Inorganic Chemistry
Communication

*Inorg. Chem.* **2010**, *49*, 2035–2037 **2035**
DOI: 10.1021/ic902481y

# Europium Complexes of a Novel Ethylenedioxythiophene-Derivatized Bis(pyrazolyl)pyridine Ligand Exhibiting Efficient Lanthanide Sensitization

**Julie M. Stanley, Xunjin Zhu, Xiaoping Yang, and Bradley J. Holliday***

*Department of Chemistry and Biochemistry and Center for Electrochemistry,*
*The University of Texas at Austin, 1 University Station, A5300, Austin, Texas 78712-0165*

Received December 14, 2009

A new class of highly luminescent nine-coordinated europium(III) tris($\beta$-diketonate) bis[(ethylenedioxythiophene)pyrazolyl]pyridine (**L**) complexes has been synthesized and the photophysical properties studied: **1** = Eu(hfac)$_3$(**L**); **2** = Eu(tta)$_3$(**L**); **3** = Eu(btfac)$_3$(**L**). The solid-state structure of complex **1** has been determined by single-crystal X-ray crystallography and shows the geometry of the local coordination environment around the Eu$^{III}$ ion to be a slightly distorted tricapped trigonal prism. Luminescence lifetimes were found to be 581, 473, and 576 $\mu$s for complexes **1**−**3**, respectively. Absolute quantum yields for complexes **1**−**3** were measured as 16.4 ± 1.4%, 27.5 ± 1.2%, and 22.2% ± 0.3%, respectively.

Luminescent lanthanide complexes have interesting photophysical properties that have been utilized in areas such as biological probes and sensors, fluoroimmunoassays, and emitting layers in polymer light-emitting diodes.[1−4] Shielding of the *f* orbitals by the $5s^2$ and $5p^6$ shells results in narrow linelike emissions of optically pure colors and long radiative lifetimes. However, the *f*−*f* transitions that result in light emission from the lanthanide are spin- and parity-forbidden, thus requiring the use of antenna molecules to indirectly excite the metal center.[5]

This indirect excitation, also known as the antenna effect, takes advantage of coordinated ligands that transfer energy from ligand-centered excited states to the metal center, resulting in lanthanide ion luminescence. In 1942, Weissmann observed that the use of organic ligands in europium complexes increased the luminescence intensity from the lanthanide ion when the complexes were irradiated with ultraviolet (UV) light.[6] Ideal ligands, also referred to as sensitizers, include multidentate, aromatic chromophores that maximize the efficiency of the energy-transfer process, which is crucial in the development of systems that result in high quantum yields from lanthanide-centered emission. For this to occur, the energy of the excited state of the ligand must be greater than, but of similar energy to (within 2000 cm$^{-1}$), that of the lanthanide excited state.[7] Other important factors in accomplishing efficient energy transfer include limitation of the nonradiative energy loss and maximization of the population of the triplet excited state of the sensitizing ligand.[5]

Seminal work by de Bettencourt-Dias on the functionalization of the sensitizing ligands with thiophene and thiophene derivatives[7−10] has demonstrated a decrease in the energy level of the triplet state of the ligand and an increase in the luminescence quantum yield when these groups are present. These effects are attributed to the increased conjugation of the system and the enhanced spin−orbit coupling due to the presence of sulfur atoms, known as the heavy-atom effect.[5,11] The net result is an improved match between the ligand triplet excited state and the excited state of the lanthanide ion and an increase in the population of the ligand triplet excited state, which results in a more efficient energy-transfer process and higher quantum yields of lanthanide luminescence.

For our systems, we developed and synthesized a new class of luminescent compounds consisting of europium(III) tris($\beta$-diketonate) 2,6-bis[4-(3,4-ethylenedioxythien-2-yl)pyrazol-1-yl]pyridine (**L**) complexes in which the bis[(3,4-ethylenedioxythiophene)pyrazolyl]pyridine moiety serves as the metal binding site. The organic backbone is an aromatic, tris-chelating ligand bound to the lanthanide ion through the nitrogen atoms of the pyridine and pyrazole rings. The inclusion of three anionic $\beta$-diketonate ligands brings the coordination number of the trivalent europium complex to

---

*To whom correspondence should be addressed. E-mail: bholliday@cm.utexas.edu.

