

Supporting Information

A Novel Chemiluminescence from the Reaction of Singlet Oxygen with β -Diketonates of Europium(III), Neodymium(III) and Ytterbium(III)

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Content: The Supporting Information (SI) material consists of the experimental methods, and the chemiluminescence and photoluminescence spectra.

Experimental methods

General Aspects.

Vis-CL was measured with the apparatus described previously¹ using a photomultiplier sensitive between 330 and 700 nm. Near IR CL was recorded by means of a photomultiplier (cooled at -90 °C) sensitive up to 1300 nm with maximum sensitivity at $\lambda = 800$ nm. The photoluminescence spectra of the $\text{Eu}(\text{fod})_3$ were acquired on a Hitachi MPF-4 spectrofluorimeter. The CL spectra were recorded on home-built spectrometer by using high transmission monochromator and near infra-red sensitive photomultiplier.¹

1,4-Dimethylnaphthalene (Aldrich, 95%) was distilled prior to use. The endoperoxide of 1,4-Dimethylnaphthalene (DMNE) was produced by sensitized photooxygenation and was purified according to published procedures.^{2,3} DMNE was kept in a freezer at -20 °C. Lanthanide β -diketonates were synthesized as described in literature.⁴⁻⁸

Measurement of the Chemiluminescence during Decomposition of DMNE in the Presence of β -Diketonates of Europium(III), Neodymium(III) and Ytterbium(III).

Solution of DMNE and $\text{Ln}(\text{L})_3 \cdot n\text{H}_2\text{O}$ in CHCl_3 , CDCl_3 or CCl_4 was prepared at the room temperature. Then an aliquot of the endoperoxide/ $\text{Ln}(\text{L})_3 \cdot n\text{H}_2\text{O}$ mixture was put to the cuvette which was placed above the photocathode of the photomultiplier and was thermostated at the required temperature, and CL recording was started immediately. All reactions were carried out by bubbling a slow stream of argon gas through the solution. The following concentrations of the reagents in the cuvette were chosen: $[\text{DMNE}] = 3 \cdot 10^{-2}$ M, $[\text{Ln}(\text{L})_3 \cdot n\text{H}_2\text{O}] = 1 \cdot 10^{-2}$ M.

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Spectra

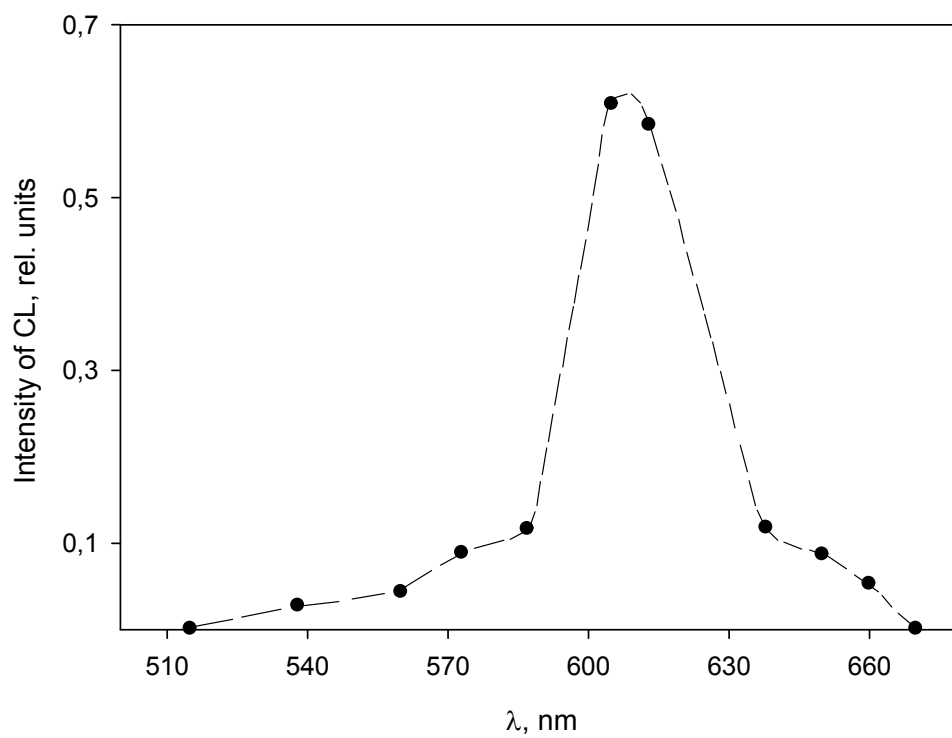


Figure S-1. Chemiluminescence spectrum taken by means of cut-off filters during decomposition of DMNE in the presence of $\text{Eu}(\text{fod})_3$ (55 °C, $[\text{DMNE}] = 3 \cdot 10^{-2} \text{ M}$, $[\text{Eu}(\text{fod})_3] = 1 \cdot 10^{-2} \text{ M}$, CHCl_3).

