

# Chemiluminescence in the oxidation of europium $\beta$ -diketonates by dimethyldioxirane

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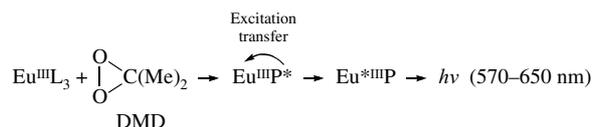
The oxidation of  $\text{Eu}(\text{FOD})_3$  and  $\text{Eu}(\text{TTA})_3$  (FOD is heptafluorodimethyloctanedionate and TTA is thenoyltrifluoroacetate) by dimethyldioxirane (DMD) is accompanied by chemiluminescence; the excitation of europium(III) occurs due to an energy released upon oxidation of the ligands.

Luminescent lanthanide complexes are widely studied as structural and analytical luminescent probes and labels in various chemical and biochemical investigations.<sup>1,2</sup> Another important feature of lanthanide chemistry is the utilization of these compounds as activators of chemiluminescence (CL) arising in chemical reactions,<sup>3–11</sup> such as oxidation of organic compounds<sup>5</sup> and decomposition of dioxetanes.<sup>1,6–10</sup> Among the compounds of lanthanides, the complexes with organic ligands such as europium  $\beta$ -diketonates, which exhibit intense fluorescence and high solubility in organic solvents, are useful for CL enhancement. A study of the CL of lanthanide chelates allows one to receive information on the mechanisms of various dark processes (e.g., quantum chain reactions) which otherwise are difficult or even impossible to explore.<sup>9,10</sup>

It is generally accepted that lanthanide  $\beta$ -diketonates are inert activators, which are excited *via* intermolecular energy transfer from the excited species formed in a chemiluminescent reaction to the metal-centered  $4f$  states. In this communication, we report a new type of lanthanide CL, when light emission arises due to the oxidation of organic ligands rather than as a result of outersphere energy transfer.

We found that the interaction of  $\text{Eu}(\text{FOD})_3$  with the powerful organic peroxide oxidant DMD<sup>12,13</sup> is accompanied by bright CL. A study of the kinetics of CL<sup>†</sup> revealed that  $\text{Eu}(\text{FOD})_3$  is not an energy acceptor, but chemically interacts with the dioxirane. In fact, regardless of the ratio between the reactants, the kinetics of CL decay has a rather complex character (Figure 1) and is characterised by the presence of two maxima (the first maximum, lasting 2–3 seconds and the second, which is considerably more prolonged and intense). Figure 1 shows that the total period of the CL decay coincides with the time of decrease of the dioxirane concentration (determined by iodometry in a control experiment) in the course of the reaction with  $\text{Eu}(\text{FOD})_3$ , and the consumption of DMD is stopped with the end of CL decay.

Iodometric analysis revealed that, regardless of the excess (from 10 to 20 equivalents) of dioxirane over a lanthanide chelate, six equivalents of DMD is consumed in the reaction with one equivalent of  $\text{Eu}(\text{FOD})_3$  so that two molecules of the dioxirane react with one molecule of the FOD ligand. The more excess of



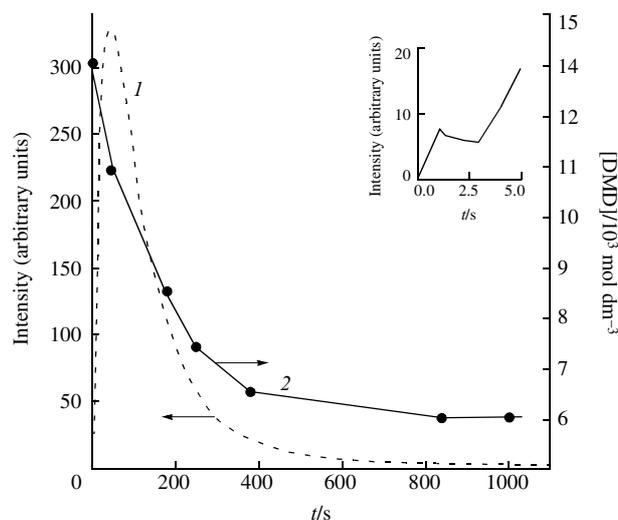
L is heptafluorodimethyloctanedionate or thenoyltrifluoroacetate  
P is the product of L oxidation by DMD

### Scheme 1

DMD over  $\text{Eu}(\text{FOD})_3$  is taken in the reaction, the shorter time is needed to reach the main maximum in the kinetic curve of CL decay. The overall time of luminescence decay also decreases with increasing DMD concentration at a constant concentration of the europium complex.

