*Anal. Chem.* **1996,** *68,* 2641−2650

# Electrogenerated Chemiluminescence. 58. Ligand-Sensitized Electrogenerated Chemiluminescence in Europium Labels

Mark M. Richter and Allen J. Bard*

*Department of Chemistry and Biochemistry, the University of Texas at Austin, Austin, Texas 78712-1167*

**The electrochemistry and electrogenerated chemiluminescence (ECL) of a series of europium chelates, cryptates, and mixed-ligand chelate/cryptand complexes were studied. The complexes were of the following general forms: $EuL_4^-$, where L = β-diketonate, a bis-chelating ligand (such as dibenzoylmethide), added as salts $(A)EuL_4$, where A = tetrabutylammonium ion or piperidinium ion ($pipH^+$); $Eu(crypt)^{3+}$, where crypt = a cryptand ligand, e.g., 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8,8,5]-tricosane; and $Eu(crypt)(L)^{2+}$ for the mixed-ligand systems. ECL was obtained for the chelates and mixed-ligand systems by reducing the complexes at a Pt electrode in the presence of peroxydisulfate in acetonitrile solutions and was attributed to the electron-transfer reaction between the reduced bound ligands and $SO_4^{\bullet-}$, followed by intramolecular excitation transfer from the excited ligand orbitals to the metal-centered 4f states. No ECL was observed under the same conditions for the europium complexes incorporating only the cryptand ligands in aqueous solution. The ECL spectra matched the photoluminescence spectra with a narrow emission band observed at 612 nm, corresponding to a metal-centered 4f−4f transition. The ECL efficiencies for the ECL-active species were low, about $10^{-1}-10^{-4}$% of that of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system under similar conditions.**

Electrogenerated chemiluminescence (ECL) involves the production of light at or near an electrode surface by electrochemically generating species capable of forming excited states.[1] The first ECL reactions involved electron transfer between electrogenerated radical cation (oxidized) and radical anion (reduced) forms of a parent species in self-annihilation reactions to form excited states.[1] Alternatively, ECL can be generated by the reaction between the oxidized or reduced forms of a parent species and a coreactant (e.g., $C_2O_4^{2-}$, $S_2O_8^{2-}$) that, upon oxidation or reduction, can undergo a chemical reaction to form strong reducing or oxidizing agents capable of undergoing highly energetic electron-transfer reactions to form excited states. For example, in the case of peroxydisulfate ($S_2O_8^{2-}$), reduction produces the strong oxidant $SO_4^{\bullet-}$, which then undergoes an electron-transfer reaction with the parent species $R^-$ to generate light, as outlined below:[2]

$$R + e^- \rightarrow R^-$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\bullet-}$$

$$R^- + SO_4^{\bullet-} \rightarrow R^* + SO_4^{2-}$$

$$R^* \rightarrow R + h\nu$$

Most of the ECL reactions studied involve organic aromatic species (hydrocarbons, heterocycles)[1] and certain transition-metal complexes, mainly $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine)[3] and analogous osmium complexes.[4] Complexes containing these metals display reasonable luminescence efficiencies, and both their redox and spectroscopic properties are well-understood.[5] $Ru(bpy)_3^{2+}$ has found growing application as an ECL-active label in diagnostics (e.g., immunoassays, DNA probes).[6,7] However, its broad emission bands can be a disadvantage in analytical applications where an ECL internal standard or multianalyte determinations are desired. Alternative labels at other wavelengths and with narrower emission bands for ECL methods are thus of interest.

We describe here ECL studies on luminescent lanthanide complexes. Many trivalent lanthanide species display high photoluminescence efficiencies (≥5% in $H_2O$), large Stokes' shifts (~300 nm), long excited-state lifetimes (on the order of several hundred microseconds), and narrow emission spectra,[8,9] all of which make them attractive as potential ECL labels. For example, lanthanide complexes have been used as fluorescent tracers or

---

(1) Faulkner, L.; Bard, A. J. In *Electroanalytical Chemistry*; Bard A. J., Ed.; Marcel Dekker: New York, 1977; Vol. 10, pp 1−95.

(2) (a) White, H. S.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6891. (b) Bolletta, F.; Rossi, A.; Balzani, V. *Inorg. Chim. Acta* **1981**, *53*, L23−L24.

(3) (a) Tokel, N.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 2862. (b) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582. (c) Wallace, W. L.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 1350. (d) Glass, R. S.; Faulkner, L. R. *J. Phys. Chem.* **1981**, *85*, 160. (e) Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 512.

(4) (a) Abruna, H. D. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *175*, 321. (b) Lee, C.-N.; Bard, A. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *244*, 319.

(5) See, for example: (a) Navon, G.; Sutin, N. *Inorg. Chem.* **1974**, *13*, 2159. (b) Gafney, H. D.; Adamson, A. W. *J. Am. Chem. Soc.* **1972**, *94*, 8238. (c) Lin, C.-T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536. (d) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815. (e) Sutin, N.; Creutz, C. *Adv. Chem. Ser.* **1978**, *No. 168*, 1.

(6) (a) Ege, D.; Becker, W. G.; Bard, A. J. *Anal. Chem.* **1984**, *56*, 2413. (b) Bard, A. J.; Whitesides, G. M. U.S. Patents 5 221 605, 1993; 5 238 808, 1993; 5 310 687, 1994.

(7) Blackburn, G. F.; Shah, H. P.; Kenien, J. H.; Leland, J.; Kamin, R. A.; Link, J.; Peterman, J.; Powell, M. J.; Shah, A.; Talley, D. B.; Tyagi, S. K.; Wilkins, E.; Wu, T.-G.; Massey, R. J. *Clin. Chem.* **1991**, *37*, 1534.

(8) Crosby, G. A.; Whan, R. E.; Allire, R. M. *J. Chem. Phys.* **1961**, *34*, 743.

(9) Sinha, A. P. B. *Spectrosc. Inorg. Chem.* **1971**, *2*, 255.

S0003-2700(96)00211-9 CCC: $12.00

labels and as probes of both chemical reactions and biomolecules.[10]

There have been numerous studies of the spectroscopic properties and electronic states of rare earth chelate complexes.[8,9] In general, optical excitation occurs as a $\pi-\pi^*$ transition in the ligand orbitals. The excitation energy is then efficiently transferred from a ligand singlet state via the ligand triplet state to the resonance energy levels of the rare earth metal center leading to the characteristic line (atomic) emission ($^5D_0 \rightarrow {}^7F_n$ ($n = 0-6$) in the case of Eu(III)).[8,9,11] Thus, excited-state formation is achieved via ligand-sensitized luminescence or the so-called "antenna" effect, since direct population of the metal orbitals by photon absorption is an inefficient process.[8,9,11,12]

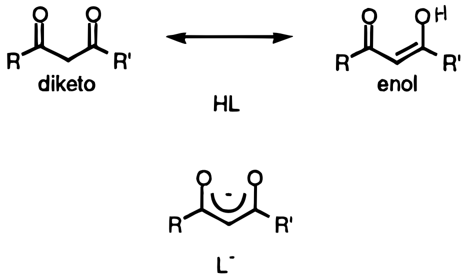
Intermolecular energy transfer from the lowest excited state of an energy donor to the ligand states of a rare earth chelate, which in turn transfers its energy intramolecularly to the central metal ion with subsequent narrow band emissions, has also been observed in spectroscopic studies.[8,13] For example, upon optical excitation, benzophenone can transfer its energy intermolecularly to Eu(III) $\beta$-diketonate chelate complexes with subsequent emission from the europium(III) metal centers.[13]

In a previous ECL study,[14] intermolecular energy transfer was observed from an exciplex (formed by the radical cation of tri-*p*-tolylamine and either the benzophenone or dibenzoylmethane radical anions) directly to a europium chelate, resulting in ECL generated via exciplex-sensitized luminescence.[14] This work differed from previous energy-transfer studies in that the excited states of the energy donor were formed electrochemically, not optically. However, no direct ECL of the Eu(III) chelate was found in that study.

Vogler and Kunkely[15] reported weak ECL using a photon-counting apparatus as a detector in Eu(TTA)$_3$(phen), Tb(TTA)$_4^-$, and Tb(TTA)$_3$(phen) (where phen = 1,10-phenanthroline and TTA$^-$ = 4,4,4-trifluoro-1-(2-thienyl)-1,5-butanediono/thenoyltrifluoroacetonato, Scheme 1). This ECL was attributed to intramolecular energy transfer from a nonemitting excited state of the intraligand orbitals to the emitting state of the metal-centered f orbitals,[15] analagous to the events that are proposed in the photochemical experiments.