(1) *Lanthanide Probes in Life, Chemical and Earth Sciences—Theory and Practice*; Bünzli, J.-C. G., Choppin, G. R., Eds.; Elsevier: Amsterdam, The Netherlands, 1989.

(2) Faulkner, S.; Natrajan, L. S.; Perry, W. S.; Sykes, D. *Dalton Trans.* **2009**, 3890–3899.

(3) de Bettencourt-Dias, A. *Dalton Trans.* **2007**, 2229–2241.

(4) Bünzli, J.-C. G. *Chem. Lett.* **2009**, *38*, 104–109.

(5) Bünzli, J.-C. G.; Piguet, C. *Chem. Soc. Rev.* **2005**, *34*, 1048–1077.

(6) Weissmann, S. I. *J. Chem. Phys.* **1942**, *10*, 214–217.

(7) de Bettencourt-Dias, A. *Inorg. Chem.* **2005**, *44*, 2734–2741.

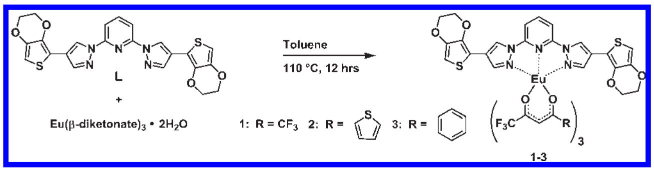
(8) de Bettencourt-Dias, A.; Viswanathan, S.; Ruddy, K. *Cryst. Growth Des.* **2005**, *5*, 1477–1483.

(9) Viswanathan, S.; de Bettencourt-Dias, A. *Inorg. Chem.* **2006**, *45*, 10138–10146.

(10) de Bettencourt-Dias, A.; Viswanathan, S.; Rollett, A. *J. Am. Chem. Soc.* **2007**, *129*, 15436–15437.

(11) Sager, W. F.; Filipescu, N.; Serafin, F. A. *J. Phys. Chem.* **1965**, *69*, 1092–1100.

**Scheme 1.** Synthesis of **1**−**3**



nine. This architecture provides a rigid environment around the europium ion, helping to limit nonradiative deactivation pathways and exclude solvent interactions that can lead to the quenching of lanthanide luminescence.[5] The exclusion of water is extremely important for lanthanide complexes because luminescence from the excited state is easily quenched by the harmonics of the O−H oscillator.[5] Our approach involves the coupling of 3,4-ethylenedioxythiophene (EDOT) to bis(pyrazolyl)pyridine in order to optimize the match between the ligand triplet excited state and the excited state of the Eu$^{III}$ ion by taking advantage of the extended conjugation resulting from the addition of the thiophene derivative and the increased electron richness of EDOT over that of thiophene alone. In addition, the sulfur atoms present in EDOT induce greater spin−orbit coupling because of the heavy-atom effect, resulting in a higher population of the ligand triplet state and a more efficient energy transfer to the metal center. Herein we report the synthesis, characterization, and photophysical properties of three nine-coordinated trivalent europium complexes: Eu(hfac)$_3$(**L**) (**1**; hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate); Eu(tta)$_3$(**L**) (**2**; tta = 2-thenoyltrifluoroacetonate); Eu(btfac)$_3$(**L**) (**3**; btfac = 4,4,4-trifluoro-1-phenyl-1,3-butanedionate).

The title ligand, **L**, was synthesized by Stille coupling of 2,6-bis(4-iodopyrazol-1-yl)pyridine and 2-(tributylstannyl)-3,4-ethylenedioxythiophene in the presence of Pd(PPh$_3$)$_2$Cl$_2$ and was characterized by melting point, $^1$H NMR, electrospray ionization mass spectrometry (ESI-MS), and elemental analysis. Complexes **1**−**3** were prepared by reacting **L** and the appropriate europium(III) tris(β-diketonate) dihydrate in toluene (Scheme 1) and were characterized by melting point, ESI-MS, and elemental analysis.

