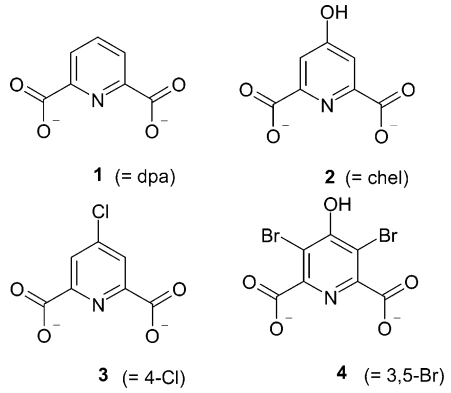
* To whom correspondence should be addressed. E-mail: mcg1@soton.ac.uk (M.C.G.), r.j.curry@surrey.ac.uk (R.J.C.).
† University of Southampton.
‡ University of Surrey.

(1) Weissman, S. I. *J. Chem. Phys.* **1942**, *10*, 214−217.
(2) Kido, J.; Okamoto, Y. *Chem. Rev.* **2002**, *102*, 2357−2368.
(3) Soini, E.; Lovgren, T. *Crit. Rev. Anal. Chem.* **1987**, *18*, 105−154.
(4) Bunzli, J. G.; Charbonniere, L. J.; Ziessel, R. F. *J. Chem. Soc., Dalton Trans.* **2000**, *12*, 1917−1923.
(5) Curry, R. J.; Gillin, W. P. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 481−486.
(6) Sloof, L. H.; Blaaderen, A. V.; Polman, A.; Hebbink, G. A.; Klink, S. I.; van Veggel, F. C. J. M.; Reinhoudt, D. N.; Hofstraat, J. W. *J. Appl. Phys.* **2002**, *91*, 3955−3980.
(7) Bhaumik, M. L.; El-Sayed, M. A. *J. Chem. Phys.* **1965**, *42*, 787−790.
(8) Hebbink, G. A.; Grave, L.; Woldering, L. A.; Reinhoudt, D. N.; van Veggel, F. C. J. M. *J. Phys. Chem. A* **2003**, *107*, 2483−2491.
(9) Hebbink, G. A.; Klink, S. I.; Grave, L.; Oude Alink, P. G. B.; van Veggel, F. C. J. M. *Chem. Phys. Chem.* **2002**, *3*, 1014−1018.

10.1021/ic051461u CCC: $33.50
Published on Web 01/26/2006

source of nonradiative relaxation can result from oxygen quenching of the ligand triplet state.[12]

Of the many types of complexes studied, the family of $Ln^{3+}(dpa)_3$ (dpa = 2,6-pyridinedicarboxylate, **1**) is of particular interest because it fully satisfies the eight- and nine-coordination requirements of Ln^{3+}. This is in contrast to the β-diketone ligands that are commonly used to chelate Ln^{3+} and require an additional "neutral" ligand to obtain full coordination.[2] As such, $Ln^{3+}(dpa)_3$ complexes are of particular interest for use in aqueous environments in which emission can be observed from the Ln^{3+} ion that would normally be quenched by OH oscillations of coordinated water molecules. Complexes of Eu^{3+} and Tb^{3+} are a primary focus because of their visible emission and hence their applications in the study of biological systems and immunoassays.



Previous studies on $Eu^{3+}(dpa)_3$ [Eu(**1**)$_3$] complexes have either compared them to other ligands with respect to the sensitization of the ion or explored the effects of varying the Eu^{3+}-to-dpa binding ratio.[13−20] Despite the potential of modifying the 3,4 and 5 positions of the dpa ligand, only one such report has been forthcoming. This studied the behavior of 4-substituted $Tb^{3+}(dpa)_3$ analogues[21] and showed the potential of such an approach for developing millisecond luminescence probes for analytical studies in aqueous environments. As mentioned by Lamture et al.,[21] extending the work to include Eu^{3+} is of interest because of its unique red emission, though it was predicted that the effects would be complex to describe as a result of the presence of multiple emitting states. As such, no further reports have been forthcoming.

