Inorganic Chemistry

Communication

pubs.acs.org/IC

Increased Antenna Effect of the Lanthanide Complexes by Control of a Number of Terdentate N-Donor Pyridine Ligands

Yuk-Wang Yip,[†,‡] Hongli Wen,[‡,§] Wing-Tak Wong,[†] Peter A. Tanner,*[,∥] and Ka-Leung Wong*[,⊥]

[⊥]Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, People's Republic of China

[†]Department of Applied Biology & Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, People's Republic of China

[§]Department of Biology & Chemistry, City University of Hong Kong, Kowloon Tong, Hong Kong, People's Republic of China

[∥]Department of Science & Environmental Studies, Faculty of Arts and Sciences, The Hong Kong Institute of Education, Tai Po, Hong Kong SAR, People's Republic of China

Supporting Information

ABSTRACT: Three europium complexes with the terdentate N-donor ligand 2,6-bis(1*H*-pyrazol-3-yl)pyridine (**L**) have been synthesized, and their crystal structures have been determined. The ligand/metal ratios in these complexes are 3, 2, and 1. The photophysical properties of the complexes indicate more efficient ligand sensitization of europium emission for the homoleptic complex.

A driving force for the synthesis of new lanthanide(III) complexes, especially those of europium and terbium, relates to their visible photoluminescent properties.[1] In the recent 2 decades, such luminescent materials have shown extensive application not only in optoelectronics but also in the detection of various biological, bioactive molecules and for in vitro imaging.[2] Lanthanide ions are attractive substitutes for the more commonly used organic fluorophors because their complexes are photochemically stable and exhibit long luminescence lifetimes and sharp emission peaks because of forced electric-dipole transitions.[3] Because lanthanide $4f^N-4f^N$ transitions are Laporte-forbidden, the direct excitation of electrons in tripositive lanthanide ions is weak. One way to overcome this shortcoming, and greatly enhance the luminescence intensity,[4] is to employ a sensitizing chromophore or antenna as a ligand in a lanthanide complex.[5]

The choice of the appropriate ligand for efficient energy transfer to the lanthanide ion after excitation has attracted much attention. The binding strength of the ligands, ultraviolet (UV) absorption properties, absence of high-frequency vibrational modes,[6] and location of donor excited states of the ligand identity[7] are important criteria to be considered.[8] Tailoring of excited-state energies by substituents associated with coordinating N-donor ligands has yielded increased emission quantum yields.[9] Aromatic pyridine ligands[10] are competent candidates to become sensitizing agents for enhancing lanthanide ion luminescence because of their ability to bind strongly to the lanthanide ions and show strong UV absorption. The 2,6-bis(1*H*-pyrazol-3-yl)pyridine (**L**) ligand, especially, plays an effective role in promoting lanthanide emission, as was previously demonstrated for Tb^{3+}.[11] We have employed this ligand in order to investigate the importance of the coordination number and type upon sensitization of emission from Eu^{3+}. It has long been realized[12] that, despite of their instabilities, 1:2 and 1:3 complexes exhibit higher luminescence yields than 1:1 complexes because the higher number of chromophores linked to the lanthanide ion facilitates high absorption of incident radiation and consequent efficient energy transfer to Ln^{3+}. A quantitative appraisal of this subject is made in the present study.

Herein, we have synthesized complexes with different metal/ligand **L** ratios (1:1, 1:2, and 1:3) for Gd^{3+} and Eu^{3+}. The literature method was employed to prepare 3-(2-pyridyl)pyrazole and **L**.[13] Lanthanide complexes were prepared by the self-assembly of europium(III) chloride or nitrate hexahydrate (1.0 equiv) with **L** in a methanol solution (see the Supporting Information, SI). The six lanthanide complexes are designated as **Ln1:L1**, **Ln1:L2**, and **Ln1:L3** to indicate Ln:L ratios, where Ln = Eu, Gd (Chart S1 and Figure 1). The crystal structures of the europium complexes have been determined, and the photophysical properties have been examined in solution and in the solid state at room and liquid-nitrogen temperature. The antenna effect is demonstrated to be the most effective for **Eu1:L3**.

