

## Electrogenerated chemiluminescence. XXI. Energy transfer from an exciplex to a rare earth chelate

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- (18) Compound IIIa is reported to be unstable.<sup>7a</sup>
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- (21) In recent attempts we have been unable to prepare the pure phenyl ester of 5,5-dimethyluciferin by the method described earlier.<sup>3</sup>
- (22) Numbers reported are mean values of several experiments; errors are estimated to be about 10% or less.
- (23) Insufficient data were presented to prove that on the scale of operations chosen (0.7  $\mu$ l of CO<sub>2</sub> produced in 6.5 ml of glycylglycine buffer at pH 7.8;<sup>15</sup> 0.9  $\mu$ l of CO<sub>2</sub> in 3.7 ml of phosphate buffer at pH 7.2)<sup>16</sup> that (1) the carbon dioxide could be recovered in reasonable amounts from the aqueous phase, in competition with exchange, and (2) the carbon dioxide produced from the luciferin was not swamped by atmospheric carbon dioxide. Also, control runs in which bubbles of carbon dioxide are passed through solutions (either aqueous or DMSO + *tert*-butoxide) are not close to the processes occurring in bio- or chemiluminescence in which carbon dioxide is produced in true solution—molecule by molecule. See also ref 3 and "Chemiluminescence and Bioluminescence," M. J. Cormier, D. M. Hercules, and J. Lee, Ed., Plenum Press, New York, N.Y., 1973, pp 358–359.
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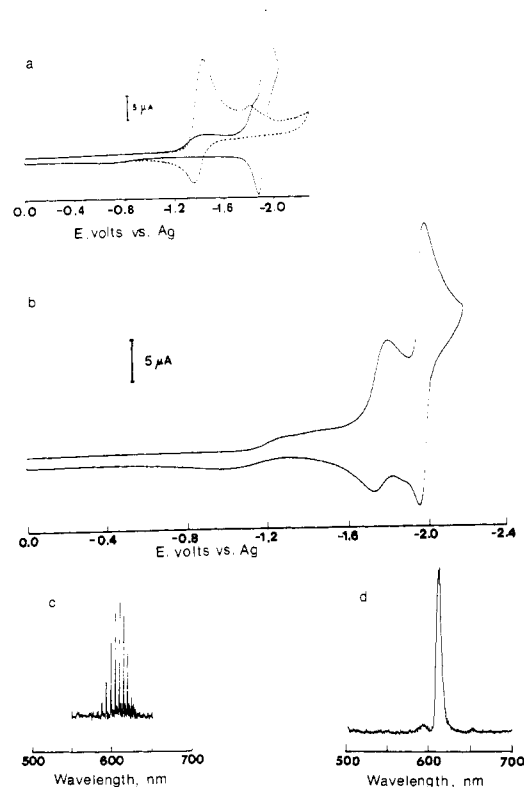
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## Electrogenerated Chemiluminescence. XXI. Energy Transfer from an Exciplex to a Rare Earth Chelate

Sir:

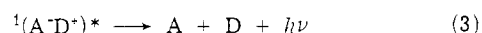
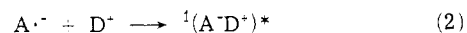
Intermolecular energy transfer from the lowest triplet ( $n, \pi^*$ ) state of a carbonyl compound (*e.g.*, benzophenone) to the ligand of a rare earth chelate, which in turn intramolecularly transfers its energy to the central metal ion with subsequent narrow band emission from the metal ion, has been reported by several investigators.<sup>1–5</sup> For example, El-Sayed and Bhaumik<sup>2,3</sup> showed this "inter-intra" molecular energy transfer from photoexcited benzophenone to a Eu(III) chelate, while Wildes and White<sup>4</sup> described sensitized chemiluminescence of lanthanide chelates by energy transfer from the excited species generated by dissociation of dioxetane. We report here the observation of intermolecular energy transfer from an excited charge-transfer complex (an exciplex or heteroexcimer) directly to a europium chelate. The exciplex was produced by the electron transfer reaction of electrogenerated radical ions<sup>6</sup> under conditions where the triplet states cannot be formed and to our knowledge is the first reported example of intermolecular exciplex-sensitized luminescence.