The solid-state structure of **1** was confirmed by single-crystal X-ray crystallography (Figure 1A).[12] The geometry around the nine-coordinated Eu$^{III}$ ion is a slightly distorted tricapped trigonal prism in which the metal ion lies at the center (Figure 1B). It is defined by six oxygen atoms from the β-diketonate ligands and three nitrogen atoms from **L**. The average Eu$^{III}$−N and Eu$^{III}$−O bond distances are 2.600 and 2.412 Å, respectively, and fall within the ranges [2.52−2.68 Å (Eu$^{III}$−N) and 2.31−2.50 Å (Eu$^{III}$−O)] reported for similar structures.[13−16]

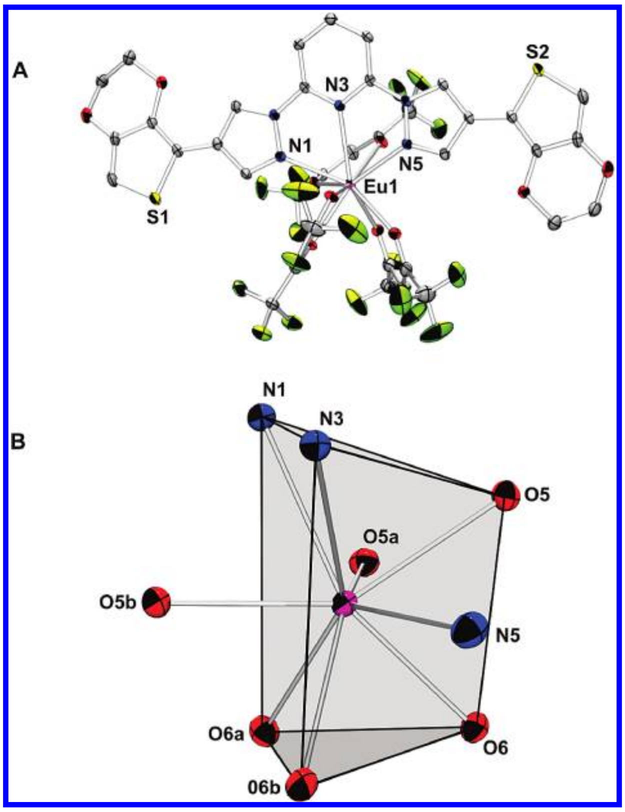


**Figure 1.** (A) ORTEP diagram of **1** showing the labeling scheme of selected atoms at a 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Eu1−O6 2.362(3), Eu1−O5b 2.395(3), Eu1−O5a 2.411(3), Eu1−O6b 2.412(3), Eu1−O6a 2.423(3), Eu1−O5 2.481(3), Eu1−N1 2.559(4), Eu1−N5 2.563(4), Eu1−N3 2.630(4); N1−Eu1−N5 118.74(12), N1−Eu1−N3 61.21(11), N5−Eu1−N3 60.71(12), O6−Eu1−N1 145.89(11), O5b−Eu1−N1 68.98(11), O5a−Eu1−N1 70.70(11), O6b−Eu1−N1 138.34(11), O6a−Eu1−N1 107.05(12), O5−Eu1−N1 81.91(11), O6−Eu1−N5 75.40(12), O5b−Eu1−N5 107.05(12), O5a−Eu1−N5 139.69(12), O6b−Eu1−N5 66.62(12), O6a−Eu1−N5 131.17(12), O5−Eu1−N5 73.47(12), O6−Eu1−N3 134.29(11), O5b−Eu1−N3 70.13(12), O5a−Eu1−N3 127.07(11), O6b−Eu1−N3 97.08(11), O6a−Eu1−N3 144.87(11), O5−Eu1−N3 82.92(11). (B) Coordination environment around Eu$^{III}$ in **1**.

**Table 1.** Photophysical Properties of **L** and Europium(III) Complexes **1**−**3** in CH$_2$Cl$_2$ at Room Temperature

| compound | $\lambda_{ex}$ (nm) | $\Phi_{fl}$ (%) | $\Phi_{Eu^{III}}$ (%) | $\tau$ (μs) |
|---|---|---|---|---|
| **L** | 339 | 29.2 ± 1.3 | | |
| **1** | 332 | 6.1 ± 0.7 | 16.4 ± 1.4 | 581 |
| **2** | 343 | 0.8 ± 0.3 | 27.5 ± 1.2 | 473 |
| **3** | 330 | 1.4 ± 0.4 | 22.2 ± 0.3 | 576 |