X-ray diffraction analysis reveals that **Eu1:L1**, **Eu1:L2**, and **Eu1:L3** crystallize in the space groups $P2_12_12_1$, $P2_1/c$, and $P\bar{1}$, respectively (Table S1). The **Gd1:L1** complex is isostructural with **Eu1:L1**, and in both, the Ln^{3+} ion is nine-coordinate to one chlorine atom, one terdentate chelating ligand **L** (to one pyridinyl and two pyrazolyl nitrogen atoms), and five aqua oxygen atoms in a distorted tricapped trigonal-prismatic structure lower than D_{3h} symmetry (see Figure S1). The charge is balanced by two chloride ions present in the void of the lattice, held in place by hydrogen bonding. The Eu−O distances (which are similar to those for Gd−O) are between 2.44 and 2.47 Å, with Eu−N distances between 2.52 and 2.60 Å and the much longer Eu−Cl distance at 2.81 Å. The complex **Eu1:L2** crystallizes in the space group $P2_1/c$ and contains two tridentate ligands, along with two hydrates and one chloride ion in the nine-coordinated environment of Eu^{3+}, with the remaining chloride ions existing in the lattice void. The Eu−O distances are 2.45 Å and 2.50 Å, with Eu−N distances between 2.53−2.62 Å. The homoleptic complex Eu1:L3 crystallizes in the space group $P\bar{1}$. The poorer quality of the crystal presented a less accurate

Received: May 7, 2012
Published: June 19, 2012

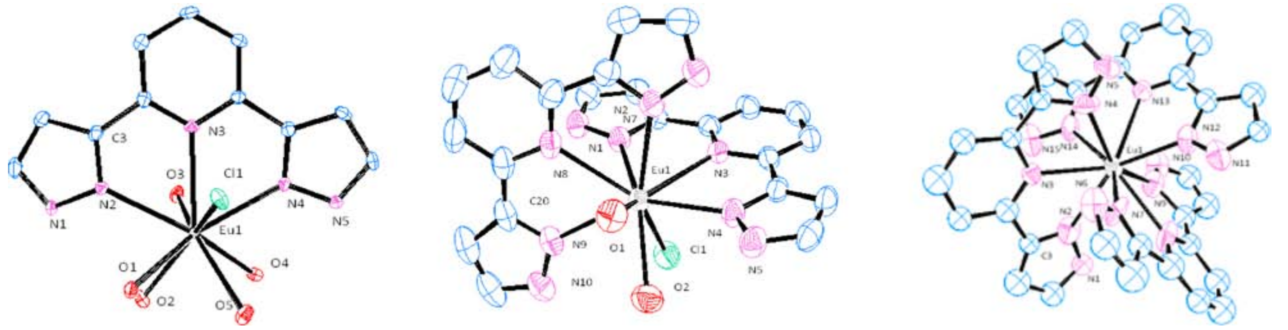

Figure 1. ORTEP plots of **Eu1:L1**(left), **Eu1:L2** (middle), and **Eu1:L3** (right). Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and atoms in the lattice void are omitted for clarity.

crystal structure determination. The ligand **L** saturates the nine-coordinated geometry of Eu^{3+}, with Eu−N distances in the range from 2.53 to 2.68 Å (mean 2.556 Å). Bardwell et al.[11] have previously reported the complexes $[ML_3][PF_6]_3$ (M = Eu, Gd, Ho), which crystallize in the space group $C2/c$. In those cases, the lanthanide cation M^{3+} lies on a C_2 axis, although the chelating coordination of the nonplanar tridentate ligands **L** is similar to that in **Eu1:L3**. The Eu−N bond distances in $[EuL_3][PF_6]_3$ of 2.52−2.60 Å (mean 2.552 Å) lie in a range fairly similar to those in **Eu1:L3**. There is a dihedral angle of ca. 4−11° between the adjacent planes in the Eu^{3+} complexes. The bite angle in these complexes (Table S1; ca. 61−63°) is similar to that for $[ML_3][PF_6]_3$. The packing diagrams of the complexes are included in the SI.