Electroluminescence studies by Heller and co-workers[16] and Doblhofer and Gerischer[17] showed that lanthanide-based emissions can be generated electrochemically under nonaqueous conditions at platinum cathodes, and Haapakka and co-workers[18] have observed the electroluminescence of Dy(III), Sm(III), and Tb(III) 2,6-[bis[*N,N*-bis(carboxymethyl)amino]methyl]-4-benzoylphenol chelates at oxide-covered aluminum electrodes. This type of high-voltage electroluminescence is thought to involve the direct formation of the excited states at the electrode surface rather than electron-transfer chemiluminescent reactions of electrochemically generated reactants.

Scheme 1



| R | R' | L⁻ | LH |
|---|---|---|---|
| $C_6H_5$ | $C_6H_5$ | DBM⁻ | DBMH |
| $C_6H_5$ | $CH_3$ | BA⁻ | BAH |
| $C_4H_4S$ | $CF_3$ | TTA⁻ | TTAH |
| $C_6H_5$ | $CF_3$ | BTA⁻ | BTAH |
| $CF_3$ | $CF_3$ | HFAC⁻ | HFACH |
| $CH_3$ | $CH_3$ | ACAC⁻ | HACAC |

The work described herein involves the ECL of a series of Eu(III) complexes incorporating $\beta$-diketonate, cryptand, and mixed-cryptand/$\beta$-diketonate ligand systems and to our knowledge is the first report of the direct ECL of a rare earth chelate or complex. The mechanism is proposed to parallel that found in the spectroscopic studies with electrochemical formation of ligand excited states followed by rapid sensitization of the metal center.

## EXPERIMENTAL SECTION

**Materials.** All chemicals were reagent grade and were used without further purification. 1,1-Diphenyl-1,3-propanedione (dibenzoylmethane, DBMH), 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (thenoyltrifluoroacetone, TTAH), 1-phenyl-1,3-butanedione (benzoylacetone, BAH), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone, HFACH), tetrabutylammonium hydroxide (TBAOH), piperidine (pip), 4,7,13,16,21,24-hexaoxa-1,10-diazacyclo-[8,8,8]hexacosane ([2.2.2]), 4,7,13,16,21-pentaoxa-1,10-diazabicyclo-[8,8,5]tricosane ([2.2.1]), and $EuCl_3 \cdot 6H_2O$ were purchased from Aldrich. 4,4,4-Trifluoro-1-phenyl-1,3-butanedione (benzoyltrifluoroacetone, BTAH) was purchased from Sigma. (pipH$^+$)[Eu(DBM)$_4$]$\cdot H_2O$ (where pipH$^+$ = piperidinium ion) was synthesized by the method of Workman[19] and was recrystallized several times from absolute methanol, filtered, washed with cold ethanol, and stored in a vacuum desiccator prior to use. Purity was established by melting point (180−182 °C)[19,20] and elemental analysis [Calcd (%): C, 68.24; H, 4.67; N, 1.22. Found (%): C, 68.58; H, 4.94; N, 1.22]. Eu(TTA)$_3$(phen), Eu[2.2.1](NO$_3$)$_3$, and Eu[2.2.2](NO$_3$)$_3$

---

(10) (a) Templeton, E. F. G.; Pollak, A. *J. Lumin.* **1989**, *43*, 195. (b) Horrocks, W. D. W.; Sudnick, D. R. *Acc. Chem. Res.* **1982**, *14*, 384. (c) Soini, E.; Hemmilä, I. *Clin. Chem.* **1979**, *25*, 353. (d) Mushrush, G. W.; Stalick, W. M.; Watkins, J. R., Jr.; Deanhault, M. C. *J. Less-Common Met.* **1986**, *126*, 363.

(11) Bryden, C. C.; Reilley, C. N. *Anal. Chem.* **1982**, *54*, 610, and references therein.

(12) Sabbatini, N.; Perathoner, S.; Balzani, V.; Alpha, B.; Lenh, J.-M. In *Supramolecular Photochemistry*; Balzani, V., Ed.; D. Reidel Publishing Co: Norwell, MA, 1987; p 187, and references therein.

(13) (a) Bhaumik, M. L.; El-Sayed, M. A. *J. Phys. Chem.* **1965**, *69*, 275. (b) Wildes, P. D.; White, E. H. *J. Am. Chem. Soc.* **1971**, *93*, 6286.

(14) Hemingway, R. E.; Park, S.-M.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *95*, 200.

(15) Vogler, A.; Kunkely, H. In *High-Energy Processed in Organometallic* Chemistry; Suslik, K. S., Ed.; ACS Symposium Series 333; American Chemical Society: Washington, DC, 1987; pp 155−168.

(16) Heller, A.; French, K. W.; Haugsjaa, P. O. *J. Chem. Phys.* **1972**, *56*, 2368.

(17) Doblhofer, K.; Gerischer, H. *J. Electroanal. Chem.* **1975**, *65*, 101.

(18) (a) Kankare, J.; Fäldén, K.; Kulmala, S.; Haapakka, K. *Anal. Chim. Acta* **1992**, *256*, 17. (b) Kankare, J.; Haapakka, K.; Kulmala, S.; Näntö, V.; Eskola, J.; Takalo, H. *Anal. Chim. Acta* **1992**, *266*, 205.

(19) Workman, N. *J. Chem. Educ.* **1971**, *48*, 303.

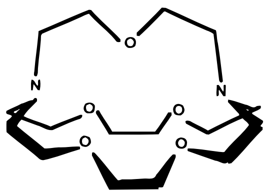
(20) Bauer, H.; Blanc, J.; Ross, D. L. *J. Am. Chem. Soc.* **1964**, *86*, 5125.

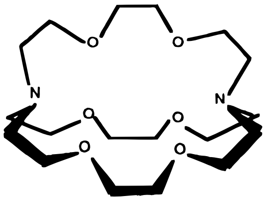
were synthesized and purified by the literature method.[21] Tetra-*n*-butyl ammonium fluoroborate ($TBABF_4$) (Sachem, Austin, TX) or tetra-*n*-butyl ammonium hexafluorophosphate ($TBAPF_6$) was used as the supporting electrolyte. $TBABF_4$ was recrystallized twice from ethyl acetate, dried in vacuo (100 °C), and stored in a vacuum desiccator prior to use. $TBAPF_6$ was recrystallized twice from 4:1 ethanol/water, dried in vacuo (100 °C), and stored in a vacuum desiccator prior to use. The acetonitrile (MeCN) was spectroquality (Burdick & Jackson) and stored over activated molecular sieves. Deionized water from a Millipore Milli-Q system was used throughout.

**$(TBA)_2S_2O_8$.** Tetra-*n*-butylammonium peroxydisulfate was prepared by a metathesis reaction between TBAOH (1.0 M solution in methanol) and $(NH_4)_2S_2O_8$ (Fischer Scientific). In a fume hood, a methanolic solution of TBAOH was added dropwise to an aqueous solution containing excess $(NH_4)_2S_2O_8$. The reaction mixture was then flushed with dry nitrogen to remove $NH_3$ and extracted three times with $CH_2Cl_2$; the organic layer was treated with activated charcoal and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under vacuum to afford the product.

**TBA Salts of $Eu^{III}L_4^-$.** Tetrabutylammonium salts of tetrakis-($\beta$-diketonato)europium(III) were prepared by slight modifications of the literature procedures.[20,21] Eight millimoles of $\beta$-diketone bis-chelating ligand (LH, Scheme 1) and 8 mmol of TBAOH were added to 25 mL of 95% ethanol. The solution was warmed to ~70 °C, and a solution of 2 mmol of $EuCl_3{\cdot}6H_2O$ in 10 mL of $H_2O$ was added dropwise with stirring. In all cases, a precipitate immediately formed. The mixture was cooled in an ice bath and the crystals were collected by vacuum filtration, washed with cold ethanol and water, and recrystallized from ethyl acetate to afford analytically pure crystals as determined by melting point[20,21] and elemental analyses. Elemental analysis of $(TBA)Eu(HFAC)_4$ ($HFAC^- =$ 1,1,1,5,5,5-hexafluoro-2,4-pentanediono/hexafluoroacetylacetonato, Scheme 1) was less than satisfactory and was performed on two samples prepared and purified independently. Satisfactory elemental analyses (±0.4% for C, H, and N; Galbraith, Knoxville, TN) were obtained for the remainder of the complexes incorporating $\beta$-diketonate bis-chelating ligands ($L^-$, Scheme 1), e.g., $(TBA)Eu(DBM)_4$, Calcd (%): C, 70.83; H, 6.26; N, 1.09. Found (%): C, 70.45; H, 6.19; N, 1.08.