In this paper, we report a study on the effects of modification of the Eu(**1**)$_3$ ligand with respect to the sensitization and emission of Eu^{3+}. In doing so, we describe the preparation and characterization of a number of 4-substituted (**1**−**3**) dpa analogues and one 3,5-disubstituted (**4**) dpa analogue. We present a detailed spectroscopic characterization of their UV absorbance, photoluminescence excitation (PLE), photoluminescence (PL), and emission lifetime. We use these data to discuss the effect of such substitution on the ligand sensitization of Eu^{3+} and its emission.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 or a Bruker DPX 400 spectrometer. Chemical shifts (δ) are quoted relative to residual solvent peaks. ^{13}C NMR spectra were fully proton decoupled. Peaks are quoted in chemical shift, ppm (δ): s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (J) are quoted in hertz. Infrared spectra were obtained using a Golden Gate sampling attachment on a Mattson Satellite 3000 Fourier transform infrared instrument. Masses are quoted as the lowest isotopic mass (for instance, ^{35}Cl and ^{79}Br if these elements are involved). For compounds that were soluble in methanol, electrospray (ES) mass spectra were recorded on a Micromass Platform II single-quadrupole mass spectrometer. The instrument is calibrated with a mixture of sodium and cesium iodide. The operating conditions were as follows: capillary, 3.50 kV; HV lens, 0.5 kV; cone voltage, 20 V; source temperature, 110 °C; ES eluant, 100% acetonitrile at 100 μL min^{-1}; nitrogen drying gas, 300 L h^{-1}; nebulizing gas, 20 L h^{-1}. Ten-microliter injections of $\approx$1−10 μL mL^{-1} solutions were made using a Hewlett-Packard HP1050 autosampler. Negative-ion data were recorded under identical conditions except for different polarity voltages and capillary voltages of −3.0 kV. Elemental analyses were performed by Medac Ltd. of Brunel Science Centre, Coopers Hill Lane, Englefield, Egham, Surrey, TW20 0JZ U.K. Melting points were measured on an Electrothermal melting point apparatus and are uncorrected. All of the solvents and reagents used were of reagent grade, obtained from Aldrich, and were used without any further purification except where specified.

Preparation of Ligands. Chelidamic Acid (2·2H$^+$).[22] This was prepared following the procedure of Horvath et al.[22] to give white crystals (99% yield). Mp: >240 °C (lit.[22] 265 °C; lit.[23] 250−255 °C). IR (ATR, ν/cm^{-1}): 3603 (s), 3441 (s), 3122 (m), 3004 (w), 2852 (w), 2699 (w), 2448 (br), 1714 (br), 1607 (s), 1467 (m), 1422 (m), 1393 (s), 1336 (s), 1259 (m), 1131 (m), 934 (s), 783 (s). ^{1}H NMR (400 MHz, D_2O): δ 7.59 (2H, s, CH_2). ^{13}C NMR (100 MHz, D_2O): δ 178.2 (*C*−OH), 172.5 (*C*═O(OH), 164.0 (*C*═O(OH), 151.5 (*C*−COOH), 116.8 (*C*H).

4-Chloropyridine-2,6-dicarboxylic Acid.[24−26][24−26] This was prepared by following literature procedures.[24,25] The reaction of

(10) Hasegawa, Y.; Murakoshi, K.; Wada, Y.; Yanagida, S.; Kim, J.; Nakashima, N.; Yamanaka, T. *Chem. Phys. Lett.* **1996**, *248*, 8−12.
(11) Iwamuro, M.; Adachi, T.; Wada, Y.; Kitamura, T.; Yanagida, S. *Chem. Lett.* **1999**, *28*, 539−540.
(12) Prendergast, F. G.; Lu, J.; Callahan. P. J. *J. Biol. Chem.* **1983**, *258*, 4075−4078.
(13) Grenthe, I. *Acta Chem. Scand.* **1964**, *17*, 9.
(14) Murray, G. M.; Sarrio, R. V.; Peterson, J. R. *Inorg. Chim. Acta* **1990**, *176*, 233−240.
(15) Brayshaw, P. A.; Harrowfield, J. M.; Sobolev, A. N. *Acta Crystallogr.* **1995**, *C51*, 1799−1802.
(16) Lis, S.; Choppin, G. R. *J. Alloys Compd.* **1995**, *225*, 257−260.
(17) Binnemans, K.; van Herck, K.; Görller-Walrand, C. *Chem. Phys. Lett.* **1997**, *266*, 297−302.
(18) Arnaud, N.; Vaquer, E.; Georges, J. *Analyst* **1998**, *123*, 261−265.
(19) Werts, M. H. V.; Jukes, R. T. F.; Verhoeven, J. W. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1542−1548.
(20) Sendor, D.; Hilder, M.; Juestel, T.; Junk, P. C.; Kynast, U. H. *New J. Chem.* **2003**, *27*, 1070−1077.
(21) Lamture, J. B.; Zhou, Z. H.; Kumar, A. S.; Wensel, T. G. *Inorg. Chem.* **1995**, *34*, 864−869.
(22) Horvath, G.; Rusa, C.; Kontos, Z.; Gerencser, J.; Huszthy, P. *Synth. Commun.* **1999**, *29*, 3719−3731.
(23) Fitton, A. O.; Smalley, R. K. *Practical Heterocyclic Chemistry*; Academic Press: London, 1968; pp 74−75.
(24) Markees, D. G.; Kidder, G. W. *J. Am. Chem. Soc.* **1956**, *78*, 4130−4134.
(25) Iglesias, C. P.; Elhabiri, M.; Hollenstein, M.; Buenzli, J.-C. G.; Piguet, C. *J. Chem. Soc., Dalton Trans.* **2000**, *13*, 2031−2044.
(26) Markees, D. G.; Kidder, G. W. *J. Am. Chem. Soc.* **1956**, *78*, 4130−4134.