The emitter of CL is an excited  $\text{Eu}^{\text{III}}$  ion since the CL spectrum recorded in the reaction of DMD with  $\text{Eu}(\text{FOD})_3$  corresponds (Figure 2) to the photoluminescence spectrum of europium (570–650 nm). The yield of CL (20 °C, acetone,  $[\text{Eu}(\text{FOD})_3]_0 = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{DMD}]_0 = 6 \times 10^{-3} \text{ mol dm}^{-3}$ ) was calculated from the ratio of the total amount of light evolved in the reaction to the initial DMD concentration to be  $6 \times 10^{-7} \text{ einstein mol}^{-1}$ . Unfortunately, it is impossible to calculate the europium excitation yield since the photoluminescence intensity considerably decreases during the reaction with DMD.

The CL behaviour appeared to be sensitive to the presence of water. When the reaction was carried out in wet acetone, an almost threefold decrease in CL intensity was observed. This effect is expectable since  $\text{H}_2\text{O}$  is known to quench the luminescence of lanthanides. However, the duration of CL decay is also significantly shortened (by a factor of 4–6) in the presence of water, indicating that the latter influences the chemical inter-



**Figure 1** Kinetics of (1) CL decay and (2) consumption of DMD in the reaction with  $\text{Eu}(\text{FOD})_3$  (acetone, 20 °C,  $[\text{Eu}(\text{FOD})_3] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{DMD}] = 1.4 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $\text{N}_2$  atmosphere). Insert: the initial fast flash of CL intensity.

<sup>†</sup> CL was recorded using a FEU-140 photomultiplier on a photometric setup. In a typical procedure, a solution of  $\text{Eu}(\text{FOD})_3$  in acetone was added to an acetone solution of DMD. The concentrations of reactants were varied in the ranges  $(5\text{--}100) \times 10^{-4} \text{ mol dm}^{-3}$  for  $\text{Eu}(\text{FOD})_3$  and  $(1\text{--}25) \times 10^{-3} \text{ mol dm}^{-3}$  for DMD. The reactions were carried out at 20 °C in a nitrogen atmosphere. DMD as an acetone solution was stored at –24 °C over molecular sieves 4 Å before use.  $\text{Eu}(\text{FOD})_3$  was dehydrated according to the published method.<sup>14</sup> The reactions were carried out in anhydrous acetone, which was obtained by boiling over  $\text{K}_2\text{CO}_3$  for several hours followed by distillation from molecular sieves. In order to test the influence of water on the CL behaviour, in a control experiment, a small amount of twice distilled water was added to anhydrous acetone solutions of the reactants before the reaction so that the overall reaction volume contained ca. 1%  $\text{H}_2\text{O}$ . The solvent effect on the CL behaviour was tested using dry co-solvents such as benzene,  $\text{CCl}_4$ , MeCN, ethyl acetate, MeOH and *tert*-butanol added to acetone in a 12.5:1 ratio.

action of the europium chelate with the dioxirane, presumably due to the ability of H<sub>2</sub>O to act as a donor of hydrogen bonds or possible coordination of water to the metal. In fact, solvents with hydrogen bond donor capacity, such as MeOH and *tert*-butanol, significantly accelerate the rate of CL decay as compared with acetone and MeCN. On the other hand, the solvent polarity is also important for this chemiluminescent reaction. Thus, the CL decays faster in weakly polar benzene or carbon tetrachloride compared with more polar acetone, acetonitrile and ethyl acetate.

The europium complex is oxidised by DMD as follows from NMR and UV-spectroscopic data. The UV spectrum of the reaction product (acetone was evaporated from the system, and the residue was dissolved in CCl<sub>4</sub>) showed no intense absorption of Eu(FOD)<sub>3</sub> at  $\lambda_{\max} = 290$  nm, whereas a new weaker absorption band appeared at  $\lambda_{\max} = 420$  nm. The <sup>1</sup>H NMR spectrum [the residue was dissolved in a CDCl<sub>3</sub>–MeOH (2.5:1) mixture] showed a new signal at 3 ppm instead of that at 6 ppm attributed to the proton of the CH group<sup>14</sup> (the signal of *tert*-butyl at 1.1 ppm remained unchanged). The photophysical characteristics of the reaction product are also completely different from those of the initial europium chelate. The new compound emits much less intense fluorescence upon irradiation with ultraviolet light at 390 nm: the photoluminescence spectrum taken after the reaction with DMD showed a drastic decrease in the photoluminescence intensity (PL-I) of europium (by more than two orders of magnitude), as compared with initial Eu(FOD)<sub>3</sub>. A redistribution of photoluminescence bands of europium is also observed (Figure 2).