**$Eu[2.2.1](L)^{2+}$.** The mixed ligand complexes $Eu[2.2.1](L)^{2+}$ (where $L^- = DBM^-$, $HFAC^-$, $TTA^-$, $BA^-$ (1-phenyl-1,8-butanediono/benzoylacetonato, Scheme 1), and $BTA^-$ (4,4,4-trifluoro-1-phenyl-1,3-butanediono/benzoyltrifluoroacetonato, Scheme 1) were synthesized by a modification of the method of Nocera et al.[22] for the synthesis of $Tb[2.2.1](ACAC)^{2+}$ (where $ACAC^- =$ 2,4-pentanediono/acetylacetonato, Scheme 1).


[2.2.1]


[2.2.2]

$Eu[2.2.1](NO_3)_3$ (0.1 mmol) was placed in ~20 mL of MeCN in a 50-mL beaker and warmed to ~50 °C. Upon addition of a slight excess of chelating ligand (0.2 mmol), the Eu(III) cryptate became soluble, and in all cases except HFACH, a change in color from clear to light yellow was observed, indicative of enolate ($L^-$) formation (in the case of HFACH, no color change could be observed) with a concomitant increase in visible emission when irradiated with a long-wavelength (383 nm) hand-held UV light (Model UVGL-25 Mineralight lamp, UVP Inc., San Gabriel, CA). In fact, no emission characteristic of the metal center was observed before addition of the diketone ligands due to both the poor solubility of the cryptates in MeCN and their poor luminescence efficiency.[12] Upon cooling, the solutions were used immediately.

**Methods.** Cyclic voltammetric experiments were performed utilizing a Bioanalytical Systems (West Lafayette, IN) Model-100A electrochemical analyzer. ECL experiments employed a Princeton Applied Research 175 universal programmer (PAR, Princeton, NJ), a Model 173 potentiostat/galvanostat, and an Omnigraphic 2000 *x*−*y* recorder (Houston Instruments, Austin, TX). A Model CH120 charge-coupled device (CCD) camera (Photometrics, Phoenix, AZ) cooled to −110 °C was used to acquire ECL spectra and to obtain the ECL emission intensities used in the calculation of ECL efficiencies. The CCD camera and the configuration of the experiment have been described in detail elsewhere.[23] Solutions used to obtain ECL spectra and ECL emission intensities incorporated 4 mM europium complex, 10 mM $S_2O_8^{2-}$, and 0.1 M $TBABF_4$. In these experiments, light intensities were integrated over a period of 30 min for the chelate complexes and 3 h for the mixed-ligand systems. Cyclic voltammetry coupled with photon detection used the PAR electrochemical apparatus described above in conjunction with a Hamamatsu C1230 photon counter (Bridgewater, NJ) equipped with a Hamamatsu R928-P photomultiplier tube cooled to −15 °C. The output was channeled to the *y* axis of the *x*−*y* recorder to afford ECL vs potential displays.

All electrochemical and ECL experiments employed a conventional three-electrode configuration. The cell was designed to fit in front of the entrance slit to the CCD spectrometer and had a total volume of 4−5 mL. A platinum disk electrode (0.2-cm diameter) was employed as the working electrode with a Pt wire as the auxiliary electrode and a silver wire as the quasi-reference electrode (AgQRE). After a series of experiments, ferrocene was added as an internal reference ($Fc/Fc^+ = 0.665$ V vs NHE)[24] and potentials recorded were referenced accordingly. Experiments were carried out in MeCN solutions containing 0.1 M $TBABF_4$ or $TBAPF_6$ or in aqueous solutions containing 0.1 M $NaClO_4$. All solutions were deoxygenated with argon for several minutes, and the experiments were run under an Ar atmosphere.

Absorption spectra were recorded with an Aminco Bowman/Milton Roy Spectronic 3000 array spectrophotometer. Luminescence spectra were measured using an SLM Aminco SPF-500 spectrofluorometer. Relative luminescence quantum yields, $\phi_R$, were measured in deaerated (Ar bubbled for 20 min) MeCN

---

[21] (a) Melby, L. R.; Rose, N. J.; Abramson, E.; Laris, J. C. *J. Am. Chem. Soc.* **1964**, *86*, 5117. (b) Gansow, O. A.; Triplett, K. B. U.S. Patent 4 257 955, 1981.

[22] Yu, J.-A.; Lessard, R. B.; Bowman, L. E.; Nocera, D. G. *Chem. Phys. Lett.* **1991**, *187*, 263.

[23] McCord, P.; Bard, A. J. *J. Electroanal. Chem.* **1991**, *318*, 91.

[24] (a) Gennet, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2787. (b) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2855.

Table 1. Voltammetric Potentials for Europium Complexes and Ligands[a]

| complex or ligand | $E_p^a$ (V vs Fc/Fc$^+$)[b] oxidation (V) | $E_{1/2}$ (V vs Fc/Fc$^+$) reductions (V) |
|---|---|---|
| (pipH$^+$)Eu(DBM)$_4$ | +0.45[c] | −1.68[c,e], −2.41 |
| (TBA)Eu(DBM)$_4$ | +0.55[c] | −2.42 |
| (TBA)Eu(TTA)$_4$ | +0.78[c] | −2.12[c,e] |
| (TBA)Eu(HFAC)$_4$ | +1.01[c] | −2.72[c,e] |
| (TBA)Eu(BA)$_4$ | +0.52[c] | −2.82[c,e] |
| (TBA)Eu(BTA)$_4$ | +1.35[c] | −2.36[c,e] |
| Eu[2.2.2](NO$_3$)$_3$ | | −0.21[f] |
| Eu[2.2.1](NO$_3$)$_3$ | | −0.44[f] |
| Eu[2.2.1](DBM)(NO$_3$)$_2$ | | −0.56 |
| Eu[2.2.1](BA)(NO$_3$)$_2$ | | −0.58 |
| Eu[2.2.1](TTA)(NO$_3$)$_2$ | | −0.64 |
| Eu[2.2.1](BTA)(NO$_3$)$_2$ | | −0.83 |
| Eu[2.2.1](HFAC)(NO$_3$)$_2$ | | |
| DBMH | +0.43[c] | −1.58[d], −1.78*c*, −2.44[d] |
| DBM$^-$ | +0.43[c] | −2.44[d] |
| TTAH | +0.72[c] | −1.17[d], −2.04[d] |
| TTA$^-$ | +0.71[c] | −2.08[c] |
| BAH | +0.50[c] | −2.10[d], −2.64[d] |
| BA$^-$ | +0.49[c] | −2.61[c] |
| BTAH | +1.11[c] | −1.22[d], −2.24[d] |
| BTA$^-$ | +1.20[c] | −2.20[c] |
| HFACH | +0.94[c] | −1.00[d] |
| HFAC$^-$ | +1.00[c] | −2.62[c] |
| [2.2.2] | +0.65[c] | |
| [2.2.1] | +0.49[c] | |

[a] Potentials (except where noted) were recorded vs Fc/Fc$^+$ in 0.1 M TBAPF$_6$ in MeCN at a scan rate of 100 mV/s. [b] Anodic peak potential ($E_p^a$). [c] Irreversible wave. [d] Quasi-reversible wave. [e] Cathodic peak potential ($E_p^c$). [f] Potentials recorded vs SCE in 0.1 M NaClO$_4$ in H$_2$O at a scan rate of 200 mV/s.

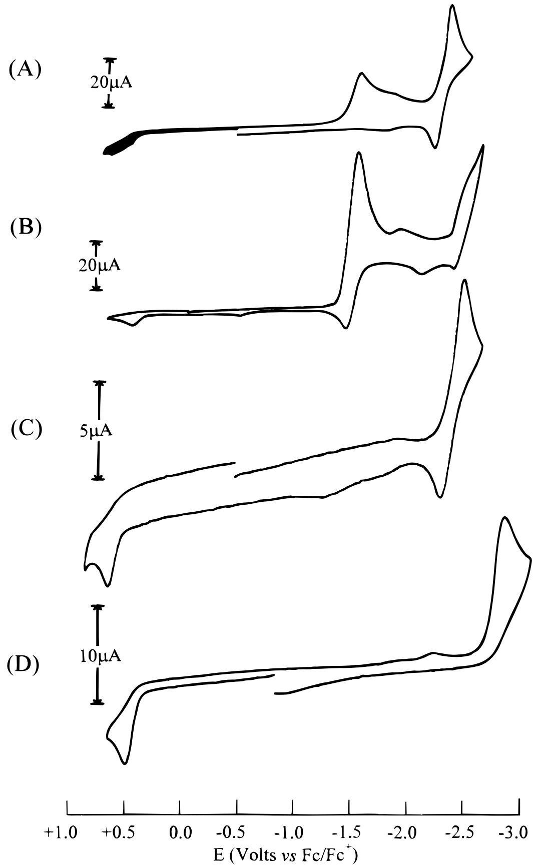


Figure 1. (A) Cyclic voltammograms of (A) (pipH$^+$)Eu(DBM)$_4$, (B) DBMH, (C) (TBA)Eu(DBM)$_4$, and (D) (TBA)Eu(BA)$_4$. Solutions were 1 mM in complex (MeCN/0.1 M TBAPF$_6$); scan rate, 200 mV/s.