chelidamic acid with phenylphosphene dichloride followed by quenching with methanol gave dimethyl 4-chloropyridine-2,6-dicarboxylate (60% yield) Mp: 137−138 °C (lit.[24] 142−143 °C). The ester was then hydrolyzed in an aqueous ethanolic solution. The addition of hydroxide followed by acidification gave 4-chloropyridine-2,6-dicarboxylic acid (**3**·2H+) (97% yield). Mp: 215−217 °C (lit.[26] 218−219 °C). IR (ATR, ν/cm^{-1}): 3478 (w), 3376 (w), 3097 (br), 1883 (w), 1813 (w), 1722 (s), 1679 (m), 1571 (s), 1480 (w), 1442 (w), 1410 (w), 1313 (s), 1211 (s), 1179 (s), 1050 (m), 996 (m), 894 (s). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.14 (2H, s, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.1 (*C*═O(OH), 151.7 (*C*−COOH), 147.1 (*C*−Cl), 124.8 (CH_2).

3,5-Dibromo-4-hydroxypyridine-2,6-dicarboxylic Acid Dihydrate (4·2H$^+$ + 2H$_2$O). Synthesis was carried out from chelidamic acid monohydrate following the procedure described by Lieben and Lerch.[28] It was crystallized as white needles (77% yield). Mp: 325−326 °C (dec). IR (Golden Gate, ν/cm^{-1}): 3380−3442, 3038−3118 (OH), 1691 (CO), 1580 (C═C). ^{1}H NMR (300 MHz, D_2O): product contains only exchanging protons. ^{13}C NMR (75 MHz, D_2O): δ 138.7 (C, C1), 138.0 (C, C3), 164.28 (C, C4). Elem anal. Calcd for $C_7H_7Br_2NO_7$: C, 22.30; H, 1.87; N, 3.72. Found: C, 22.27; H, 1.66; N, 3.51.

Preparation of Complexes. Triethylammonium Europium(III) Tris(pyridine 2,6-dicarboxylate) (Eu^{3+}(dpa)$_3$, Where dpa = 1). A solution of pyridine-2,6-dicarboxylic acid (0.305 g, 1.8 mmol) in methanol (50 mL) was added to a solution of $Eu^{III}(OAc)_3$ (0.200 g, 0.6 mmol) in methanol (50 mL) with stirring. The solutions became turbid when mixed, but upon the addition of triethylamine (0.50 mL, 3.6 mmol), the suspension dissolved and the solution became clear. Stirring was continued at room temperature for 2 days, and then the solvent was evaporated under reduced pressure to yield a clear oil. This was dissolved in hot methanol (distilled) and triturated in acetone to give a white solid, which was filtered and recrystallized from hot methanol dried under high vacuum to yield white crystals (450 mg, 70.9%). Mp: 252−253 °C. IR (Golden Gate, ν/ cm^{-1}): 2600−3250 (br, OH), 1612 (s, C═O), 1571 (s, C═C), 1580 (s, C═C). ^{1}H NMR (300 MHz, DMSO): δ 2.08 (9H, t, 7.1 Hz, N−CH_2−CH_3), 4.51 (2H, d, 7.7 Hz Ar$C_{3,5}H$), 4.80 (6H, qt, 7.1 Hz, NCH_2), 5.20 (1H, t, 7.5 Hz, ArC_4H). ^{13}C NMR (75 MHz, D_2O): δ 9.63 (CH_3, NCH_2CH_3), 47.04 (CH_2, NCH_2), 83.69 (CH, Ar*C*$_3$H), 138.95 (C, ArC_2), 150.34 (ArC_4H), 165.78 (C, *C*═O). Elem anal. Calcd for $Eu^{III}(dpa)_3^{3-}$-$(TEAH)_3^{3+}(TEA)_{0.5}(H_2O)_{2.5}$: C, 48.19; H, 6.40; N 8.74. Found: C, 48.39; H, 6.49; N, 8.60.

