J|A|C|S
COMMUNICATIONS

Site-Isolated Luminescent Europium Complexes with Polyester Macroligands: Metal-Centered Heteroarm Stars and Nanoscale Assemblies with Labile Block Junctions

Jessica L. Bender,[†] Perry S. Corbin,[†] Cassandra L. Fraser,*,[†] David H. Metcalf,[†]
Frederick S. Richardson,[†] Edwin L. Thomas,[‡] and Augustine M. Urbas[‡]

Department of Chemistry, University of Virginia, McCormick Road, P.O. Box 400319, Charlottesville, Virginia 22904-4319, and Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received March 7, 2002

Luminescent block copolymers with selectively positioned chromophores are prepared in a single step by chelation of dibenzoylmethane and bipyridine macroligands to europium(III) ions. Placement of metals at the block junction in the molecular architecture implies localization of metals at microdomain boundaries upon self-assembly into hierarchically structured composites. Many lanthanide complexes are noted for their luminescence arising from f−f transitions generated by direct metal excitation, or more commonly via the “antenna effect”, namely, energy transfer from ligand excited states to the metal.[1] Europium-based systems are of special interest for optical excitation and emission studies because they exhibit high luminescent quantum efficiencies, and the details of Eu(III) (4f−4f) excitation and emission spectra and excited state reaction kinetics are particularly sensitive to structural details of the coordination environment. These features have been exploited in biological contexts—e.g., in time-resolved fluoroimmunoassays[2] and structural probes[1a]—and also make lanthanide chromophores (Eu, red; Tb, green) the focus of organic light emitting diode (OLED) materials for new display technologies.[3] To facilitate processing and to enhance properties, it is advantageous to “package” luminophores in polymer shells.[4] Metal site isolation in polymer matrixes may prevent self-quenching and inhibit ready access by small molecules such as water, which dissipates energy nonradiatively through OH stretching modes. Self-assembly of inorganic/organic composites, selective positioning of functionality on small length scales, and the ability to respond to environmental stimuli and transition between distinct states are attractive features for advanced materials.[5] A molecular design that shows much promise for addressing these challenges is described.

One class of ligands that has figured prominently in both fundamental studies and applications development involving lanthanides is the β-diketonates.[6] Numerous derivatives are known and steric and electronic properties are easily modified by modular syntheses. Tris(dibenzoylmethane)Eu(III) and other β-diketonate complexes are common[7] and easily produced by reaction of the ligand with $EuCl_3$ in the presence of a base (e.g., Et_3N). For extension to a polymeric analogue, dibenzoylmethane was functionalized with a hydroxyl site (dbmOH, **1**) for generating a biocompatible poly(lactic acid) macroligand (dbmPLA, **2**; M_n(NMR) = 8.4 kDa; M_w(MALLS) = 7.0 kDa, PDI = 1.12) by tin-catalyzed ring opening polymerization (Figure 1).[8] A Eu(III) complex, Eu(dbmPLA)$_3$, **3**, was prepared by using a mixed solvent system to accommodate both the metal salt and the polymer.

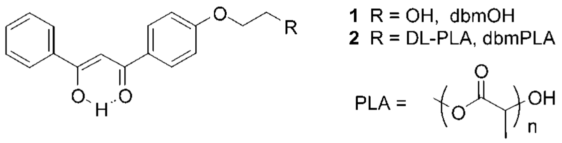

Figure 1. Dibenzoylmethane initiator **1** and PLA macroligand **2**.

As a preliminary screen of sample homogeneity and luminescence properties, unpolarized emission spectra (Figure 2a) and lifetime data (Table 1) were recorded for Eu(dbmPLA)$_3$ (**3**) and Eu(dbm)$_3$, for comparison. Analysis of the emission decay for these species reveals both short and longer lifetime components. Given the Lewis acidity of six-coordinate Eu(III) dbm complexes and the variety of Lewis basic groups in the reaction medium, there are many plausible explanations for the multiple species that are observed. Residual solvent (H_2O, CH_3OH), hydroxyl groups on the polymer chain ends, or other oxygen donors on the main chain could serve as donor ligands (Figure 2a, X), increasing the coordination number of certain Eu centers and perhaps shortening their luminescence lifetimes. Interestingly, the relative weighting of the longer lifetime component (Table 1, RW$_2$) is greater for polymeric complex **3** relative to Eu(dbm)$_3$, and for films versus solutions of **3**. The previously noted polymer shell effect may explain these observations.[4]

Because lanthanide tris(dbm) complexes readily form higher coordinate adducts with additional donor ligands,[7,9] they are an ideal platform for metal template assisted block copolymer synthesis. Provided that traditional coordination chemistry extends to polymeric ligands, when two different kinds of macroligands (e.g., dbm and bpy[10]) are combined with lanthanide salts, heteroarm stars with metals at the block junction can form in a single step. In films, these systems are expected to form nanoscale assemblies with metals at the microdomain interfaces, presenting new possibilities for photonic materials in optical information processing.[11] Moreover, because Eu and other lanthanides are labile metals, facile ligand dissociation can cause the block copolymer to fragment at the block junction.[12] For films, this implies a transition from microstructured materials to macrophase-separated homopolymer blends (i.e., of Eu(dbmA)$_3$ and bpyB$_2$) in the affected regions.