solutions at room temperature using the literature method[25] with Ru(bpy)$_3^{2+}$ as the standard, $\phi_{ref} = 0.0682$.[25]

## RESULTS

**Electrochemistry. Chelates.** Voltammetric potentials for the europium(III) chelates and the free β-diketone (LH and L$^-$) ligands are given in Table 1. Without exception, the free protonated ligands display two reductions and one oxidation in the potential window from +1.00 to −2.80 V vs Fc/Fc$^+$. A typical cyclic voltammogram of DBMH is shown in Figure 1B. The reductions in each case are quasi-reversible with the lone oxidation being irreversible. The nature of the substituents attached to the β-diketonate core (i.e., CF$_3$, C$_6$H$_5$, CH$_3$, C$_4$H$_3$S, Scheme 1) determine the energy of the LUMO and this is reflected in the observed potentials for reduction: BAH (−2.10 V) < DBMH (−1.58 V) < BTAH (−1.22 V) < TTAH (−1.17 V) < HFACH (−1.00 V). β-Diketones exist as tautomers, and the ratio of diketo to enol depends on the nature of the system in question (Scheme 1). DBMH and similar ligands exist almost exclusively in the enol form.[26] Upon reduction, both forms produce the enolate species (L$^-$). Previous electrochemical investigations on β-diketone ligands, most notably DBMH,[26] have characterized the nature of the reduction processes. For DBMH, for example, the cyclic voltammogram in MeCN shown in Figure 1B is similar to that reported in dimethyl sulfoxide (DMSO) with TBAP as electrolyte and a static Hg drop as the working electrode,[26] suggesting the same mechanism in both solvents. Reduction waves are observed at −1.58, −1.75, and −2.44 V vs Fc/Fc$^+$ (Table 1, Figure 1B), assigned to initial reduction of DBMH to the radical anion, followed by formation and subsequent reduction of the pinacol (DBMH$_2$)$_2$ and enolate (DBM$^-$), respectively.[26] Except for HFACH, all of the free ligands display reductive electrochemistry similar to DBMH (Table 1). With HFACH, a second reduction (corresponding to reduction of the enolate ion) is not seen. To demonstrate that the second reduction wave is due to the enolate ion, the TBA enolate salts were prepared.[26,27] The enolate ions (Table 1) display a single reduction at potentials comparable to those observed for the second wave in the parent (LH) ligands and represents reduction of the enolate to the radical dianion.[26]

A cyclic voltammogram of the chelate (pipH$^+$)Eu(DBM)$_4$ is shown in Figure 1A. It is characterized by an irreversible oxidation wave at +0.45 V vs Fc/Fc$^+$, attributed to oxidation of the ligand. This oxidation wave occurs at the potential seen for the unbound enolate ligand (Table 1), suggesting little interaction between metal and ligand orbitals. A chemically reversible reduction is observed at −2.41 V vs Fc/Fc$^+$ corresponding to reduction of the bound enolate ligands (Figure 1A),[14,15] again by comparison to the free L$^-$ behavior (Table 1).[26] No waves are observed ≤−500 mV where the thermodynamic reduction of free Eu$^{3+}$ occurs.[28] In (TBA)Eu(DBM)$_4$, an irreversible oxidation at

---

(25) (a) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583. (b) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853.

(26) (a) Buchta, R. C.; Evans, D. H. *J. Electrochem. Soc.* **1970**, *117*, 1494. (b) Buchta, R. C.; Evans, D. H. *Anal. Chem.* **1968**, *40*, 2181.

(27) β-Diketone ligand and tetrabutylammonium hydroxide (1 M in methanol, Aldrich) were reacted in 95% ethanol in stoichiometric amounts and evaporated to dryness. They were then washed and recrystallized from anhydrous diethyl ether to afford pale yellow crystals.[26]

$+0.55$ V vs Fc/Fc$^+$ is observed, similar to that in the piperidinium analog but at slightly more positive potentials (Figure 1C), perhaps because of ion-pairing effects.[29] The irreversible wave that appears at $-1.68$ V in the (pipH$^+$)Eu(DBM)$_4$ voltammogram does not appear in the voltammograms of the TBA system. In (pipH$^+$)Eu(DBM)$_4$, this shoulder is perhaps due to traces of free ligand or other impurities, despite the excellent agreement with melting point and elemental analysis data. Controlled potential electrolysis was performed with (pipH$^+$)Eu(DBM)$_4$ (1 mM) in MeCN/0.1 M TBAPF$_6$ in a two-compartment stirred cell utilizing Pt mesh working and auxilliary electrodes and a AgQRE. The potential was stepped to a potential on the shoulder, $-1.9$ V vs Fc/Fc$^+$. The irreversible wave at $-1.8$ V gradually disappeared with no change in the bound-ligand wave at $-2.41$ V, indicating that this species is probably free ligand or an electroactive impurity in the sample.

A ligand-centered reduction is observed with all of the chelates in the range $-2.0$ to $-2.8$ V vs Fc/Fc$^+$ corresponding to reduction of the coordinated L$^-$ ligand; these occur at potentials comparable to those in the unbound L$^-$ species. For example, a cyclic voltammogram of (TBA)Eu(BA)$_4$ is shown in Figure 1D. It displays a ligand-based oxidation at potentials comparable to those observed in the DBM$^-$ chelates. The reduction at $-2.82$ V vs Fc/Fc$^+$ is assigned to reduction of the bound BA$^-$ ligand and, when compared to the DBM$^-$ chelates, clearly shows the dependence of this reduction on the nature of the L$^-$ ligand. The small, irreversible wave at $-2.4$ V is presumably due to decomposition products since it is absent when the scan direction is reversed before oxidation of Eu(BA)$_4^-$ can occur.

**Cryptates.** Cyclic voltammetric data for the [2.2.2] and [2.2.1] cryptand ligands and the Eu[2.2.2](NO$_3$)$_3$ and Eu[2.2.1](NO$_3$)$_3$ cryptate complexes are given in Table 1. The free ligands are insoluble in aqueous solution and display no reduction waves in MeCN to $-2.8$ V vs Fc/Fc$^+$. However, an irreversible oxidation is observed at $+0.65$ and $+0.49$ V for the [2.2.2] and [2.2.1] ligands in MeCN, respectively. The Eu cryptates are insoluble in MeCN and thus water was used as a solvent. The electrochemistry of the Eu(III) cryptates has been previously reported in aqueous solutions utilizing a hanging mercury drop working electrode.[30] Cyclic voltammograms obtained with a Pt electrode show chemically reversible reduction waves (corresponding to the Eu$^{3+/2+}$ couple)[30] with the [2.2.2] cryptate at slightly more positive potentials (Table 1).

**Mixed-Ligand Systems.** The electrochemistry of the mixed-ligand Eu[2.2.1](L)$^{2+}$ complexes was complicated because of free ligand in solution. In most cases, a reduction wave was observed at potentials more positive than $-0.800$ V vs Fc/Fc$^+$ corresponding to Eu(III) reduction, followed closely by ligand reduction. The assignment of the first reduction to Eu(III/II) was made by comparison to the Eu[2.2.1]$^{3+}$ cryptate.[30] An Eu(III/II) wave was found for all ligands except for the HFAC$^-$ complex (Table 1).

**Spectroscopy. Chelates.** Spectroscopic data for the Eu chelates are given in Table 2. The absorption spectra of the complexes are characterized by high-intensity ligand-centered (LC) bands characteristic of the $\beta$-diketone (LH) ligands. The absorption maxima of these transitions occur at wavelengths near those of the free ligands. Photoexcitation of the complexes into their LC absorption bands ($\lambda_{ex}^{max}$ = 339 nm) resulted in an emission spectrum characteristic of the rare earth ion with a narrow band ($^5D_0 \rightarrow {}^7F_2$ transition) at ~612 nm (Figure 2). Photoluminescence quantum efficiencies ($\phi_R$) for the complexes (Table 2) follow the order (TBA)Eu(BTA)$_4$ > (TBA)Eu(TTA)$_4$ > (TBA)Eu(DBM)$_4$ > (TBA)Eu(BA)$_4$ > (pipH$^+$)Eu(DBM)$_4$ > (TBA)Eu(HFAC)$_4$. These results suggest that the energy-transfer efficiency from the ligand-centered level to the luminescent metal-centered levels is larger for the BTA$^-$ and TTA$^-$ complexes than those containing other $\beta$-diketonate ligands. In general, photoemission in europium chelates containing suitable organic ligands results from energy transfer from an excited ligand singlet state to the metal center.[8,9,11] A simplified MO picture (ignoring multiplicities) of this process is given in Figure 3 (steps 1−3).