Triethylammonium Europium(III) Tris(4-hydroxypyridine-2,6-dicarboxylate) (Eu^{3+}(chel)$_3$, Where chel = 2). A solution of chelidamic acid (0.362 g, 1.8 mmol) in methanol (50 mL) was added to a solution of $Eu(OAc)_3$ (0.200 g, 0.6 mmol) in methanol (50 mL) with stirring. The solutions became turbid when mixed, but upon the addition of triethylamine (0.5 mL, 3.6 mmol), the suspension dissolved and the solution became clear and yellow in color. The reaction was stirred at room temperature for 2 days, and then the solvent was evaporated under reduced pressure to yield a clear sticky gum. The gum was triturated in heptane (10 mL) and acetone (10 mL) to yield a white solid, which was crystallized from hot methanol to give a white powder (450 mg, 74.9%). Mp: 202−204 °C (dec). IR (Golden Gate, ν/cm^{-1}): 3250−2600, 2700−3200 (br w, OH), 1723 (s, CO), 1575 (m, C═C). ^{1}H NMR (300 MHz, D_2O): δ 1.22 (9H, t, 7.4 Hz, NCH_2CH_3), 2.90 (2H, br s, CH_2), 3.18 (6H, q, 7.4 Hz, NCH_2). ^{13}C NMR (75 MHz, D_2O): δ 10.80 (NCH_2CH_3), 49.24 (NCH_2), 70.00 (CH). Elem anal. Calcd for $Eu^{III}(chel)_3^{3-}(TEAH)_3^{3+}(TEA)_{0.25}(H_2O)_{1.5}$: C, 46.13; H, 6.09; N, 8.34. Found: C, 46.35; H, 6.07; N, 8.11.

Triethylammonium Europium(III) Tris(4-chloropyridine-2,6-dicarboxylate) (Eu^{3+}(4-Cl)$_3$, Where 4-Cl = 3). A solution of 4-chloropyridine-2,6-dicarboxylic acid (0.363 g, 1.8 mmol) in methanol (50 mL) was added to a solution of $Eu^{III}(OAc)_3$ (0.200 g, 0.6 mmol) in methanol (50 mL) with stirring. The solutions became turbid when mixed, but upon the addition of triethylamine (0.5 mL, 3.6 mmol), the suspension dissolved and the solution became clear and yellow in color. The reaction was stirred at room temperature for 2 days, and the solvent was then evaporated under reduced pressure to yield a yellow solid. This solid was crystallized in hot methanol (distilled) and filtered to yield pale yellow crystals (450 mg, 70.9%). Mp: 200−202 °C. IR (Golden Gate, ν/cm^{-1}): 2200−2750 (br, OH), 1569 (s, C═C), 733 (s, C−Cl). ^{1}H NMR (300 MHz, D_2O): δ 1.19 (9H, br s, N−CH_2−CH_3), 3.15 (6H, br s, NCH_2), 4.13 (2H, br s, Ar−CH_2). ^{13}C NMR (75 MHz, D_2O): δ 10.87 (CH_3, NCH_2CH_3), 49.32 (CH_2, NCH_2), 84.88 (CH, Ar−CH_2), 138.70 (C, C1), 163.00 (C, C3), 168.21 (C, C4). Elem anal. Calcd for $Eu^{III}(4\text{-}Cl)_3^{3-}(TEAH)_3^{3+}(TEA)_{1.1}$: C, 42.95; H, 5.57; N, 7.83. Found: C, 42.96; H, 5.63; N, 7.63.

Triethylammonium Europium(III) 3,5-Dibromo-4-hydroxypyridine-2,6-dicarboxylate Hexahydrate (Eu^{3+}(3,5-Br), Where 3,5-Br = 4). Europium oxide (0.102 g, 0.29 mmol) was converted to europium chloride by dissolution in a hydrochloric acid solution (0.87 mL, 2 M, 1.74 mmol). The europium chloride solution formed was then added to a solution of 3,5-dibromochelidamic acid (0.570 g, 1.74 mmol) in water (100 mL) and stirred. Potassium hydroxide (0.196 g, 3.49 mmol) was added, but the reactants were slow to dissolve. Dissolution was achieved by stirring the mixture overnight. The colorless, clear solution was stirred at room temperature for a further day, and then the water was removed by evaporation under reduced pressure to yield a microcrystalline powder (216 mg, 62.3%). Mp: 320 °C (dec). IR (Golden Gate, ν/cm^{-1}): 3500−2300 (br, OH), 1618 (s, C═O). ^{1}H NMR (300 MHz, D_2O): only exchanging protons seen. Elem anal. Calcd for $Eu^{III}(3,5\text{-}Br)_1$-$(H_2O)_3$: C, 15.46; H, 1.11; N, 2.58. Found: C, 15.59; H, 1.16; N, 2.31.

Spectroscopic Measurements. Optical characterization of each of the complexes was carried out in solutions of methanol or water as indicated using UV-quartz 10-mm cuvettes. Absorption spectra were obtained using a Varian Cary 500 spectrophotometer with a spectral resolution of ±0.1 nm over the wavelength range of 190−1000 nm. PL spectra, PLE spectra, and PL decay transients (emission lifetime measurements) were recorded using a Cary Eclipse spectrophotometer with a xenon flash lamp source and a photomultiplier tube detector with a similar resolution. The emission lifetime was calculated with the Cary Eclipse software provided with the instrument, using a least-squares analysis fitting for both single- and double-exponential decay. In all cases, only a single-exponential decay was found, with the system resolution being 3 μs. All spectra were corrected for sample concentration, with care taken to use low concentrations when studying the properties of the ligand.