To test these ideas, namely, if metal-centered heteroarm star block copolymers and their nanostructured films can be produced, and whether changes at the molecular level can be transmitted to assembly structures, the five-arm heteroarm star Eu(dbmPLA)$_3$-

---

* Author to whom correspondence should be addressed. E-mail: fraser@virginia.edu.
[†] University of Virginia.
[‡] Massachusetts Institute of Technology.

10.1021/ja0261269 CCC: $22.00

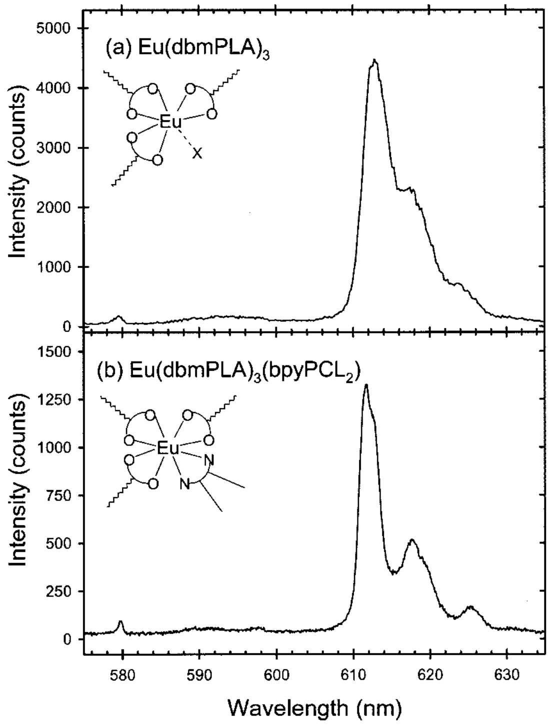

Figure 2. Emission spectra for (a) Eu(dbmPLA)$_3$ **3** and (b) Eu(dbmPLA)$_3$(bpyPCL$_2$) **4** in CH_2Cl_2 solution (excitation λ: 465.8 nm).

Table 1. Luminescence Lifetimes[a] (τ_1 and τ_2) for Europium Dibenzoylmethane Complexes and Their Bipyridine Adducts

complex	τ_1 (ms)	RW$_1$[b] (%)	τ_2 (ms)	RW$_2$[b] (%)
Eu(dbm)$_3$	0.021	86	0.302	14
Eu(dbmPLA)$_3$ (**3**)	0.108	52	0.349	48
Eu(dbmPLA)$_3$[c] (**3**) film	0.119	13	0.371	87
Eu(dbm)$_3$(bpy)	0.102	100		
Eu(dbmPLA)$_3$(bpyPCL$_2$) (**4**)	0.111	100		

[a] 1 mM CH_2Cl_2 solutions monitored at 612 nm after excitation at 465.8 nm. [b] Relative weighting (RW) of component in double exponential fits. [c] Cast from CH_2Cl_2 by slow evaporation onto a glass substrate.

(bpyPCL$_2$) (**4**) was targeted (PCL = poly(ϵ-caprolactone); M_n(NMR) = 7.4 kDa; M_w(MALLS) = 6.7 kDa, PDI = 1.07).[8] In contrast to the homoleptic Eu complexes, lifetime data for both Eu(dbm)$_3$(bpy) and the block copolymer complex Eu(dbmPLA)$_3$(bpyPCL$_2$) exhibit single-exponential decay, consistent with single Eu species. Additional evidence for sample homogeneity for **4** is provided by the relative sharpness of the emission intensity feature arising from the $^5D_0 \rightarrow {}^7F_0$ transition observed at 579.7 nm (Figure 2b). The sharpness of this nondegenerate transition indicates that all the Eu sites in the sample have essentially identical ligand coordination and structural environments. In metal template assisted block copolymer synthesis, energetic benefits of chelation are balanced against the tendency of dissimilar polymers to separate from each other. Adduct and, thus, block copolymer formation may be favored for the dbmPLA/bpyPCL$_2$ combination because they are comparable polyesters. For dissimilar polymers, mixtures may be observed at equilibrium, with solvent playing a significant role.