Table 2. Spectroscopic Data for a Series of Europium Complexes[a]

| complex | $\lambda_{abs}^{max}$ (nm) | $\lambda_{em}^{max}$ (nm)[b] | $\phi_R$ (%)[c] | rel ECL eff (%)[d,e] |
|---|---|---|---|---|
| (pipH$^+$)Eu(DBM)$_4$ | 346 | 611 | 8.20 | 0.62 |
| (TBA)Eu(DBM)$_4$ | 348 | 611 | 16.3 | 0.30 |
| (TBA)Eu(HFAC)$_4$ | 304 | 612 | 7.90 | $4.8 \times 10^{-2}$ |
| (TBA)Eu(BA)$_4$ | 315 | 611 | 10.8 | $8.8 \times 10^{-2}$ |
| (TBA)Eu(TTA)$_4$ | 338 | 612 | 83.9 | $2.9 \times 10^{-2}$ |
| (TBA)Eu(BTA)$_4$ | 317 | 611 | 101 | $5.4 \times 10^{-2}$ |
| Eu[2.2.2](NO$_3$)$_3$ | 220[f] | 612[f] | 0.03[g] | |
| Eu[2.2.1](NO$_3$)$_3$ | 211[f] | 612[f] | | |
| Eu[2.2.1](DBM)$^{2+}$ | 344 | 612 | 0.0153 | $9.8 \times 10^{-4}$ |
| Eu[2.2.1](BA)$^{2+}$ | 311 | 612 | 0.106 | $2.68 \times 10^{-4}$ |
| Eu[2.2.1](TTA)$^{2+}$ | 348 | 614 | 0.0847 | |
| Eu[2.2.1](HFAC)$^{2+}$ | 275 | 612 | 3.83 | |
| Eu[2.2.1](BTA)$^{2+}$ | 329 | 613 | 0.115 | |

[a] Spectra were recorded in CH$_3$CN at room temperature. [b] Excitation wavelength, 339 nm. [c] Error ±8%. [d] Relative ECL efficiencies as compared to Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$.[2,3] [e] Error ±20%. [f] Recorded in H$_2$O at room temperature. [g] From ref 31 [recorded in D$_2$O at room temperature vs Ru(bpy)$_3^{2+}$ (0.028 in H$_2$O)].

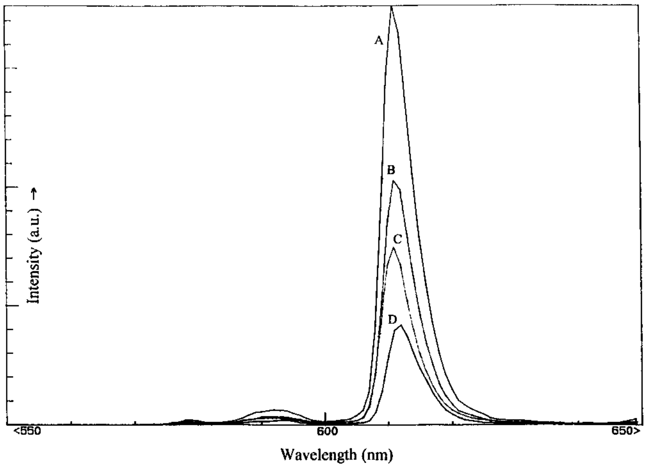


Figure 2. Fluorescence spectra of (A) (pipH$^+$)Eu(DBM), (B) (TBA)-Eu(DBM)$_4$, (C) (TBA)Eu(BA)$_4$, and (D) (TBA)Eu(HFAC)$_4$. Solutions were 0.1 mM in complex (CH$_3$CN); excitation wavelength, 339 nm.

**Cryptands.** The spectroscopy of the Eu[2.2.2]$^{3+}$ and Eu[2.2.1]$^{3+}$ cryptands has been studied in detail.[31] Both display extremely weak absorption in the visible region, with peaks above

---

(28) *Standard Potentials in Aqueous Solutions*; Bard, A. J., Parsons, R., Jordan, J., Eds.; Marcel Dekker: New York, 1985; pp 624−625.

(29) Noro, J.; Sekine, T. *Bull. Chem. Soc. Jpn.* **1993**, *64*, 1647.

(30) Gansow, O. A.; Kauser, A. R.; Triplett, K. M.; Weaver, M. J.; Yee, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 7087.

(31) Sabbatini, N.; Dellonte, S.; Ciano, M.; Bonazzi, A.; Balzani, V. *Chem. Phys. Lett.* **1984**, *107*, 212, and references therein.

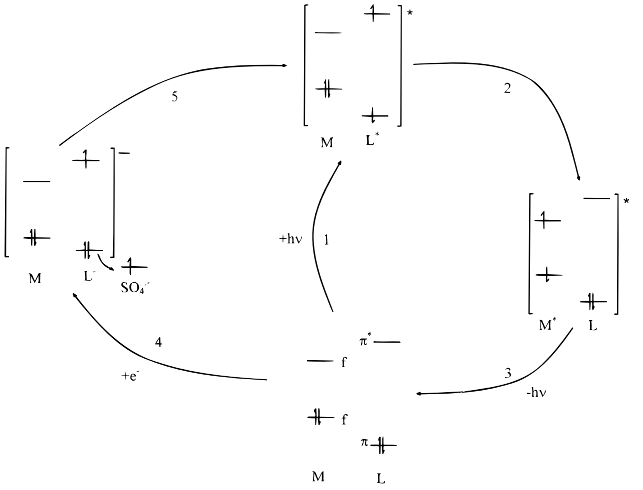


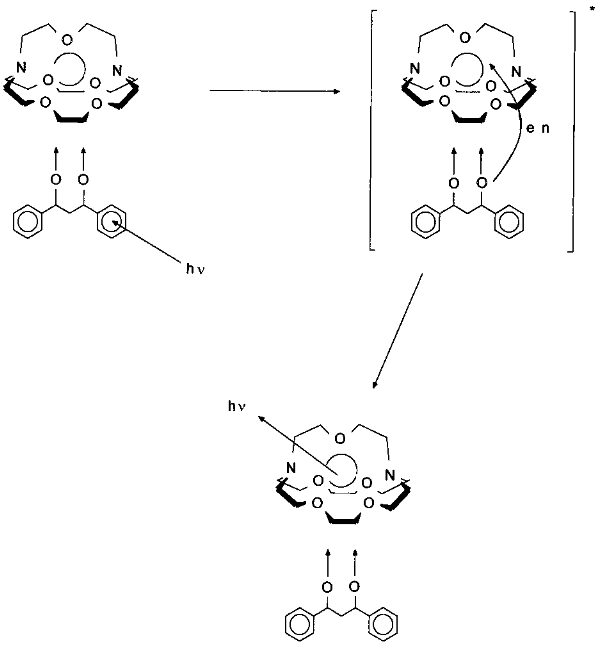
Figure 3. Simplified molecular orbital scheme (ignoring spin multiplicities) for (1) photexcitation pathway and proposed mechanism for generation of ECL, (2) intramolecular energy transfer from ligand orbitals to resonance levels of Eu(III) metal center, (3) 4f−4f metal-centered emissions, (4) electrochemical reduction of Eu(III) to Eu(II), and (5) interaction of strong oxidant $SO_4^{\bullet -}$ with the ligand-centered HOMO to produce $SO_4^{2-}$ and an excited ligand orbital.

290 nm assigned as charge transfer in origin. The cross section for absorption is small for both the europium ion and the cryptand ligands, and the subsequent emission intensities are much weaker than those observed in the $\beta$-diketonate chelate complexes (<5% in $D_2O$) since efficient intramolecular energy transfer does not take place.[31]

**Mixed-Ligand Systems.** Luminescence attributed to intramolecular energy migration from phenylcarboxylates and the $\beta$-diketonate ligand acetylacetonato (2,4-pentanediono) ($ACAC^-$) to a $Tb^{3+}$ ion residing in the [2.2.1] cryptand has recently been observed.[22,32] A related system incorporating the $DBM^-$ ligand and the proposed energy migration pathway is shown in Scheme 2. In their spectroscopic studies on the $Tb[2.2.1](ACAC)^{2+}$ systems, Nocera et al.[22,32] observed a 3-fold increase in emission intensity upon coordination to the $ACAC^-$, because $ACAC^-$ has a greater cross section for absorption than the cryptand ligands, resulting in better intramolecular energy transfer from the triplet levels of the bound $ACAC^-$ to the rare earth ion.[22,32] A shift in the absorption band to longer wavelengths in the UV region is observed for the mixed-ligand $Eu[2.2.1](L)^{2+}$ systems compared to that for the cryptands alone (Table 2). These bands correlate closely with those observed for the free LH ligands, and as observed in the $Tb[2.2.1](ACAC)^{2+}$ system,[22,32] an increase in emission intensity is obtained upon addition of the $L^-$ diketonate ligands (Table 2) as compared to $Eu[2.2.1]^{3+}$, which displays no appreciable emission intensity in MeCN.