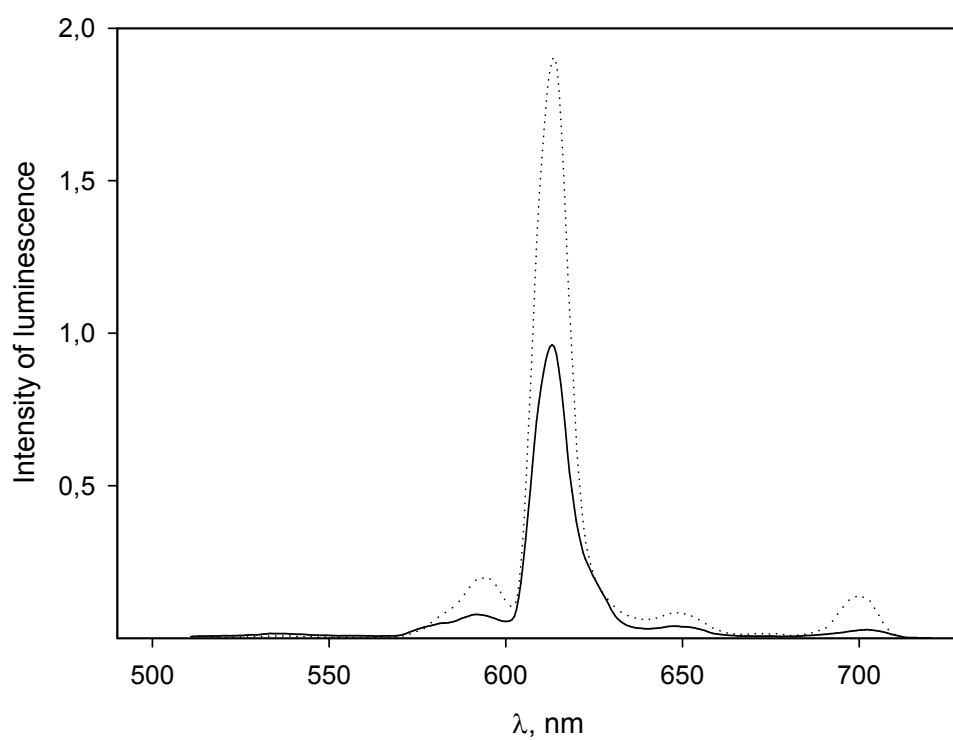


Figure S-2. Luminescence spectrum of Eu(fod)_3 ($\lambda_{\text{exc}} = 400 \text{ nm}$, $[\text{Eu(fod)}_3] = 1 \cdot 10^{-2} \text{ M}$, CDCl_3) in the absence (solid line) and in the presence (dotted line) of $1 \cdot 10^{-2} \text{ M}$ DABCO.

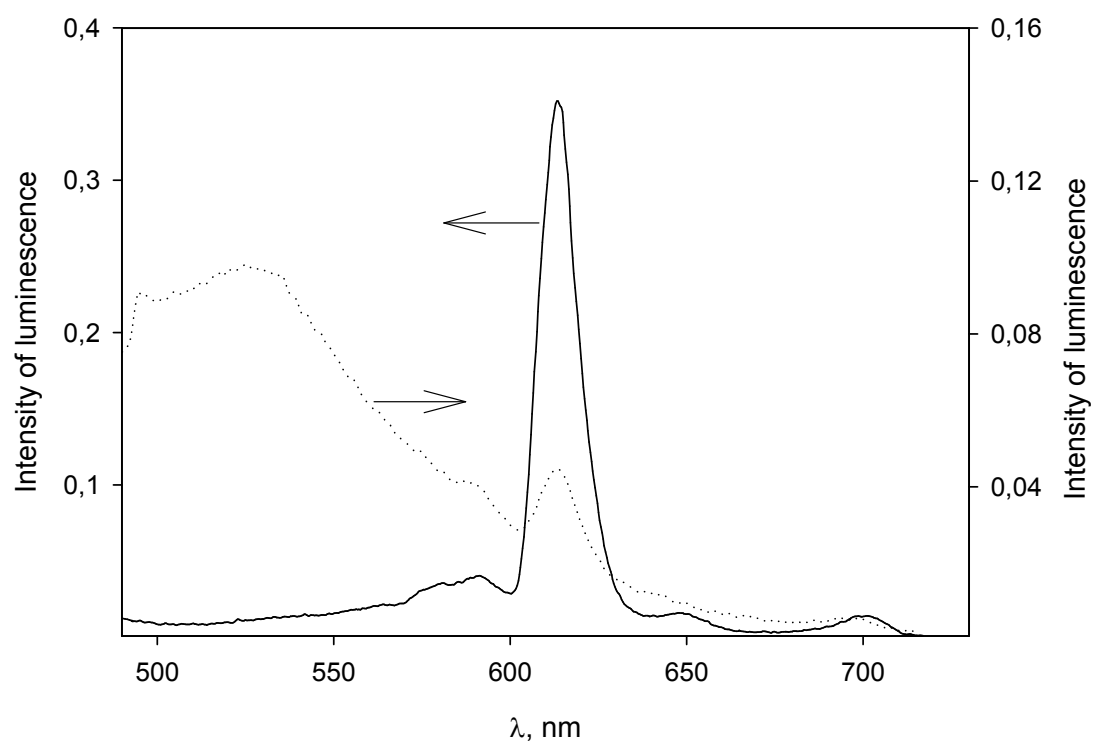


Figure S-3. 1, Photoluminescence spectrum (solid line) of $\text{Eu}(\text{fod})_3$ ($\lambda_{\text{exc}} = 465 \text{ nm}$, $[\text{Eu}(\text{fod})_3] = 1 \cdot 10^{-2} \text{ M}$, CHCl_3); 2, photoluminescence spectrum (dotted line) of the reaction mixture ($\lambda_{\text{exc}} = 465 \text{ nm}$) taken after chemiluminescent decomposition of DMNE in the presence of $\text{Eu}(\text{fod})_3$ (55°C , $[\text{DMNE}] = 6 \cdot 10^{-2} \text{ M}$, $[\text{Eu}(\text{fod})_3] = 1 \cdot 10^{-2} \text{ M}$, CHCl_3). Note the different scaling of the ordinate axes.