Results

Absorbance. The absorption spectrum for each complex dissolved in methanol is shown in Figure 1. As previously noted for Tb^{3+} analogues, the energy of the electronic band edge of the ligand absorption is reduced as the 4 position of the pyridine is substituted in the order H > Cl > OH.[21]

(27) George, M. R.; Grossel, M. C.; Orton, J. B. In preparation.
(28) Carnall, W. T.; Fields, P. R.; Rajnak, K. *J. Chem. Phys.* **1968**, *49*, 4450−4455.

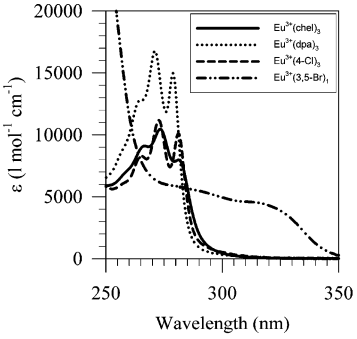


Figure 1. Absorption spectra of europium(III) tris(dipicolinate) [Eu(**1**)$_3$] and its analogues (in methanol).

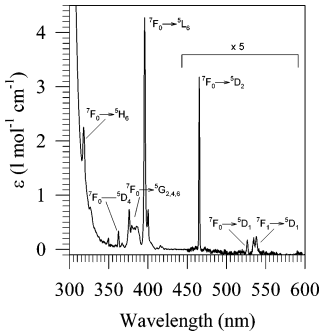


Figure 2. Absorption spectra of europium(III) tris(dipicolinate) [Eu(**1**)$_3$] (in water) showing the low absorption coefficient of intra-atomic f−f transitions (as labeled). [Note: At wavelengths above 450 nm, the intensity has been multiplied by a factor 5 for clarity.]

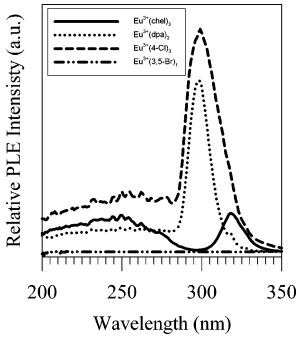


Figure 3. PLE spectra of europium(III) tris(dipicolinate) [Eu(**1**)$_3$] and its analogues, dissolved in methanol, obtained using the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ 615-nm emission.

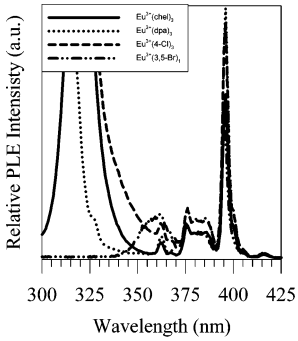


Figure 4. PLE spectra of europium(III) tris(dipicolinate) [Eu(**1**)$_3$] and its analogues, dissolved in methanol, obtained using the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ 615-nm emission.

However, in our case the effect of the OH substitution is significantly less than that reported for the Tb^{3+} complexes. Also shown is the absorption spectrum of the Eu(**4**) complex. In this case, a broad absorption feature can be observed extending to wavelengths above 350 nm. This may be due to the substitution of Br at the 3 and 5 positions, further enhancing the effect of the OH group in the 4 position on the pyridine ring. Careful inspection of this spectrum reveals the presence of a peak situated at ∼280 nm (evidenced by a shoulder at this point) that coincides with the $\pi \rightarrow \pi^*$ absorption seen for the other complexes. The effect of dissolving the complexes in water was to reduce the strength of the $\pi \rightarrow \pi^*$ absorption of the ligand by ∼10% with little further change to the absorption spectra.

Because of the forbidden nature of the 4f−4f intra-atomic transitions, direct absorption of the Eu^{3+} ion is too weak to measure at the low concentrations required to observe the ligand $\pi \rightarrow \pi^*$ transitions in full. As such, a number of high-concentration solutions were used to obtain the direct absorption of the complexed Eu^{3+} ion. Figure 2 shows the absorption spectrum of the Eu(**1**)$_3$ complex dissolved in water. A number of intra-atomic 4f−4f transitions can be clearly identified and are labeled for ease of discussion. Transitions at wavelengths below 320 nm are overlapped by the onset of the ligand absorption and so cannot be resolved. The presence of a doublet absorption peak at ∼535 nm (due to the $^7F_1 \rightarrow {}^5D_1$ transition) confirms the 1:3 E u^{3+}-to-ligand ratio in this complex.[17] It also shows that at room temperature there is a significant population of the $^7F_1$ level as a result of thermal excitation.