**Electrogenerated Chemiluminescence. $Eu(TTA)_3(phen)$.** Very weak ECL in rare earth chelates was first reported by Vogler and Kunkely[15] by potential cycling of the species $Eu(TTA)_3(phen)$, $Tb(TTA)_4^-$, and $Tb(TTA)_3(phen)$ in MeCN and $CH_2CH_2$ with $TBABF_4$ electrolyte. No ECL emission spectra characteristic of the metal centers were reported, however. ECL was detected by utilizing a photomultiplier tube with bandpass and cutoff filters to obtain an approximate location of the ECL peaks.[15] We reinvestigated $Eu(TTA)_3(phen)$ due to its high luminescence

Scheme 2. Photophysical Processes for the **$\beta$-Diketonate ($L^-$) Ligand**[a]



[a] In this case, $L^- = DBM^-$. The absorption of photons by $DBM^-$ is followed by intramolecular energy transfer (en) to the rare earth center, followed by luminescence from the 4f orbitals of the metal center in the covalently linked $La^{III}[2.2.1](L)^{2+}$ system (La refers to a trivalent lanthanide metal ion such as Tb or Eu).

quantum efficiency [~48% vs $Ru(bpy)_3^{2+}$].[33] As seen previously,[15] this complex displays no oxidation waves and two irreversible reductions (both assigned as ligand-based processes) in the potential range +2.0 to −2.8 V vs $Fc/Fc^+$. Thus, despite the intense photoluminescence efficiency, the electrochemistry, i.e., lack of oxidation and the irreversible nature of the reduction waves, suggests that this is a poor candidate for annihiliation ECL (i.e., excitation via electron transfer of oxidized and reduced forms). An alternative approach involves application of a coreactant to generate the oxidant.[2] Weak emission was obtained with $S_2O_8^{2-}$, using a single-photon-counting apparatus (Hamamatsu R928P photomultiplier tube cooled to −15 °C) as a detector. However, the light intensity was so weak that no spectrum could be obtained using the CCD. Most of the emission originated at the Pt auxilliary electrode, probably by a high-voltage electroluminescent mechanism,[16−18] since ECL was not observed at the working electrode during controlled-potential sweeps to positive potentials. Several solvent systems were employed in attempts to improve both ECL efficiency and find conditions where the reduction waves were more reversible (e.g., DMF, THF, MeCN/$H_2O$), but these were unsuccessful. On the basis of these results, we feel the only previous report of direct ECL from a rare earth chelate may have been largely electroluminescence.[15]

**Chelates.** When the potential of the platinum electrode was swept to −2.20 V vs AgQRE in MeCN solutions containing chelate and $(TBA)_2S_2O_8$, emission was observed at potentials corresponding to reduction of the chelate complexes as shown in Figure 4. The ECL spectra for the $BA^-$, $DBM^-$, and $HFAC^-$ chelates (Figure 5) were essentially the same as those for the photoluminescence and thus correspond to 4f−4f metal-centered transitions. $(pipH^+)$-$Eu(DBM)_4$ exhibits an ECL emission spectrum at intensities

---

(32) Pikramenou, Z.; Yu, J.-A.; Lessard, R. B.; Ponce, A.; Wong, P. A.; Nocera, D. G. *Coord. Chem. Rev.* **1994**, *132*, 181.

(33) Richter, M. M.; Bard, A. J., unpublished results.

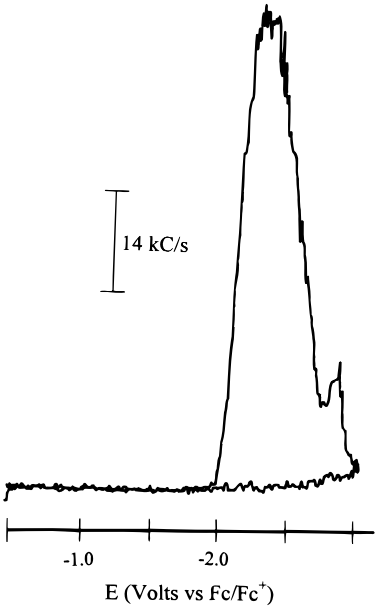


Figure 4. ECL emission for the reduction of 2 mM (TBA)Eu(TTA)$_4$ and 10 mM (TBA)$_2$S$_2$O$_8$ in MeCN/0.1 M TBAPF$_6$. Scan rate, 100 mV/s.

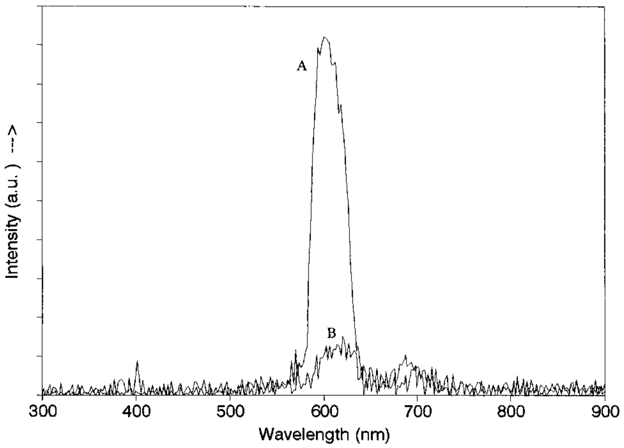


Figure 5. ECL spectra of (A) (TBA)Eu(DBM)$_4$ and (B) (TBA)Eu(BA)$_4$ in CH$_3$CN/S$_2$O$_8{}^{2-}$. Solutions were 4 mM in chelate, 10 mM in S$_2$O$_8{}^{2-}$, and 0.1 M in TBABF$_4$. The potential was continuously pulsed between 0.0 and 2.5 V vs AgQRE with a pulse duration of 1 s and an acquistion time of 30 min.

comparable to those observed with (TBA)Eu(DBM)$_4$. ECL was not observed in MeCN solutions containing only S$_2$O$_8{}^{2-}$, free $\beta$-diketone ligand, and S$_2$O$_8{}^{2-}$ or with the chelate complexes in the absence of S$_2$O$_8{}^{2-}$. The ECL could not be observed visually, even to the dark-adapted eye. When the CCD camera was focused directly on the surface of the electrode, integrated light intensities and an image of the light being generated at the electrode surface could be obtained. In all cases, light could be observed only at the Pt disk electrode, indicating that all of the chelates undergo ECL processes, forming the same excited states electrochemically as are formed photochemically. Only emissions for complexes containing DBM$^-$, BA$^-$, and HFAC$^-$ were sufficiently intense that spectra could be obtained with a CCD camera/monochromator.[23] Spectra could only be obtained after integrating for 30 min, indicating that the ECL efficiencies of the rare earth chelates are relatively small. In the TTA$^-$ and BTA$^-$ systems, discoloration of the solution occurred upon prolonged electrolysis ($\leq$30 min), suggesting the formation of decomposition products. At longer times ($\geq$1 h), the complexes incorporating HFAC$^-$ and BA$^-$ also showed signs of decomposition, in line with the labile nature of rare earth coordination compounds.[34]

The relative ECL efficiency was obtained by comparing the integrated intensity of the chelate/S$_2$O$_8{}^{2-}$ reaction system to that of the Ru(bpy)$_3{}^{2+}$/S$_2$O$_8{}^{2-}$ reference system. The integrated ECL intensities of the systems were measured in MeCN utilizing 1 mM complex, 10 mM S$_2$O$_8{}^{2-}$, and 0.1 M TBABF$_4$. The efficiency was estimated by comparing the ratios of the integrated emission intensity to the number of coulombs consumed in the reduction of the chelate, resulting in values in the range of $10^{-1}$–$10^{-4}$% (Table 2).

