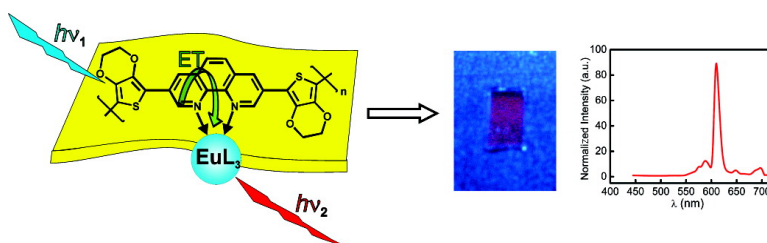


Photoluminescent Europium-Containing Inner Sphere Conducting Metallopolymer

Xiao-Yan Chen, Xiaoping Yang, and Bradley J. Holliday

J. Am. Chem. Soc., **2008**, 130 (5), 1546-1547 • DOI: 10.1021/ja077626a

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 2 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Photoluminescent Europium-Containing Inner Sphere Conducting Metallopolymer

Xiao-Yan Chen, Xiaoping Yang, and Bradley J. Holliday*

Department of Chemistry and Biochemistry and Center for Nano and Molecular Science and Technology,
The University of Texas at Austin, 1 University Station, A5300, Austin, Texas 78712-0165

Received October 3, 2007; E-mail: bholliday@cm.utexas.edu

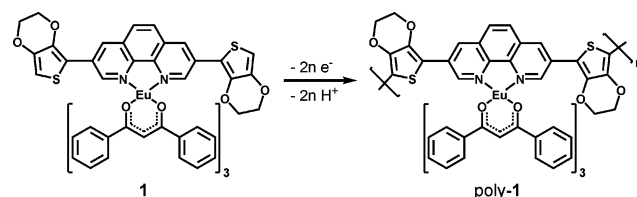
The development of light-emitting materials for solid-state lighting applications has been a topic of intense research activity in recent years.¹ Polymer light-emitting diodes (PLEDs), in particular, have been studied extensively since the first fabrication of a functioning diode utilizing a conjugated polymer as the electroluminescent material in 1990.² Compared to inorganic electroluminescent materials, polymer materials have several attractive features including mechanical strength, flexibility, ease of processing, and the potential to be of low cost.³

While many advances have been made, long-standing issues including limited lifetime, low quantum efficiencies, and poor color purity continue to plague many conjugated polymer materials/devices. For example, high photoluminescence efficiencies (>50%) often do not translate into high PLED electroluminescence efficiencies (<5%) due to formation of non-emissive triplet excitons.⁴ Additionally, obtaining high color purity from organic polymer materials is difficult due to broad emission peaks.⁵ These drawbacks of conjugated polymers have triggered efforts to use lanthanide ions as the emissive materials in PLEDs.⁶ If successful, the energy of the singlet and triplet excited states can be harvested to excited states of the *f* orbitals of the lanthanide ions and subsequently generate light. In theory, internal efficiencies of 100% should thus be possible. In addition, lanthanide metal ions exhibit extremely sharp emission bands due to the shielding of the 4*f* orbitals by the 5*s* and 5*p* shells.

Seminal work in this area has primarily focused on polymer systems doped or blended with lanthanide complexes.⁶ However, blending may not always give rise to uniformly dispersed and thermodynamically stable compositions. A more effective, but much less explored, approach involves the covalent coupling of a lanthanide complex to a polymer backbone.⁷ This route rules out phase separation or aggregation during device processing/operation. Furthermore, energy transfer in a covalently bound system is anticipated to be more efficient due to the close proximity of the two components. Despite such encouraging premises, only non-conducting polymers with the lanthanide complex linked as a pendant unit have been explored.⁷ Conducting polymers have been used in many device applications including electrical conductors, nonlinear optical devices, sensors, batteries, and memory devices and should therefore offer advantages in electroluminescent applications. Herein, we report the first example of a new class of photoluminescent conducting metallopolymers with direct electronic communication between the metal center and the polymer backbone.