The onset of the ligand absorption at longer wavelengths in the Eu^{3+}(chel)$_3$ [Eu(**2**)$_3$], Eu^{3+}(4-Cl)$_3$ [Eu(**3**)$_3$], and Eu^{3+}(3,5-Br)$_1$ [Eu(**4**)] complexes has significantly reduced the number of intra-atomic transitions that could be clearly assigned. However, in each case, the $^7F_1 \rightarrow {}^5D_1$ transition could be identified and the data are consistent with the Eu^{3+}-to-ligand ratios given by single-crystal X-ray diffraction studies of these complexes that are being reported elsewhere.[27]

Excitation Spectra. To obtain further information about the interaction between the ligands and the Eu^{3+} ion, PLE spectra were obtained. Figure 3 shows the PLE spectrum for each of the complexes dissolved in methanol, obtained at 615 nm ($^5D_0 \rightarrow {}^7F_2$ Eu^{3+} emission). Dissolving the complexes in water again had little effect on the PLE spectra. For the case of Eu(**1**)$_3$ and Eu(**3**)$_3$, intense peaks are observed centered ∼295 and 300 nm, respectively. This can be assigned to the excitation of the $\pi \rightarrow \pi^*$ transition of the ligands, followed by an energy-transfer process to the Eu^{3+} ion as described above. That this is not the result of a direct excitation of the Eu^{3+} ion (e.g., $^7F_0 \rightarrow {}^5F_2$ at ∼300 nm) can be confirmed by examining the PLE spectrum of the Eu(**4**) complex. In this case, no energy transfer occurs and the Eu^{3+} emission is only sensitized by direct excitation of the ion, with no sensitization being observed at wavelengths below 340 nm. Additionally, the strength of the PLE signal is orders of magnitude stronger than that observed for direct excitation of the Eu^{3+} ion (Figure 4). The PLE spectrum of Eu(**2**)$_3$ shows similar behavior to that observed for Eu(**1**)$_3$ and Eu(**3**)$_3$. In this case, the $\pi \rightarrow \pi^*$ ligand-sensitized excitation

peak has been further red-shifted to ~320 nm as previously observed in Tb^{3+} analogues by the action of the OH group.[21] The movement of this excitation peak correlates with the observed shift in the absorption spectra in Figure 1. It is also much weaker than the equivalent peak observed for the Eu(**1**)$_3$ and Eu(**3**)$_3$ complexes, being only 1.5 times higher in intensity than that of the direct excitation at ~400 nm shown in Figure 4. This would indicate that the presence of the OH group combined with the red shift of the $\pi \rightarrow \pi^*$ transition has led to a significant reduction in the energy-transfer efficiency or that the OH group is effectively quenching Eu^{3+} once energy transfer occurs.

At wavelengths below 300 nm, there exists a broad excitation peak centered at ~250 nm for each of the complexes (with the exception of Eu(**4**)). It is noticeable that the intensity of this broad peak is comparable for each complex even though it is significantly lower than the higher energy peak (~300 nm) for the Eu(**1**)$_3$ and Eu(**3**)$_3$ complexes. If, as discussed above, the presence of the OH group leads to a reduction in energy transfer in the Eu(**2**)$_3$ complexes, we would also expect this peak to be reduced in comparison with the spectra of the other complexes (assuming the standard model, which describes energy transfer as occurring from ligand triplet states following an ISC process from excited singlet states). That it is not suggests that direct energy transfer from highly excited ligand states into Eu^{3+} may occur in these complexes before relaxation to the lowest excited π^* state can take place. If this is the case, then this process must take place with a rate constant faster than $\sim 10^{10}$ s^{-1} to efficiently compete with vibrational relaxation of the ligand. This would also imply that energy transfer can occur from singlet states in these complexes. To further clarify this observation, further ultrafast spectroscopy measurements are required.

The PLE spectra of the complexes at wavelengths above 350 nm are shown in Figure 4. At these wavelengths, the excitation peaks correspond to direct excitation of the Eu^{3+} ion using the transitions described in Figure 2. Close inspection reveals that direct sensitization of Eu(**2**)$_3$ results in a smaller emission signal than that for the Eu(**1**)$_3$ and Eu(**3**)$_3$ complexes and is identical with that observed for the Eu(**4**) complex. In the latter complex, it is known that, in addition to the OH group present on the ligand, water is directly coordinated with Eu^{3+}, which will strongly quench the emission. Given the close match with the PLE spectrum of Eu(**2**)$_3$, we believe that the OH group on the ligand is indeed contributing to the nonradiative decay of the excited Eu^{3+} and is responsible for the reduction in ligand-sensitized emission observed in this complex, as is observed in Figure 3. Furthermore, the similar intensities of the PLE spectra for the Eu(**1**)$_3$ and Eu(**3**)$_3$ complexes indicate that the effect of substitution with Cl solely at the 4 position of the pyridine ring is of minimal benefit in further reducing nonradiative decay. If any effect is to be observed, full substitution of the ring is required.