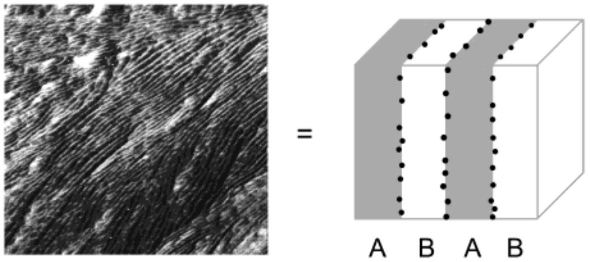

Figure 3. Representative phase contrast AFM image of a Eu(dbmPLA)$_3$(bpyPCL$_2$) block copolymer film (swelled with water vapor prior to analysis to enhance contrast) with a schematic representation of the lamellar morphology (A = PCL, B = PLA, ● = Eu center).

As further confirmation of adduct formation, AFM studies were conducted to determine whether Eu(dbmPLA)$_3$(bpyPCL$_2$) films undergo microphase separation. Thin films of **4** were cast from 5% CH_2Cl_2 solution by slow evaporation on a mercury surface. Phase contrast images show a lamellar microstructure with a period of 17.5 nm (Figure 3). When ordered films of **4** were heated, morphological changes consistent with thermally induced ligand dissociation and fragmentation of the block copolymer at the block junction were noted. More detailed investigation of this phenomenon, additional spectroscopic analyses, and further compositional and architectural modification are underway.

Acknowledgment. We thank the National Science Foundation (CHE-9733466, MIT Center for Materials Science and Engineering) and the Petroleum Research Fund, administered by the ACS, for partial support for this work. John E. McAlvin, Siddhartha R. Shenoy, and Xufeng Wu are acknowledged for setting the stage for this work.

Supporting Information Available: Experimental details for the synthesis of Eu complexes, the measurement of emission spectra and lifetimes for Eu complexes, and the AFM study of thin films of **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Richardson, F. S. *Chem. Rev.* **1982**, *82*, 541. (b) Parker, D.; Williams, J. A. G. *J. Chem. Soc., Dalton Trans.* **1996**, 3613. (c) Sabbatini, N. *Coord. Chem. Rev.* **1993**, *123*, 201. (d) de Sá, G. F.; Malta, O. L.; de Mello Donegá, C.; Simas, A. M.; Longo, R. L.; Santa-Cruz, P. A.; da Silva, E. F. *Coord. Chem. Rev.* **2000**, *196*, 165.
(2) Elbanowski, M.; Makowska, B. *J. Photochem. Photobiol. A: Chemistry* **1996**, *99*, 85.
(3) For example, see: (a) Male, N. A. H.; Salata, O. V.; Christou, V. *Synth. Met.* **2002**, *126*, 7. (b) Yu, G.; Liu, Y.; Wu, X.; Zhu, D.; Li, H.; Jin, L.; Wang, M. *Chem. Mater.* **2002**, *12*, 2537.
(4) Kawa, M.; Frechét, J. M. J. *Chem. Mater.* **1998**, *10*, 286 and references therein.
(5) (a) Muthukumar, M.; Ober, C. K.; Thomas, E. L. *Science* **1997**, *277*, 1225. (b) Scott, B. J.; Wirnsberger, G.; Stucky, G. D. *Chem. Mater.* **2001**, *13*, 3140. (c) Manners, I. *Science* **2001**, *294*, 1664.
(6) Otway, D. J.; Rees, W. S., Jr. *Coord. Chem. Rev.* **2000**, *210*, 279.
(7) For example, see: Richardson, F. S.; Brittain, H. G. *J. Am. Chem. Soc.* **1981**, *103*, 18 and references therein.
(8) Corbin, P. S.; Webb, M. P.; McAlvin, J. E.; Fraser, C. L. *Biomacromolecules* **2001**, *2*, 223 and references therein.
(9) Batista, H. J.; de Andrade, A. V. M.; Longo, R. L.; Simas, A. M.; de Sá, G. F.; Ito, N. K.; Thompson, L. C. *Inorg. Chem.* **1998**, *37*, 3542 and references therein.
(10) (a) Fraser, C. L.; Smith, A. P. *J. Polym. Sci, Part A: Polym. Chem.* **2000**, *38*, 4704. (b) Schubert, U. S.; Heller, M. *Chem. Eur. J.* **2001**, *7*, 5252.
(11) Horie, K.; Ushiki, H.; Winnik, F. *Molecular Photonics: Fundamentals and Practical Aspects*; Wiley-VCH: Tokyo, 2000.
(12) For other examples of dynamic structural motifs, see: Ramström, O.; Lehn, J.-M. *Nature Rev. Drug Discovery* **2002**, *1*, 26.

JA0261269