In electrogenerated chemiluminescence (ecl) and radical ion chemiluminescence (cl) reactions, excited states are formed by an energetic electron transfer reaction; frequently these are excited states of the acceptor (A) or donor (D) species themselves



**Figure 1.** (a) Cyclic voltammogram of 1 mM Eu(DBM)<sub>3</sub> · pip and 0.1 M TBAP acetonitrile at a platinum disk electrode with a scan rate of 200 mV/sec. Dotted line is reduction of free ligand, DBMH; (b) cyclic voltammogram of TPTA-benzophenone with Eu(DBM)<sub>3</sub> · pip in acetonitrile. Scan rate was 200 mV/sec at the platinum disk electrode. Solution contained 1.2 mM TPTA, 1.1 mM benzophenone, 1.6 mM Eu(DBM)<sub>3</sub> · pip, and 0.1 M TBAP; (c) ecl spectrum obtained from solution in (b) with pulse duration, 1 sec; (d) fluorescence spectrum of Eu(DBM)<sub>3</sub> · pip in acetonitrile, with excitation at 421 nm.

In many cases, however, longer wavelength (red-shifted from the excited singlet A or D peaks by about 6000 cm<sup>-1</sup>), structureless, emission is also observed and this has been identified as originating from an exciplex directly formed in the radical ion reaction.<sup>6–10</sup>



In some cases, where the energy of the radical ion reaction is less than that necessary to form excited singlet or triplet states of A and D, *e.g.*, for the case of the reaction of tri-*p*-tolylamine (TPTA) radical cation and either benzophenone (BP) or dibenzoylmethane (DBMH) radical anion, only exciplex emission is observed. If the europium chelate Eu(DBM)<sub>3</sub> · piperidine or Eu(DNM)<sub>3</sub> · piperidine (where DBM is dibenzoylmethide and DNM is dinaphthoylmethide) is added to the TPTA-BP or TPTA-DBMH ecl systems, emission characteristic of Eu(III) is observed, and we describe experiments below which demonstrate that this emission is a result of energy transfer from the exciplex.

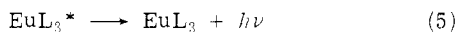
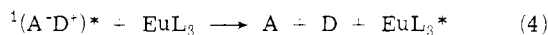
Experimental techniques in the ecl studies followed previous practice;<sup>6,9,10</sup> details on chelate preparation, solvent purification, and apparatus are available.<sup>11</sup> Spectroscopic and electrochemical data for the Eu chelates as well as TPTA, BP, and DBMH are given in Table I. Consider an ecl experiment with a solution containing 1.2 mM TPTA, 1.1 mM BP, 1.6 mM Eu(DBM)<sub>3</sub> · piperidine and 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) in acetonitrile at a Pt electrode (Figure 1). A cyclic voltammogram of the chelate (Figure 1a) is characterized by a reversible one-electron reduction wave at -1.94 V; the small waves at -1.43 and

**Table I.** Electrochemical and Spectroscopic Data

Compound	$E_{p,red}^a$	$E_{p,ox}^a$	$E_T$ , eV	$\Delta H^\circ$ , <sup>b</sup> eV	$h\nu$ , nm
Eu(DBM) <sub>3</sub> ·pip	-1.94	n.o. <sup>c</sup>		2.78	612 <sup>f</sup>
Eu(DNM) <sub>3</sub> ·pip	-1.68	n.o. <sup>c</sup>		2.52	610 <sup>f</sup>
TPTA	n.r. <sup>c</sup>	1.00	2.9 <sup>d</sup>		
BP	-1.75	n.o. <sup>c</sup>	2.97 <sup>e</sup>	2.59	~490 to 700 <sup>g</sup>
DBMH	-1.43	n.o. <sup>c</sup>	2.77 <sup>e</sup>	2.27	~550 to 730 <sup>g</sup>

<sup>a</sup> Solutions contained about 1.0 mM depolarizer and 0.1 M TBAP in acetonitrile. Potentials vs. Ag reference electrode. <sup>b</sup> For reaction of reduced form with TPTA·<sup>+</sup>, calculated from  $-\Delta H^\circ = E_{p,red} - E_{ox} + 0.16$  eV.<sup>12</sup> <sup>c</sup> n.r. = not reduced, n.o. = not oxidized, in region of interest. <sup>d</sup> From ref 8. <sup>e</sup> From ref 13. <sup>f</sup> Emission peak obtained by optical excitation. <sup>g</sup> Ecl emission from the electron transfer reaction of TPTA·<sup>+</sup> and corresponding anions;  $\lambda_{max}$  values were 581 nm for (TPTA·<sup>-</sup>-BP·<sup>-</sup>) and 665 nm for (TPTA·<sup>-</sup>-DBMH·<sup>-</sup>).