Attempts were also made to produce ECL by alternate pulsing of the electrode potential between the cathodic peak potential of the chelate reduction and the anodic peak potential of several added electroactive donor species via an annihilation type mechanism:[1]

$$A + e^- \rightarrow A^-$$

$$D - e^- \rightarrow D^+$$

$$A^- + D^+ \rightarrow A^* + D$$

$$A^* \rightarrow A + h\nu$$

(where D represents the donor and A the europium chelate complex, EuL$_4{}^-$). The donors used were *N*,*N*-dimethyl-*p*-toluidine ($E_{1/2} = +0.51$ V in CH$_2$Cl$_2$ vs SCE), 10-methylphenothiazene ($E_{1/2} = +0.58$ V in CH$_2$Cl$_2$ vs SCE), and tris(4-bromophenyl)amine ($E_{1/2} = +1.04$ V in CH$_2$Cl$_2$ vs SCE), all of which have been shown to produce ECL in the Mo$_6$Cl$_{14}{}^{2-}$ system.[35] ECL experiments were performed on MeCN solutions of the $\beta$-diketonate complexes containing equimolar concentrations of chelate and D. No ECL emission was observed upon pulsing a Pt electrode between potentials appropriate to ensure production of electrogenerated species D$^+$ and A$^-$ with either the CCD camera focused on the electrode surface or a single-photon-counting system. As noted above, these complexes display an irreversible oxidation at around +1.0 V vs Fc/Fc$^+$, presumably due to oxidation of the $\beta$-diketonate ligands attached to the Eu$^{3+}$ metal center which may, in part, account for the lack of ECL. However, even when the potential of the donor oxidation was at less positive potentials than that of the chelates, no ECL was observed, confirming earlier experiments with (pipH$^+$)Eu(DBM)$_4$.[14] Lack of chelate emission from all systems indicates that the population of the emitting chelate electronic states in this manner is not an energetically favorable process compared to oxidation with SO$_4{}^{\bullet-}$.[14]

**Cryptates.** We also investigated the possibility of ECL with europium cryptates, where the organic cage structure of the cryptand can shield the encapsulated metal ion from the solvent and slow decomposition. Because the cryptates are insoluble in acetonitrile, the ECL experiment was carried out in an aqueous solution containing 4 mM europium crypate salt, 10 mM (NH$_4$)$_2$S$_2$O$_8$, and 0.1 M NaClO$_4$ by pulsing the potential of the Pt working electrode into the background of the solvent ($\sim$−1.5 V vs SCE) to ensure reduction of both the peroxydisulfate (S$_2$O$_8{}^{2-}$)

---

(34) (a) Karraker, D. G. *J. Chem. Educ.* **1970**, *47*, 424. (b) Johnson, O. *J. Chem. Educ.* **1970**, *47*, 431. (c) Friedman, H. G.; Choppin, G. R.; Feuerbacher, D. G. *J. Chem. Educ.* **1964**, *41*, 355.

(35) Mussell, R. D.; Nocera, D. G. *Polyhedron* **1986**, *5*, 47.

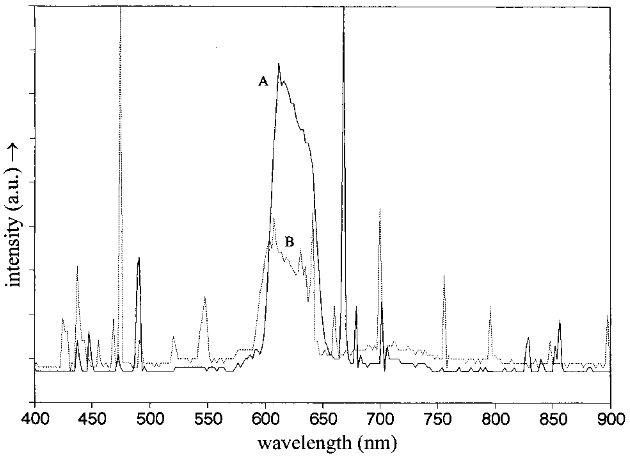


Figure 6. ECL spectra of (A) Eu[2.2.1](DBM)$^{2+}$ and (B) Eu[2.2.1](BA)$^{2+}$. Solutions were 4 mM in complex, 10 mM in $S_2O_8^{2-}$, and 0.1 M in $TBABF_4$. The potential was continuously pulsed between 0.0 and 2.5 V vs AgQRE with a pulse duration of 1 s and an acquistion time of 3 h.

and the cryptate molecule. No ECL emission was observed above background, even after prolonged integration with the CCD camera (>3 h).

**Mixed-Ligand Systems.** ECL was also observed when $\beta$-diketonate ligands were present in the cryptate systems, i.e., with Eu[2.2.1](DBM)$^{2+}$ and Eu[2.2.1](BA)$^{2+}$ (Figure 6). The spectra consisted of a single narrow band centered at ~612 nm, identical to those obtained in photoluminescence and characteristic of europium-centered emissions. ECL was observed in these systems under the same conditions described above for the chelates by pulsing the potential of the working electrode to −2.1 V vs AgQRE and measuring the intensity with the CCD camera. ECL was not visible to the dark-adapted eye, and the spectra could be obtained only after integration for a period of 3 h (as opposed to 30 min for the chelate systems). Relative estimated ECL efficiencies of $10^{-4}$% (±20%) were obtained (compare to $Ru(bpy)_3^{2+}/S_2O_8^{2-}$). These values are 2 orders of magnitude below those obtained in the $EuL_4^-$ chelates. One reason for this lower intensity in the mixed-ligand systems may be the number of $\beta$-diketonate ligands bound to the metal center (4:1, chelates/mixed-ligand systems, respectively).

## DISCUSSION

For organic and transition-metal complexes like $Ru(bpy)_3^{2+}$, ECL is usually interpreted on the basis of an energetic electron-transfer reaction.[1,2,36] In the ECL reaction scheme involving reduction in the presence of $S_2O_8^{2-}$, for example, the strongly oxidizing intermediate $SO_4^{\bullet-}$ removes an electron from the bonding orbital of the reduced complex, resulting in the excited state which then undergoes radiative emission to the ground state. In the case of electrogenerated $Ru(bpy)_3^{2+}$, electrochemical reduction results in the addition of an electron to the LUMO, which is $\pi^*$ in nature, while the ($SO_4^{\bullet-}$) abstracts an electron from the filled $t_{2g}$ metal orbitals. Thus, the emissive excited state is formed directly in the electron-transfer reaction. However, in contrast to the d orbitals of the transition elements, the f orbitals do not contribute significantly to bonding and hence to complexation in the lanthanide ions.[34] Because the f electrons lie deeply buried within the d, p, and s electronic shells, there is little metal/ligand orbital interaction and hence the broadening effects of ligand vibrations are minimized. Thus, the f−f spectra of the lanthanides are sharp or atomic-like. Vogler and Kunkely[15] concluded that the electron transfer among electrogenerated species formed a nonemitting excited state, presumably centered on the ligand part of the molecules, since no metal-centered electrochemistry was observed in either the Eu or Tb systems. This nonemitting state then underwent intramolecular energy transfer to the metal f orbitals to form the emitting excited states, analogous to what is observed photochemically in an "antenna" or ligand-sensitized luminescence mechanism (Figure 3).[12] This mechanism is plausible for this ECL, especially in complexes of Tb where the metal orbitals are too high to be accessible for reduction at potentials accessible in acetonitrile (~3.0 V vs Fc/Fc$^+$).

In the Eu chelates incorporating $\beta$-diketonate-type ligands, no reduction is observed in the cyclic voltammetry at ~−0.50 V, where one would expect the Eu$^{3+/2+}$ couple to occur and which is observed in Eu cryptate complexes such as those studied here.[21] This suggests that the metal f orbitals are screened by the ligand orbitals, resulting in redox behavior characteristic of ligand-based processes at even more negative potentials. This is an indication that direct formation of metal-centered excited states is not possible in these systems and that ECL occurs via a ligand-sensitization mechanism such as that described above, where nonemissive ligand excited states are formed from which intramolecular energy transfer takes place (Figure 3, steps 4 and 5 followed by 2 and 3).

$$Eu^{III}(L^-)_3L^{\bullet 2-} + SO_4^{\bullet -} \rightarrow Eu^{III}(L^-)_3L^{-*} \rightarrow Eu^{III*}(L^-)_4^-$$

The absence of ECL in the Eu[2.2.2]$^{3+}$ and Eu[2.2.1]$^{3+}$ complexes suggests a non-energy-transfer route is not available in these, however. The cryptands display a metal-centered reduction at ~−0.50 V vs Fc/Fc$^+$ assignable to the Eu$^{3+/2+}$ couple, suggesting direct access to the metal-centered orbitals. The ligand orbitals in the [2.2.2] and [2.2.1] cryptands are of such energies as to not be observed in the potential range used. The lack of ECL shows that even though the quenching effects of bound solvent molecules on the excited-state Eu$^{3+}$ are minimized by encapsulation and decomposition is reduced, the ligand orbitals are too high to take part in the sensitization of the metal ion. This leads us to conclude that the organic $\beta$-diketonate ligands that produce high luminescence efficiency are also necessary in the ECL process.