The photophysical properties of **L** have been studied in solution and under a variety of conditions, the details of which have been summarized in Table 1. At room temperature (Figure 2A), the absorption spectrum closely follows the excitation spectrum and displays a broad band ($\lambda_{max}$ = 339 nm) that is red-shifted compared to that of 2,6-bis(pyrazol-1-yl)pyridine ($\lambda_{max}$ = 304 nm) because of the extended conjugation caused by the presence of the EDOT moieties. The emission spectrum displays a broad band ($\lambda_{max}$ = 378 nm) corresponding to ligand fluorescence, confirmed by a small Stokes shift and a short excited-state lifetime. Upon cooling to 77 K in a solvent glass, an increase in the emission intensity and the presence of a previously absent vibrational structure can be seen. These observations are attributed to the reduction of thermal nonradiative pathways available for energy loss. Ligand phosphorescence is seen (Figure 2B) from 484 to 650 nm, and the energy of the ligand triplet state is measured as 20 700 cm$^{-1}$, which is 3700 cm$^{-1}$ greater than that of the

---

[12] Crystal data for **1**: C$_{38}$H$_{20}$EuF$_{18}$N$_5$O$_{10}$S$_2$, $M$ = 1264.67, triclinic, space group $P\bar{1}$, $a$ = 13.175(3) Å, $b$ = 13.625(3) Å, $c$ = 14.527(3) Å, α = 68.77(3)°, $\beta$ = 78.73(2)°, $\gamma$ = 68.60(2)°, $V$ = 2257.1(8) Å$^3$, $Z$ = 2, $D_{calcd}$ = 1.861 g cm$^{-3}$, $\mu$ = 1.618 mm$^{-1}$, $T$ = 153(2) K, R1 = 0.0418, R2 = 0.1014.

[13] Holz, R. C.; Thompson, L. C. *Inorg. Chem.* **1988**, *27*, 4640–4644.

[14] De Silva, C. R.; Wang, R.; Zheng, Z. *Polyhedron* **2006**, *25*, 3449–3455.

[15] Li, X.-L.; Dai, F.-R.; Zhang, L.-Y.; Zhu, Y.-M.; Peng, Q.; Chen, Z.-N. *Organometallics* **2007**, *26*, 4483–4490.

[16] Ziessel, R.; Diring, S.; Kadjane, P.; Charbonnière, L.; Retailleau, P.; Philouze, C. *Chem. Asian J.* **2007**, *2*, 975–982.

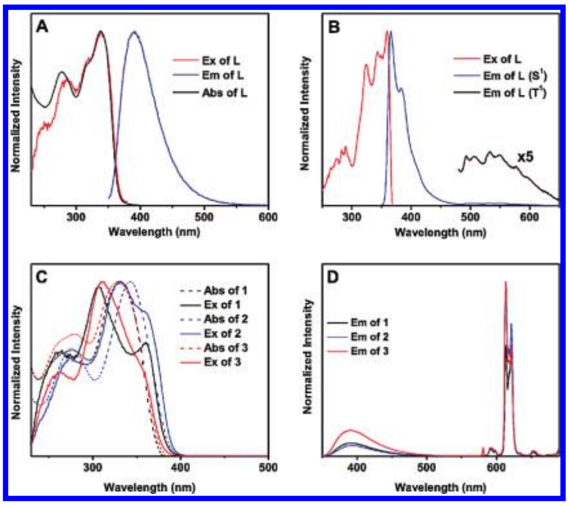


**Figure 2.** (A) Excitation, emission, and absorption spectra of **L** at room temperature in $CH_2Cl_2$. (B) Excitation, emission, and absorption spectra of **L** at 77 K in 2-methyltetrahydrofuran. (C) Excitation and absorption spectra of **1**−**3** at room temperature in $CH_2Cl_2$. (D) Emission spectra of **1**−**3** at room temperature in $CH_2Cl_2$.

$Eu^{III}$ $^5D_0$ excited state (17 000 $cm^{-1}$).[17] Although the energy difference is slightly higher than the optimal value previously reported,[7,18] the probability of an efficient energy transfer from the ligand to the metal center is still high.