PL Spectra. The emission spectrum for each complex is shown in Figure 5. Each of these was obtained by excitation using the Eu^{3+} $^7F_0 \rightarrow {}^5L_6$ 396-nm transition to allow comparison between the complexes. For each complex, three main emission bands are observed to peak at ~590 nm ($^5D_0 \rightarrow {}^7F_1$), 615 nm ($^5D_0 \rightarrow {}^7F_2$), and 690 nm ($^5D_0 \rightarrow {}^7F_4$). In the case of Eu(**4**), an additional peak is observed at ~580 nm corresponding to the ($^5D_0 \rightarrow {}^7F_0$) transition, again confirming the Eu-to-ligand ratio.[19]

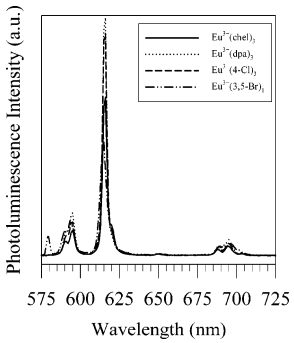


Figure 5. PL spectra of europium(III) tris(dipicolinate [Eu(**1**)$_3$] and its analogues, dissolved in methanol, excited using the Eu^{3+} $^7F_0 \rightarrow {}^5L_6$ 396-nm transition.

Table 1. Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ 615-nm Emission Lifetimes for the Complexes with Dipicolinic Acid and Its Analogues

	Eu(**1**)$_3$		Eu(**2**)$_3$		Eu(**3**)$_3$	
	298 nm	396 nm	318 nm	396 nm	300 nm	396 nm
τ_{water} (ms)	1.70	1.71	1.16	1.19	1.40	1.47
$\tau_{methanol}$ (ms)	2.63	2.90	1.92	1.93	1.30	1.34

It is known that the nature of magnetic dipole transitions is independent of the crystal field surrounding the metal ion. We can therefore use the $^5D_0 \rightarrow {}^7F_1$ 590-nm emission to assess the effect of modification of the ligands on the emissions at other wavelengths. In the case where the Eu^{3+}-to-ligand ratio is 1:3, there is little variation of the emission line strength of the 615-nm ($^5D_0 \rightarrow {}^7F_2$) transition, with it being ca. 6 times that of the invariant $^5D_0 \rightarrow {}^7F_1$ transition. For the case of the Eu(**4**) complex, however the line strength is reduced to ca. 3 times that of the $^5D_0 \rightarrow {}^7F_1$ transition as a result of the significantly reduced symmetry of the ligand field.

No emission was observed from the ligands in this study or from transitions within the Eu^{3+} ion other than those shown in Figure 5. Excitation of the complexes at the PLE peaks observed in Figure 3 had no effect on the shape of the emission spectra.

Emission Lifetime. The emission lifetime was measured for each of the Eu-to-ligand 1:3 complexes (in both water and methanol) at 615 nm, exciting the Eu^{3+} ion both indirectly and directly at ~300 and 396 nm, respectively, and the results are reported in Table 1. Figure 6 shows the luminescence decay transients of the complexes, dissolved in methanol, when sensitized via the ligand (exciting at the PLE peaks for each complex shown in Figure 2). The emission lifetime did not vary when the excitation wavelength was changed from ~300 to 200 nm. The effect of the solvent on the Eu^{3+} emission lifetime can be clearly seen (Table 1), with the lifetime increasing for the case of Eu(**1**)$_3$ and Eu(**2**)$_3$ when water is replaced with methanol. This arises from the reduction of nonradiative relaxation of the excited

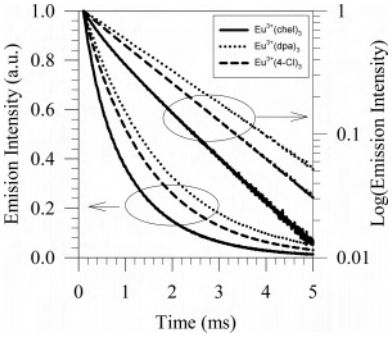


Figure 6. Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ 615-nm emission intensity decay for europium(III) tris(dipicolinate) [Eu(**1**)$_3$] and its analogues dissolved in methanol.

Eu^{3+} ion through coupling with OH vibrational modes. This effect is further exemplified when these two complexes are compared, with the lifetime of the emission from Eu(**2**)$_3$ always being less than that from Eu(**1**)$_3$ (because of the presence of the OH group in the 4 position in the former).

The lifetime of the Eu(**3**)$_3$ complex follows the opposite trend, decreasing when dissolved in methanol in comparison with its behavior in water. The reason for this is unclear, and further work is required to fully understand this effect.