The solution-state electronic absorption, emission, and excitation spectra were recorded for the Eu^{3+} complexes at room temperature. The UV-absorption bands of the complexes (Figure S2) were ∼8 nm red-shifted after complexation. The excitation spectra (Figure S3) of the complexes presented bands similar to those of their absorption spectra, located at ∼240−280 and 330 nm, attributed to intraligand excitations. The emission lifetimes on a nanosecond scale at ca. 405 nm ($S_1 \rightarrow S_0$), and on a microsecond scale at ca. 450 nm ($T_1 \rightarrow S_0$), were measured in a glassy 2-methyltetrahydrofuran matrix at 77 K for the gadolinium complexes **Gd1:L*x*** (x = 1−3; Figure S4). The values were found to be similar and were 32 ± 1 ns for singlet-state emission and 7.2 ± 0.3 μs for triplet-state emission, with the triplet states located between 440 and 460 nm. The emission bands are blue-shifted by 45 nm compared with those at room temperature. Given the similarity of the ligand excited-state energies, ligand absorption strengths (∼17000 M^{-1} cm^{-1}), and ligand emission lifetimes in the different complexes, it is instructive to determine the sensitization efficiencies of the $Eu^{3+5}D_0$ luminescent state, η_{sens}, in each case. This quantity is related to the overall quantum yield upon ligand excitation, Q^{L}_{Eu}, which we have determined by the integrating sphere method,[14] by the equation[15]

$$Q^{L}_{Eu} = \eta_{sens} Q^{Eu}_{Eu} = \eta_{sens} \tau_{obs}/\tau_{rad} \quad (1)$$

where Q^{Eu}_{Eu} represents the intrinsic quantum yield (i.e., employing direct excitation into Eu^{3+} energy levels) and τ_{obs} and τ_{rad} are the observed and radiative (or natural) lifetimes of the $^5D_0$ state. The latter can be estimated if the spontaneous emission probability in vacuo of the magnetic-dipole-allowed $^5D_0 \rightarrow {}^7F_1$ transition is assumed to be constant (i.e., 14.65 s^{-1}), with constant energy for the transition. This value needs to be corrected by the (cube of the) refractive index of the crystal, and taking the value 1.6 gives the radiative lifetime of the $^5D_0 \rightarrow {}^7F_1$ transition as 16.7 ms. The radiative lifetime of the $^5D_0$ state (in ms) may then be estimated by a comparison of integrated areas, I, as follows:[15]

$$(\tau_{rad})^{-1} = [I_{TOT}/I_{^5D_0 \rightarrow {}^7F_1}]/16.7 \quad (2)$$

where I_{TOT} denotes the entire area of the $^5D_0 \rightarrow {}^7F_J$ transitions. Thus, from measurements of the $^5D_0$ lifetime (τ_{obs}), overall quantum efficiency Q^{L}_{Eu}, and integrated spectral areas, it is possible to estimate the sensitization efficiency (η_{sens}) of $Eu^{3+5}D_0$ luminescence by coordinated ligands.

A comparison of the luminescence quantum efficiencies of europium complexes has previously been based upon the energy of the respective ligand triplet state and the europium emissive states.[12] However, the number of coordinated ligands and their geometry and electronic structure should be taken into account in the various energy-transfer pathways.[5,16] In the present study, the triplet-state energies of the studied complexes are very similar (as determined from the corresponding gadolinium complexes), so that the sensitization efficiency variations are thus not affected by variation in the triplet-state energies. Furthermore, the distances between the pyridine ring and Eu^{3+} metal ion are similar for these nine-coordinated lanthanide complexes with various numbers of 2,6-bis(1*H*-pyrazol-3-yl)pyridine ligands, as well as the absorption extinction coefficients of the ligands in the three series of complexes.

298 K (a) and 77 K (b) visible emission spectra of the complexes are shown in Figure 2. All features correspond to luminescence from the $^5D_0$ state, and the terminal multiplets are marked in the figures. The figures have been arbitrarily scaled so that the area under the bands due to the $^5D_0 \rightarrow {}^7F_1$ transition is the same in each case. As mentioned above, this transition gains nearly all of its intensity via the magnetic-dipole mechanism. By contrast, the $^5D_0 \rightarrow {}^7F_2$, $^7F_4$ transitions occur by the Judd forced electric-dipole mechanism[17] because of the mixing of odd orbital character from other electron configurations into $4f^6$. A comparison of the relative areas of the $^5D_0 \rightarrow {}^7F_2$ transition in the figures then provides a guide to the extent of this mixing and to the deviation from centrosymmetry for the complexes. Thus, it is observed that **Eu1:L1** and **Eu1:L2** are more unsymmetrical than **Eu1:L3**, which is also evident from the structures in Figure 1. In fact, the crystallographic site symmetry of Eu^{3+} in all of the complexes is C_1, but from the spectra, the approximate symmetry of **Eu1:L3** appears to involve a pseudo-3-fold axis (Figure S6). The ratios of the integrated areas $I_{TOT}/I_{^5D_0 \rightarrow {}^7F_1}$ are compiled in the second row of Table 1 from the 298 K spectra, and they are similar to those measured at 77 K.