The photoluminescent properties of complexes **1**−**3** have been studied and are summarized in Table 1. Each of the complexes is highly luminescent as a solid and in solution, emitting a bright-red color when irradiated with a hand-held UV lamp ($\lambda_{ex}$ = 365 nm). The absorption spectra of complexes **1**−**3** are similar to that of the free ligand (**L**), with the minor differences being attributed to contributions from the bound $\beta$-diketonate ligands (Figure 2C). Through monitoring of the emission intensity at 612 nm with varied excitation wavelengths, the excitation spectrum was recorded. The excitation profile of each complex closely mimics that of its corresponding absorption spectrum, demonstrating that energy transfer occurs from **L** and the $\beta$-diketonate ligands to the $Eu^{III}$ ion. The emission profiles of complexes **1**−**3** display a broad band from 350 to 500 nm due to residual ligand fluorescence and characteristic sharp peaks of $^5D_0 \rightarrow {}^7F_{0-4}$ transitions of the $Eu^{III}$ ion from 575 to 725 nm (Figure 2D). The symmetry of the coordination environment around the $Eu^{III}$ ion is low in solution, which is consistent with the X-ray crystal structure and confirmed by the domination of the spectra by the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition. The absence of splitting in the $^5D_0 \rightarrow {}^7F_0$ transition indicates that there is only one local symmetry environment around the $Eu^{III}$ ion present.[19] Absolute quantum yields of **L** and complexes **1**−**3** were measured using an integrating sphere (Table 1). We speculate that the observed trends in $\Phi$ and $\tau$ over the series of **1**−**3** are due to a combination of interrelated effects (e.g., cooperative heavy atom effect, relative energy levels, ligand $\varepsilon$) but dominated by the relative $\beta$-diketonate and $Eu^{III}$ excited-state energies. The trend of longer excited-state lifetime and lower absolute quantum yield with the larger energy gap ($\Delta E$) between the $\beta$-diketonate and the $Eu^{III}$ ion is borne out in **1**−**3** [$\Delta E$ ($\times 10^3$ $cm^{-1}$): **1**(hfac) = 5.0, **2**(tta) = 3.5, **3**(btfac) = 4.5].[20,21] The observed quantum yields fall within the ranges of thiophene-containing $Eu^{III}$ complexes previously reported: 0.1−3.6%,[7] 0.9−3.1%,[9] and 76.2%.[10]

In summary, we have demonstrated the design, synthesis, and characterization of a new class of highly luminescent lanthanide complexes that utilize a 2,6-bis(pyrazol-1-yl)-pyridine ligand functionalized with 3,4-ethylenedioxythiophene in conjunction with $\beta$-diketones to indirectly excite the europium metal center. These complexes show high quantum yields and long radiative lifetimes, supporting the general hypothesis that incorporation of thiophene, and thiophene derivatives, into sensitizing ligands promotes the enhancement of energy-transfer pathways that lead to lanthanide ion radiative emission. This is important to the expansion of the utilization of these and other similar complexes in biomedical and materials science applications. Previous work has demonstrated that similar compounds may be used to make thin films via electropolymerization.[22] Future efforts will be focused in similar directions.

**Acknowledgment.** We gratefully acknowledge the Robert A. Welch Foundation (Grant F-1631), the Petroleum Research Fund administered by the American Chemical Society (47022-G3), the National Science Foundation (Grants CHE-0639239, CHE-0741973, and CHE-0847763), the American Heart Association (Grant 0765078Y), the Center for Nano & Molecular Science & Technology at The University of Texas at Austin for financial support of this research.

**Supporting Information Available:** Experimental details for the syntheses of **L** and **1**−**3**, details of photophysical measurements, X-ray diffraction tables, and crystallographic data for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(17) Lanaerts, P.; Görller-Walrand, C.; Binnemans, K. *J. Lumin.* **2006**, *117*, 163–169.

(18) Meshkova, S. B.; Topilova, Z. M.; Bol'shoi, D. V.; Nazarenko, N. A. *J. Appl. Spectrosc.* **2000**, *67*, 893–897.

(19) Carlos, L. D.; Videira, A. L. L. *Phys. Rev. B* **1994**, *49*, 11721–11728.

(20) Klink, S. I.; Hebbink, G. A.; Grave, L.; Oude Alink, P. G. B.; van Veggel, F. C. J. M.; Werts, M. H. V. *J. Phys. Chem. A* **2002**, *106*, 3681–3689.

(21) Lenaerts, P.; Driesen, K.; Van Deun, R.; Binnemans, K. *Chem. Mater.* **2005**, *17*, 2148–2154.

(22) Chen, X.-Y.; Yang, X.; Holliday, B. J. *J. Am. Chem. Soc.* **2008**, *130*, 1546–1547.