Our approach to the development of solid-state light-emitting materials involves the design and synthesis of well-defined conducting metallopolymers that incorporate lanthanide complexes in an inner sphere, or Wolf Type II, fashion (Scheme 1).⁸ As such, we aim to take full advantage of the properties of both components with high efficiency due to the direct electronic interface this configuration creates. To accomplish this goal, the new ligand, 3,8-bis(3,4-(ethylenedioxy)thien-2-yl)-1,10-phenanthroline (**L**) in which

Scheme 1. Electrochemical Polymerization of Europium-Containing Monomer to Conducting Metallopolymer



the 1,10-phenanthroline (Phen) moiety serves as a metal binding group and 3,4-(ethylenedioxy)thiophene (EDOT) as a polymerizable group, was prepared. Additionally, we have chosen europium(III) for our initial studies considering the ease of characterization of the pure red europium emission provides (~615 nm) and the rich literature base on this class of emissive metal complexes.⁹

The europium β -diketonate complex $\text{Eu}(\text{DBM})_3(\text{H}_2\text{O})_2$, where DBM = dibenzoylmethanido, was covalently linked to the nitrogen donors from the Phen moiety of **L** to form monomer **1** (Scheme 1). This complex has been fully characterized by ¹H and ¹³C NMR spectroscopy, mass spectrometry, combustion analysis, and single-crystal X-ray diffraction (Figure 1). The molecular structure of **1** (Figure 1) is the first reported structure of a complex containing both a lanthanide ion and EDOT electropolymerizable units. The eight-coordinate Eu(III) ion lies at the center of a slightly distorted square antiprism that is defined by the six oxygen atoms from the DBM ligands and the two nitrogen atoms from **L**. The Eu–N_{av} bond distance (2.577(4) Å) is longer than the Eu–O_{av} bond distance (2.330(3) Å). This trend and these bond distances are consistent with the data of the complex $\text{Eu}(\text{DBM})_3\text{Phen}$ (Eu–N_{av} 2.656 Å; Eu–O_{av} 2.359 Å).¹⁰

Monomer **1** has been electropolymerized to form poly-**1** (Scheme 1) as an electrode-confined film onto a variety of working electrode surfaces (Supporting Information). Cyclic voltammetry of **1** over a window of +1.25 to –1.25 V (vs Fc/Fc⁺) resulted in the growth of a polymer film that has a reversible wave with $E_{1/2} = -0.55$ V. The first scan exhibits two oxidative peaks at *i*_p of ~0.4 and 1.0 V whose positions steadily become more positive with increasing

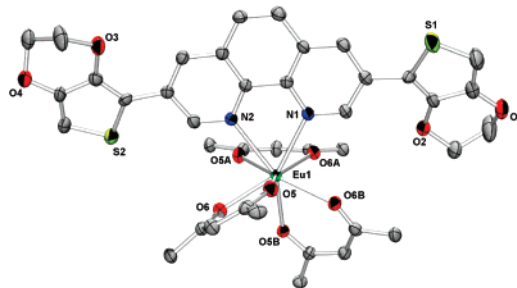


Figure 1. ORTEP diagram of **1** showing the labeling scheme of selected atoms at 30% probability level. Hydrogen atoms, solvent molecules, and phenyl rings of the dibenzoylmethanido ligands are omitted for clarity.