The effect of direct and indirect excitation on the emission lifetime can be seen for all complexes dissolved in both solvents (water and methanol). In general, it is observed that the lifetime is longer when the Eu^{3+} ion is directly excited than when it is indirectly excited. If we assume that, when the ligand is excited at the $\pi \rightarrow \pi^*$ energy (~300 nm), energy transfer occurs into the Eu^{3+} $^5D_4$ level, we can explain this as being due to the nonradiative relaxation from $^5D_4 \rightarrow {}^5D_0$ being more efficient than that from the $^5L_6$ state $\rightarrow {}^5D_0$ (direct excitation). This is also in agreement with the selection rules for intra-atomic electric-dipole transitions. In the case of Eu(**1**)$_3$ dissolved in methanol, and to a lesser degree for Eu(**3**)$_3$ dissolved in both solvents, the increase in the emission lifetime when direct excitation is used is significant. This indicates the importance of coupling to O−H groups as a means of the $^5L_6$ energy level decaying to the radiative $^5D_0$ level.

Discussion

A comparison of the absorption and PLE spectra presented in Figures 1 and 3, respectively, reveals that excitation of the ligand at the $\pi \rightarrow \pi^*$ absorption maximum (~280 nm) is not the most efficient means of sensitizing the Eu^{3+} ion. The PLE spectra indicate that excitation of the low-energy tail of the $\pi \rightarrow \pi^*$ transition should be used instead. Consideration of the Eu^{3+} energy level structure reveals a doublet energy level ($^5I_6$ and $^5H_6$) at ~285 nm.[28] The occurrence of energy transfer into this level requires an intra-atomic transition with $|\Delta J| = 6$, $|\Delta L| = 2$ or 3, and $|\Delta S| = 1$. The probability of such a transition occurring is significantly lower than a transition to the $^5F_2$ corresponding to ~300 nm ($|\Delta J| = 2$, $|\Delta L| = 0$, and $|\Delta S| = 1$) because of spin selection rules for the forbidden 4f transitions.[29] As such, we that believe that energy transfer occurs predominantly into the $^5F_2$ energy level in both the Eu(**1**)$_3$ and Eu(**3**)$_3$ complexes. However, for the Eu(**2**)$_3$ complex, there is no sensitization of Eu^{3+} at ~300 nm. In this case, we believe that energy transfer occurs into the $^5H_4$ ($|\Delta J| = 4$, $|\Delta L| = 2$, and $|\Delta S| = 1$) and $^5H_6$ ($|\Delta J| = 6$, $|\Delta L| = 2$, and $|\Delta S| = 1$) energy levels, with the reduced probability imposed by spin selection rules explaining the reduced sensitization efficiency of the Eu^{3+} ion in comparison with the other complexes. Energy transfer into these levels can also be seen as shoulders in the low-energy tails of the other PLE spectra.

However, this does not fully explain the red shift between the $\pi \rightarrow \pi^*$ absorption and PLE maxima. If, as is normally assumed, the large spin−orbit coupling (induced by the heavy-atom effect) results in efficient ISC from the excited singlet state to the triplet state from which energy transfer occurs, we would expect a strong PLE peak at the $\pi \rightarrow \pi^*$ absorption maximum. That we do not see this implies that ISC, though most probably occurring, is not very efficient in these complexes. This, in turn, implies that there are other highly efficient (nonradiative) competing relaxation routes, allowing the excited singlet state to relax.

An alternative explanation is that we are also directly exciting the triplet state of the ligand (which lies at a lower energy than the singlet state) at wavelengths greater than ca. 300 nm, though this is unlikely even with a large spin−orbit coupling induced by the heavy-atom effect.

If we compare the results obtained here with those for Tb^{3+} analogues,[21] we observe the opposite trend for the overall luminescence sensitization finding that substitution of the 4 position of the pyridine ring in the order Cl > H > OH increases the ability of obtaining sensitized emission from Eu^{3+} in contrast to OH > H > Cl for Tb^{3+}. The effect of brominating the 3 and 5 positions of the pyridine ring is inconclusive because of the incomplete saturation of Eu^{3+} with only a single ligand. It is hard to resolve whether the difference between the sensitization of Eu^{3+} and Tb^{3+} arises from poor energy transfer or increased nonradiative quenching, though the latter is clearly important in the case of Eu^{3+}. However, it is the overall ability to obtain sensitized emission that we are concerned with here, and hence the present results are of immediate value.

Acknowledgment. We thank EPSRC for a studentship (to M.R.G.).

IC051461U

(29) Peacock, R. D. *Rare Earths* (*Structure and Bonding 22): The Intensities of Lanthanide f ↔ f Transitions*; Springer-Verlag: Berlin, 1975.