Figure S5 shows the 298 K and 77 K luminescence decays of the $^5D_0$ emission (under 350 nm excitation) for the three complexes. The curves were fitted by monoexponential decay rates, and the observed lifetimes

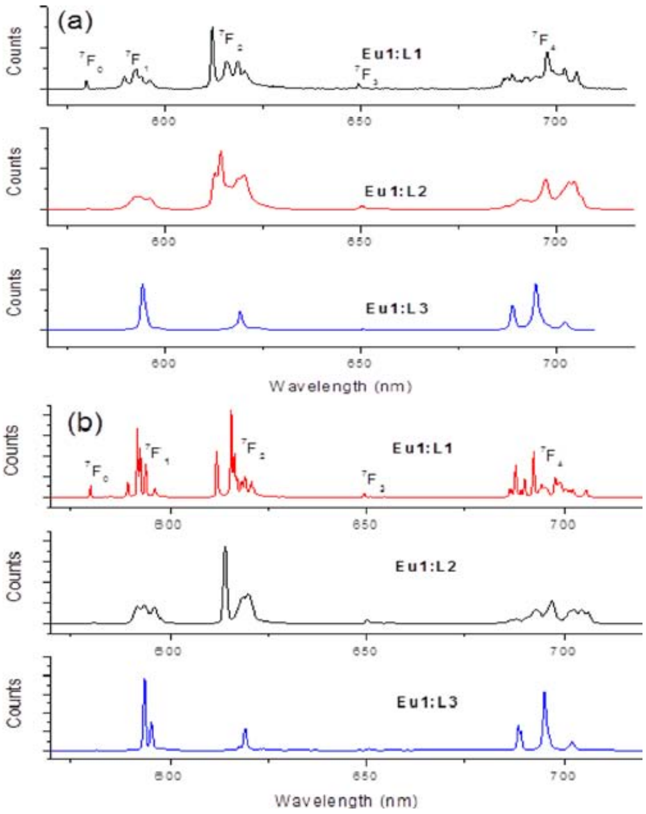

Figure 2. 298 K (a) and 77 K (b) emission spectra of europium complexes using 365 nm excitation. The ordinate is photon counts.

Table 1. Intensity and Kinetic Data for Eu1:L*x* (x = 1−3)

parameter	Eu1:L1	Eu1:L2	Eu1:L3
$I_{TOT}/I_{^5D_0\to{}^7F_1}$	7.01	8.64	3.68
$^5D_0$: $\tau_{295\ K}$ ($\tau_{77\ K}$) (ms)	0.26 (0.28)	0.81 (1.08)	2.24 (2.11)
τ_{rad} (ms)	2.38	1.93	4.54
η_{int}	0.11	0.42	0.49
Q^L_{Eu}	0.02	0.07	0.19
η_{sens}	0.18	0.17	0.39

are tabulated in row 3 of Table 1. The greatest deviation from monoexponential behavior was found for **Eu1:L2** at 77 K, so that the average lifetime has alternatively been given in this case. The values are accurate to about 10% because considerable variation with crystal quality was found. The similarity of the 298 K and 77 K lifetimes shows that nonradiative decay from $^5D_0$ exhibits a very small temperature dependence. The gap $^5D_0$−$^7F_6$ is ~12000 cm^{-1}. The gap is spanned by four quanta of the aqua intraligand stretching mode so that the calculated radiative lifetime (row 4 in Table 1: from eq 2) is most quenched for the 1:1 complex (row 5: η_{int}). The measured overall quantum efficiencies of the $^5D_0$ emission under 345 nm ligand excitation are listed in row 6, and by using eq 1, the sensitization efficiency (row 7: η_{sens}) can then be deduced. This is determined to be greatest for **Eu1:L3**.