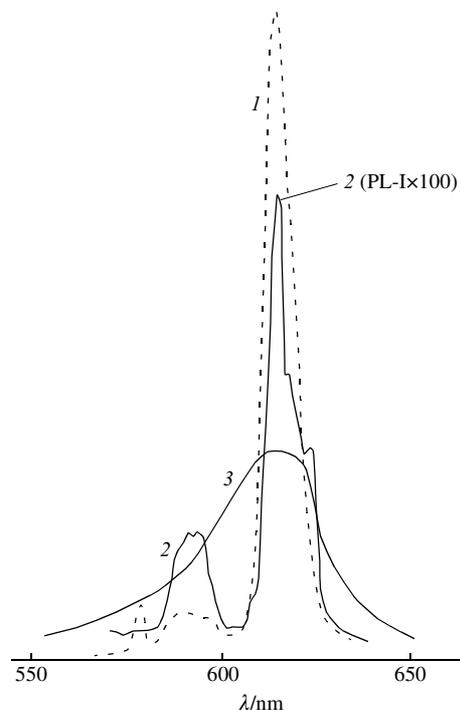
Similar results were obtained with the Eu(TTA)<sub>3</sub> complex (TTA = thenoyltrifluoroacetate). The CL emitter observed in the reaction of Eu(TTA)<sub>3</sub> with DMD is an excited europium ion (570–650 nm), and the kinetics of luminescence decay is characterised by the presence of a maximum. Eu(TTA)<sub>3</sub> is oxidised by DMD as manifested by the disappearance of its UV absorption at 343 nm in the course of the reaction. As in the case of Eu(FOD)<sub>3</sub>, six equivalents of DMD were consumed in the reaction with one equivalent of Eu(TTA)<sub>3</sub>, and the newly formed product of the chelate oxidation is more than two orders of magnitude weakly fluorescent compared with the initial europium complex.

Although the precise mechanism of the reaction of DMD with Eu(FOD)<sub>3</sub> or Eu(TTA)<sub>3</sub> remains unknown, the data obtained allow us to conclude that the excitation of europium occurs as a result of its oxidation by the dioxirane.<sup>‡</sup> The presence of a maximum in the kinetic curve of CL decay occurring upon the interaction of Eu(TTA)<sub>3</sub> and Eu(FOD)<sub>3</sub> with DMD is obviously caused by the accumulation of an intermediate (presumably of a peroxidic type) and its subsequent exothermic decomposition followed by energy transfer to the metal ion (Scheme 1).

The results of this work also testify that the  $\beta$ -diketonates of europium are not always passive and may significantly contribute to the production of CL as a result of their oxidation by peroxides. This circumstance should be taken into account when lanthanide complexes are used as 'inert' activators for studying chemi- or bioluminescent reactions.

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<sup>‡</sup> The results of this work give an example of the generation of excited states during the oxidative reactions of dioxiranes. The area of so-called oxidative CL of dioxiranes is a highly perspective avenue of their chemistry, which has begun to be explored only in recent years.<sup>13,15,16</sup>



**Figure 2** (1) Luminescence spectrum of Eu(FOD)<sub>3</sub> (acetone, 20 °C, [Eu(FOD)<sub>3</sub>]<sub>0</sub> = 3×10<sup>-3</sup> mol dm<sup>-3</sup>). (2) Luminescence spectrum of the reaction mixture taken after the reaction of Eu(FOD)<sub>3</sub> with DMD (acetone, 20 °C, [Eu(FOD)<sub>3</sub>]<sub>0</sub> = 3×10<sup>-3</sup> mol dm<sup>-3</sup>, [DMD]<sub>0</sub> = 3×10<sup>-2</sup> mol dm<sup>-3</sup>). (3) Chemiluminescence spectrum taken during the reaction of DMD with Eu(FOD)<sub>3</sub> (acetone, 50 °C, [Eu(FOD)<sub>3</sub>]<sub>0</sub> = 5×10<sup>-3</sup> mol dm<sup>-3</sup>, [DMD]<sub>0</sub> = 1.2×10<sup>-2</sup> mol dm<sup>-3</sup>, N<sub>2</sub> atmosphere).

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