-1.80 V are probably due to free ligand (DBMH), which cannot be removed from the chelate even by several recrystallizations and sublimation. A cyclic voltammogram of the reduction in a similar solution containing TPTA and BP (Figure 1b) shows that BP can be reduced without reduction of the Eu(III) complex. When the potential of the platinum electrode is pulsed, with a pulse length of 1 sec, from -1.81 V (BP·<sup>-</sup> production) to +1.06 V (TPTA·<sup>+</sup> production) the exciplex emission observed in the absence of Eu chelate (a broad band with a maximum at 581 nm) is replaced by a narrow band at 612 nm (Figure 1c); this emission corresponds to the luminescence observed from the chelate alone upon photoexcitation (Figure 1d). Note that the electron transfer reaction between TPTA·<sup>+</sup> and the reduced Eu(III) chelate does not produce ecl emission (although the energy of the reaction is sufficient to produce an excited chelate species), so that the observed emission cannot be attributed to this source (e.g., from trace amounts of reduced complex formed at the foot of its wave). Moreover trivial excitation of the chelate by the emitted light from the exciplex cannot occur, since the absorption maximum of the complex is at 2.95 eV and excitation at wavelengths of exciplex emission (ca. 2.14 eV) fails to produce chelate emission. Finally excited states of TPTA and BP cannot be formed in the electron transfer reaction since the energy of the reaction ( $\Delta H^\circ \approx 2.59$  eV) is significantly below the triplet energies of these species. The results are consistent with the formation of exciplex, reaction 2, followed by energy transfer.



Very similar results are obtained with the TPTA-DBMH-Eu(DNM)<sub>3</sub>·piperidine system. In the absence of chelate the electron transfer reaction between TPTA·<sup>+</sup> and DBMH·<sup>-</sup> ( $\Delta H^\circ \approx 2.27$  eV) produces exciplex emission (a band at 615-665 nm) and is energetically incapable of producing excited states of the parent species. When Eu(DNM)<sub>3</sub>·piperidine is added, only emission from the Eu chelate is observed.

The results suggest that the energy transfer reaction between exciplex and chelate must be a very rapid one, since the exciplex emission is quenched by millimolar amounts of chelate. Since there is essentially no overlap between the exciplex emission and chelate absorption spectra, a long range Förster-type dipole-dipole interaction is improbable, and a diffusion-controlled collisional transfer appears more probable. One possibility, suggested by a reviewer,<sup>14</sup> is that the EuL<sub>3</sub> facilitates intersystem crossing of <sup>1</sup>(A·<sup>-</sup>D<sup>+</sup>) to the triplet exciplex. Energy transfer from the triplet exciplex to

the chelate then produces EuL<sub>3</sub>\*. Finally we should point out the unique advantage of ecl or cl methods in a sensitization study of this sort. The selective formation of exciplex via the A·<sup>-</sup>/D<sup>+</sup> reaction avoids the production of excited states of A and D, required in photoexcitation experiments, which complicate the interpretation of the results.<sup>15</sup>

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- (15) Support of this research by the Army Research Office-Durham is gratefully acknowledged.

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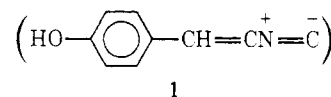
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## Cooccurrence of a Terpenoid Isocyanide-Formamide Pair in the Marine Sponge *Halichondria* sp.

Sir:

Prior to the recent isolation of two sesquiterpenoid isocyanides from marine sponges,<sup>1,2</sup> an isocyanide had only once been reported as a naturally occurring function, namely in xanthocillin (1),<sup>3</sup> a mold metabolite of *Penicillium not-*



*atum*. The postulate of a formamide precursor of this unique natural product seemed an attractive idea, but Achenbach and Grisebach's<sup>4</sup> attempt at illuminating the biogenesis of the isocyanide function in xanthocillin failed. We now have in hand strong presumptive evidence that formamides are precursors of isocyanides in the marine sponge of the genus *Halichondria*, by isolating from this animal two isocyanide-formamide pairs, one a sesqui- (80%) and the other a diterpene (20%). The structures of the sesquiterpenoids are the subject of this report.

In the course of our program on antimicrobial constituents of marine sponges, we examined the active extract of *Halichondria* sp., which was collected by trawling at a depth of 200 m off the north shore of Oahu. Methanol extraction of the sponge, followed by ether-water partition of the residue, furnished 2.3% (based on dry weight of the animal) of an oil which was separable by preparative tlc on silica gel (methylene chloride-hexane 1:1, visualized with long wavelength uv light). The major portion of the oil consists of functional derivatives 2-4 of the sesquiterpene 4-amorphene (5) in addition to two nonfunctionalized dienes, ole-