As noted above, ECL was observed when the $\beta$-diketonate ligands BA$^-$ and DBM$^-$ were incorporated into the Eu[2.2.1]$^{3+}$ framework. Although the ECL was weak, 2 orders of magnitude below that in the $EuL_4^-$ complexes under the same experimental conditions, spectra could be obtained (Figure 6). Complexes incorporating BA$^-$ and DBM$^-$ produce ECL spectra in both the chelates and mixed-ligand systems while those incorporating BTA$^-$ and TTA$^-$ do not. Experiments on the mixed-ligand HFAC$^-$ complex Eu[2.2.1](HFAC)$^{2+}$ were inconclusive since only a weak signal a few units above background was obtained. These results coupled with the lack of signal for the Eu[2.2.1]$^{3+}$ and Eu[2.2.2]$^{3+}$ cryptates further supports the ligand-sensitization mechanism. Thus, ECL seems to depend highly on the nature of the ligands

---

(36) Faulkner, L. R.; Glass, R. S. In *Chemical and Biological Generation of Excited States*; Adam, W., Cilento, G., Eds.; Academic Press: New York, 1982; p 191.

bound to the rare earth metal ions as well as the number of light-absorbing or "light-harvesting" $\beta$-diketonate-type ligands.

As has been discussed,[15] it is difficult to draw precise mechanistic conclusions in systems with extremely low ECL intensity such as these, since ECL can originate from products of side reactions (i.e., decomposition where an unbound ligand takes part in sensitization of the metal center). However, the cyclic voltammetric experiments coupled with emission detection (Figure 4) show that ECL is observed at potentials corresponding to the bound ligand-centered $EuL_4^-$ reductions. Thus, the emission can be attributed to interaction of the $SO_4^{\bullet -}$ radical with the reduced chelate complex, ultimately resulting in metal-centered emission. Despite the low ECL efficiencies, our observations, coupled with the work of Vogler and Kunkely[15] and unpublished studies,[37] indicate that ECL in the rare earths is a fairly general, if weak, phenomenon where the ligands appear to be involved directly in the ECL mechanism.

ECL efficiencies in these rare earth complexes is disappointing for application as labels, considering the intense nature of the photoluminescence quantum efficiencies. The most intense ECL emission obtained with $(pipH^+)Eu(DBM)_4$ was only 0.62% that of $Ru(bpy)_3^{2+}$ under similar conditions. The reason for the low efficiency for the Eu chelates is connected to the efficiency of production of the excited state in the electron-transfer reaction, since the photoluminescence efficiencies of these species are as high or higher than $Ru(bpy)_3^{2+}$.

According to Marcus theory, excited-state formation is expected to be favored over ground-state formation if the driving force of the electron transfer is very high (the "inverted-region" effect).[36,38] Due to the highly energetic nature of the species formed, electron transfer to form the emitting species is only one of several competing processes. For example, even if excited-state formation is energy sufficient (if the potential difference of the redox species exceeds the excitation energy), radiationless reformation of the ground state may occur. Similarly, only a small fraction of the electrogenerated products may undergo the "annihilation" reaction to form the excited states. In the case of of the self-annihilation reaction of $Ru(bpy)_3^{2+}$, it has been shown that the electrogenerated species, which undergo the annihilation electron-transfer reaction, all produce excited states. However, of these, only 1 in 20 or ~5% are believed to undergo emission.[2a,3a,b] Thus, unit efficiency of excited-state formation is observed which does not necessarily hold in other systems.

Cyclic voltammetry gives an indication of the relative stability of the reduced and oxidized forms of a species; irreversible waves are indicative of instability in a molecule. The unstable molecule undergoes a rearrangement or substitution on the time scale of the experiment, and this can compete with the electron-transfer reaction necessary to produce the emitting excited state. For example, loss of a ligand upon dissolution is a common occurence in rare earth complexes[34] due to their labile nature, and in the presence of even trace amounts of water, replacement of a coordinated ligand by a water molecule is possible.

Cyclic voltammetric experiments on the Eu chelates incorporating $\beta$-diketonate ligands showed reductions characteristic of irreversible processes (Table 1, Figure 1D) for all complexes except those incorporating $DBM^-$. Upon prolonged electrolysis in the presence of persulfate only $(pipH^+)Eu(DBM)_4$ and $(TBA)Eu(DBM)_4$ displayed little or no signs of decomposition as shown by discoloration of solution. These two systems also displayed the highest ECL emission efficiencies. The mixed-ligand chelate/cryptate systems also display irreversible electrochemistry assigned to ligand-based processes. Furthermore, under the experimental conditions for obtaining ECL spectra, discoloration of the solution occurs, indicating that at least partial loss of the $\beta$-diketonate ligand from the cryptate framework is occurring. The order of magnitude difference between $\phi_{ECL}$ in going from the chelates to the mixed-ligand systems may also be accounted for in this manner, since in the mixed-ligand systems fewer light-absorbing ligands remain to sensitize the metal center. We also postulate that the strongly oxidizing intermediate $SO_4^{\bullet -}$ removes an electron from the bonding orbital of the reduced ligand, where this interaction may itself lead to decomposition or side reactions. As was the case with the $Eu[2.2.2]^{3+}$ and $Eu[2.2.1]^{3+}$ cryptands, the mixed-ligand $BA^-$ and $DBM^-$ systems display a reversible couple at potentials characteristic of metal-centered $Eu^{3+/2+}$ reduction. This reduction coupled with the irreversible ligand-based processes at significantly more negative potentials leads to a more complicated ECL mechanism and may also lead to lower values of $\phi_{ECL}$. Orbital energies are also a factor to consider since the efficiency of the intramolecular energy transfer and hence both the photoluminescence and ECL efficiencies are dependent upon the nature of the ligands. However, while there is a correlation between the HOMO−LUMO difference (energy gap) of ML* (Figure 3; Table 2) and $\phi_R$ (as judged by spectroscopic absorbance data), there is little apparent correlation between the energy gap and the relative ECL efficiency. Energy transfer to form the M*L state (Figure 3) is apparently more efficient for $Eu(BTA)_4^-$ and $Eu(TTA)_4^-$ when these state are populated photochemically (vide infra). On the other hand, these complexes display poor ECL. In fact, $Eu(DBM)_4^-$ has the smallest energy gap (~3 eV) and a relatively low $\phi_R$ (~8%) while displaying the highest ECL efficiency (~0.6%). Thus, the importance of orbital energies on ECL is hard to quantify. In this study, complex stability and the ability of the $\beta$-diketonate ligand to undergo efficient electron transfer with $SO_4^{\bullet -}$ to form ML* appear to be more important in the efficiency of the ECL process.

## CONCLUSIONS

The electrochemical reduction of various europium complexes containing different ligand assemblies in the presence of reduced $S_2O_8^{2-}$ generates emission spectra characteristic of the metal center and, to our knowledge, is the first direct ECL in a rare earth complex where spectra are reported. The ECL appears to occur by a mechanism different from that observed in transition-metal complexes. The initial excited states formed in the ECL reaction sequence appear to be centered on the ligand portions of the molecule with subsequent intramolecular electron transfer to the metal-centered orbitals resulting in ligand sensitization of the metal center. The ECL intensity is orders of magnitude lower than that of the previously reported $Ru(bpy)_3^{2+}$ systems, limiting their practical use in analytical applications. In this instance, encapsulation within a cryptate framework does not appear to offer any advantages in terms of ECL efficiency since those systems incorporating a cryptate framework resulted in lower ECL efficiencies by at least 1 order of magnitude over the $EuL_4^-$ systems. The ECL seems to depend highly on the nature of the ligands bound to the rare earth metal, with those ligands possessing orbitals of proper energy to promote energy transfer within the

---

(37) Billadeau, M. M.; Leland, J. K.; Gudibande, S., unpublished studies.
(38) Marcus, R. A. *Rev. Mod. Phys.* **1993**, 65.

4f orbital framework leading to enhanced ECL. The number of ligands may also play a role since ECL in the mixed-ligand (cryptate/$\beta$-diketonate) systems is weaker than in the complexes incorporating solely $\beta$-diketonate bis-chelating ligands. The lack of accessibility of the f orbitals may in part account for the proposed mechanism as well as the low ECL efficiency, since $SO_4^{\bullet -}$ can remove an electron from a more readily accessible ligand, resulting in more than one pathway for the excited electron to lose its energy. Despite the low $\phi_{ECL}$ and the constraints these place on making precise mechanistic arguments, it is fairly clear from the variety of ECL active rare earth systems studied to date that the ligands play an integral role in both the ECL and photoluminescence experiments.

## ACKNOWLEDGMENT

We thank Thomas Richards, Frank Fan, and Jeff Debad for helpful discussions throughout this work and Mark Billadeau, John Leland, and Satya Gudibande of IGEN for access to their results. The support of this research by IGEN, the Texas Advanced Research Program, and the Robert A. Welch Foundation is gratefully acknowledged.

Received for review March 1, 1996. Accepted May 27, 1996.⊗

AC960211F

---

⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1996.