In conclusion, three new europium complexes with the terdentate N-donor ligand 2,6-bis(1*H*-pyrazol-3-yl)pyridine have been synthesized, and their crystal structures were determined. The complexes differ in the ligand/metal ratios, which are 3, 2, and 1. By keeping factors such as the ligand−metal distance and ligand absorptivity constant, the effects of these different ratios upon the sensitization of europium luminescence have been found from spectral, kinetic, and quantum efficiency measurements.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental methods, coordination geometry, electronic spectra, luminescence decay and crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic information is available free of charge as CIF records CCDC 868403 to 868405 and 867591 from the Cambridge Crystallographic Data Centre (CCDC) via the web link www.ccdc.cam.ac.uk/ datarequest/cif.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: peter.a.tanner@gmail.com (P.A.T.), klwong@hkbu.edu.hk (K.-L.W.).

Author Contributions

‡These authors contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge financial support from the Hong Kong RGC (GRF-503510) and HKBU (FRG1/ 22611-12/034).

■ REFERENCES

(1) dos Santos, C. M. G.; Harte, A. J.; Quinn, S. J.; Gunnlaugsson, T. *Coord. Chem. Rev.* **2008**, *252*, 2512−2527.

(2) Montgomery, C. P.; Murray, B. S.; New, E. J.; Pal, R.; Parker, D. *Acc. Chem. Res.* **2009**, *42*, 925−937.

(3) Liu, G.; Jacquier, B. *Spectroscopic Properties of Rare Earths in Optical Materials*; Tsinghua University Press & Springer: Beijing and Heidelberg, 2005.

(4) Gawryszewska, P.; Sokolnicki, J.; Legendziewicz, J. *Coord. Chem. Rev.* **2005**, *249*, 2489−2509.

(5) de Sá, D. F.; Malta, O. L.; de Mello Donegá, C.; Simas, A. M.; Longo, R. L.; SantaCruz, P. A.; Silva, E. F. *Coord. Chem. Rev.* **2000**, *196*, 165−195.

(6) Freund, C.; Porzio, W.; Giovanella, U.; Vignali, F.; Pasini, M.; Destri, S. *Inorg. Chem.* **2011**, *50*, 5417−5429.

(7) Bünzli, J. C. G.; Comby, S.; Chauvin, A.-S.; Vandevyver, C. D. B. *J. Rare Earths* **2007**, *25*, 257−274.

(8) Armelao, L.; Quici, S.; Barigelletti, F.; Accorsi, G.; Bottaro, G.; Cavazzini, M.; Tondello, E. *Coord. Chem. Rev.* **2010**, *254*, 487−505. Tanner, P. A.; Duan, C.-K. *Coord. Chem. Rev.* **2010**, *254*, 3026−3029.

(9) de Silva, C. R.; Li, J.; Zheng, Z.; Corrales, L. R. *J. Phys. Chem. A* **2008**, *112*, 4527−4530.

(10) Bencini, A.; Lippolis, V. *Coord. Chem. Rev.* **2010**, *254*, 2096−2180.

(11) Bardwell, D.; Jeffery, J. C.; Jones, P. L.; McCleverty, J. A.; Psillakis, E.; Reeves, Z.; Ward, M. D. *Dalton Trans.* **1997**, 2079−2086.

(12) Latva, M.; Takalo, H.; Mukkala, V.-M.; Matachescu, C.; Rodriguez-Ubis, J. C.; Kankare, J. *J. Lumin.* **1997**, *75*, 149−169.

(13) Lin, Y.; Lang, S. A. *J. Heterocycl. Chem.* **1977**, *14*, 345−349.

(14) de Mello, J. C.; Whittmann, H. F.; Friend, R. H. *Adv. Mater.* **1997**, *9*, 230−232. Murase, N.; Li, C. *J. Lumin.* **2008**, *128*, 1896−1903.

(15) Werts, M. H. V.; Jukes, R. T. F.; Verhoeven, J. W. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1542−1548.

(16) Bünzli, J.-C. G.; Chauvin, A.-S.; Kim, H. K.; Deiters, E.; Eliseeva, S. V. *Coord. Chem. Rev.* **2010**, *254*, 2623−2633.

(17) Judd, B. R. *Phys. Rev. B* **1962**, *127*, 750−761.