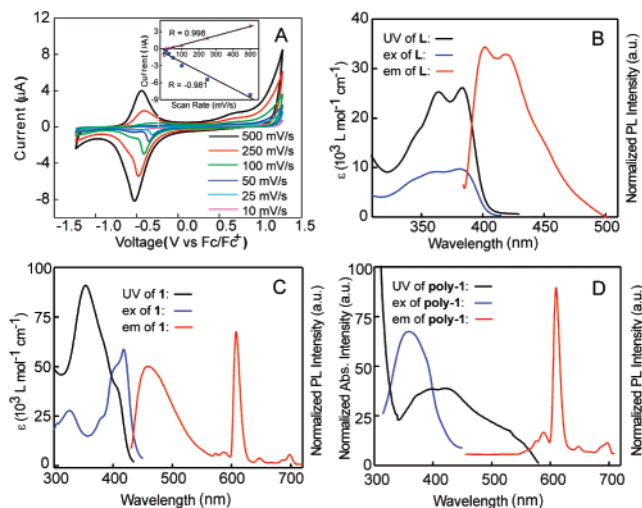


Figure 2. (A) Electrochemical scan rate dependence of poly-1 (Fc/Fc^+ is the redox couple of ferrocene). Inset: plot of linear current increase versus scan rate. (B) Photophysical properties of **L** recorded in CH_2Cl_2 at room temperature. (C) Photophysical properties of **1** recorded in CH_2Cl_2 at room temperature. (D) Photophysical properties of poly-1 recorded as a thin film on ITO coated glass at room temperature. UV = absorbance profile, ex = excitation profile, and em = emission profile.

scans (Figure S1). The resulting electroactive polymer films were characterized using electrochemical methods (Figure 2A), UV-vis spectroscopy (Figure 2D), and X-ray photoelectron spectroscopy (XPS). As shown in Figure 2A, the peak current of an electrodeposited film of poly-1 in pure electrolyte solution varies linearly with the rate of the electrochemical scan up to 500 mV/s. This behavior is indicative of a strongly adsorbed electroactive thin film which is not limited by the ionic flux of counteranions. The XPS data were used to determine the film composition and metal coordination environment (Supporting Information). The $\text{Eu } 3d_{3/2}$ and $\text{Eu } 3d_{5/2}$ peaks are observed at 1165.2 and 1135.2 eV, respectively, corresponding well to the expected values for Eu(III) bound to oxygen.¹¹ The $\text{S } 2p$ peak is also found at 164.3 eV. Quantitative XPS analysis reveals that the film has an atomic ratio of $\text{Eu}:\text{S} = 1:1.85$, which is in agreement with the stoichiometric molar ratio of the monomer (1:2.03 by XPS) and proposed film structure.

The photophysical properties of **L**, **1**, and poly-1 have been studied under a variety of conditions (Figure 2B–D). The absorption spectrum of **L** (Figure 2B) displays a broad band with some vibronic structure from 325 to 400 nm ($\lambda_{\text{max}} = 365$), which is red shifted compared to Phen ($\lambda_{\text{max}} = 290$ nm) due to the extended conjugation. Furthermore, the emission and excitation spectra are consistent with fluorescence emission ($\Phi_{\text{fl}} = 0.40$) from the direct population of the singlet excited state. The absorption maximum of **1** at 353 nm and the shoulder around 405 nm are attributed to the combination of the singlet–singlet $\pi-\pi^*$ transitions of the DBM and **L** ligands (Figure 2C). Upon selective excitation at 420 nm, the emission profile of **1** displays two distinct features: a broad band centered at 460 nm, residual fluorescence from the coordinated ligands, and the characteristic sharp peaks associated with the $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$ transitions of the Eu(III) ion between 575 and 700 nm (Figure 2C). The excitation spectrum of **1** was recorded while monitoring the emission intensity at 610 nm. The observed transitions correspond to the absorption profile of the combined $\pi-\pi^*$ transitions of the ligands at 405 nm thus confirming that energy transfer takes place from the ligands to the Eu(III) ion. The overall luminescent quantum yields for the emission from the Eu(III) ion and the coordinated ligands in **1** in CH_2Cl_2 are 0.11 and 0.21, respectively.

Figure 2D shows the photophysical profiles of a film of poly-1 deposited on ITO-coated glass. The absorption spectrum displays a very broad redox-dependent band characteristic of the extended aromatic system of a conducting metallopolymer structure which is red shifted from that of **L** and **1**. The emission spectrum measured with 375 nm as the excitation wavelength is characteristic of Eu(III) emission. The five expected components of the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions are well-resolved and the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition dominates the spectrum. This is indicative of a low-symmetry coordination environment around the Eu(III). Most notably, poly-1, shows *exclusively* the Eu(III)-centered $^5\text{D}_0 \rightarrow ^7\text{F}_j$ emission bands, and the ligand emission from the organic backbone completely disappears, presumably indicating more efficient energy transfer. The excitation spectrum of poly-1 is less broad and blue shifted relative to the absorption spectrum, suggesting that the energy transfer takes place from a localized excited state. This is consistent with energy transfer from the Phen portion of the polymer backbone to the Eu(III).

In summary, we have demonstrated the synthesis of the first photoluminescent lanthanide conducting metallopolymer. This structure, which displays pure metal-based photoluminescence via stimulated excitation, is assembled from a well-characterized europium-containing monomer via controlled electropolymerization. These results bode well for the development of high color purity PLEDs from this new class of materials. Furthermore, this approach represents a novel perspective on the use of luminescent conducting metallopolymer for a wide range of light-emitting applications.

Acknowledgment. We gratefully acknowledge the Welch Foundation (F-1631), the PRF/ACS (47022-G3), the THECB (ARP 003658-0010-2006), the UT-CNM and UT-Austin for financial support.

Supporting Information Available: Experimental details for the synthesis and characterization of **L**, **1**, and poly-1; electrochemical and spectroscopic details; X-ray diffraction tables; and crystallographic data for **1** (.cif). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) *Emissive Materials: Nanomaterials*; Advances in Polymer Science 199; Springer: Berlin, 2006 and references therein.
- (2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; MacKay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
- (3) (a) Forrest, S. R. *Nature* **2004**, *428*, 911. (b) Gustafsson, G.; Cao, Y.; Treasy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.
- (4) Segal, M.; Baldo, M. A.; Holmes, R. J.; Forrest, S. R.; Soos, Z. G. *Phys. Rev. B* **2003**, *68*, 075211/1.
- (5) Kido, J.; Okamoto, Y. *Chem. Rev.* **2002**, *102*, 2357.
- (6) (a) de Bettencourt-Dias, A. *Dalton Trans.* **2007**, 2229. (b) Zhang, T.; Xu, Z.; Qian, L.; Tao, D. L.; Teng, F.; Gao, X.; Xu, X. R. *Chem. Phys. Lett.* **2005**, *415*, 30. (c) Kang, T. S.; Harrison, B. S.; Foley, T. J.; Kniefely, A. S.; Boncella, J. M.; Reynolds, J. R.; Schanze, K. S. *Adv. Mater.* **2003**, *15*, 1093. (d) Kang, T. S.; Harrison, B. S.; Bouguettaya, M.; Foley, T. J.; Boncella, J. M.; Schanze, K. S.; Reynolds, J. R. *Adv. Funct. Mater.* **2003**, *13*, 205. (e) McGehee, M. D.; Bergstedt, T.; Zhang, C.; Saab, A. P.; O'Regan, M. B.; Bazan, G. C.; Srdanov, V. I.; Heeger, A. J. *Adv. Mater.* **1999**, *11*, 1349.
- (7) (a) Ling, Q.; Yang, M.; Wu, Z.; Zhang, X.; Wang, L.; Zhang, W. *Polymer* **2001**, *42*, 4605. (b) Lenarets, P.; Storms, A.; Mullens, J.; D'Haen, J.; Görrler-Walrand, C.; Binnemans, K.; Driesen, K. *Chem. Mater.* **2005**, *17*, 5194.
- (8) (a) Wolf, M. O. *J. Inorg. Organomet. Polym. Mater.* **2006**, *16*, 189. (b) Holliday, B. J.; Swager, T. M. *Chem. Commun.* **2005**, 23.
- (9) *Modern Aspects of Rare Earths and Their Complexes*; Sastri, V. S., Bünzli, J.-C., Rao, V. R., Rayudu, G. V. S., Perumareddi, J. R., Eds.; Elsevier: Amsterdam, 2003.
- (10) Ahmed, M. O.; Liao, J. L.; Chen, X.; Chen, S. A.; Kaldis, J. H. *Acta Crystallogr.* **2003**, *E59*, m29.
- (11) Mercier, F.; Alliot, C.; Bion, L.; Thromat, N.; Toulhoat, P. *J. Electron Spectrosc. Relat. Phenom.* **2006**, *150*, 21.

JA077626A