

SUPPLEMENTARY INFORMATION

The first registration of a green liquid-phase chemiluminescence of the divalent Eu^{2+} ion in interaction of β -diketonate complexes $\text{Eu}(\text{acac})_3 \cdot \text{H}_2\text{O}$, $\text{Eu}(\text{dpm})_3$, $\text{Eu}(\text{fod})_3$ and $\text{Eu}(\text{CH}_3\text{COO})_3 \cdot 6\text{H}_2\text{O}$ with Bu^i_2AlH in THF with the participation of oxygen

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Experimental section:

The β -diketonate complexes $\text{Eu}(\text{acac})_3 \cdot \text{H}_2\text{O}$, $\text{Eu}(\text{dpm})_3$, $\text{Eu}(\text{fod})_3$, and hexahydrate $\text{Eu}(\text{CH}_3\text{COO})_3 \cdot 6\text{H}_2\text{O}$ were used as received from Aldrich Chemical Co. Dialkylhydride Bu^i_2AlH , 73% solution in toluene was distilled according to ⁵¹. THF was distilled under argon from sodium benzophenone ketyl before use. Argon and air were purified as in ⁵¹. The CL, PL spectra and decay lifetimes were recorded on a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer (model FL-3-22) equipped with double-grating monochromators, dual lamphousing with 450W Xenon lamp and pulsed solid state laser-diode NanoLED, photomultiplier tube detector (Hamamatsu R928 PMT). Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard instrument correction, provided in the instrument software. Lifetime measurements were carried out using for excitation the Xenon flash lamp (500 Hz repetition rate) in the case of Eu^{3+} and 370 nm NanoLED (1 MHz repetition rate) in the case of Eu^{2+} . PL quantum yields (ϕ_{PL}) of the Eu^{2+} complexes in THF were determined by ratio value of integrated area under corrected luminescence spectra with using $2.0 \cdot 10^{-5}$ M solution of anthracene (scintillation pure grade) in EtOH as a reference sample ($\phi_{\text{PL}} = 0.28$).⁵² As a result, the PL quantum yields were calculated by Eq.1.

$$\frac{\phi_x}{\phi_{st}} = \frac{A_{st} \cdot n_x^2 \cdot D_x}{A_x \cdot n_{st}^2 \cdot D_{st}} \quad (1)$$

where ϕ_{st} and ϕ_x are the PL quantum yields of the sample and standard; A_x and A_{st} are absorbances at the excitation wavelength for the sample and standard; n_x and n_{st} are the refractive indexes of solvents: 1.4050 for THF and 1.3611 for EtOH;⁵³ D_x and D_{st} are the areas under the PL spectra of the sample and standard. CL quantum yields (in Einstein $\cdot\text{mol}^{-1}$) were calculated based on the ratio $S/[\text{Me}_2\text{CHC}(\text{H})=\text{O}]$, where S is a light sum (in photon $\cdot\text{mL}^{-1}$), defined as the integrated area under the CL kinetic curves in coordinates CL intensity (I_{CL} , in photon $\cdot\text{s}^{-1}\cdot\text{mL}^{-1}$) versus time (s), $[\text{Me}_2\text{CHC}(\text{H})=\text{O}] \approx 4 \cdot 10^{-4}$ M is a concentration of isobutyric aldehyde, which is formed by complete oxidation of Bu^i_2AlH by oxygen and calculated using data.⁵⁴

The kinetics of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ reduction was monitored by an increase in the PL intensity of Eu^{2+} at 560 nm ($\lambda_{\text{exc}} = 445$ nm) with an instrument Fluorolog-3 spectrofluorimeter using a time mode «Kinetics Acquisition». The integration time for all experiments was 10 s. The kinetics of CL was carried out in the original chemiluminometer⁵⁴ in cylindrical Pyrex CL-cell (reactor) closed with a penicillin cap. As a light detector was photomultiplier tube "FEU-39". Calibration of the chemiluminometer was carried out as in ⁵⁵.

In a typical experiment, transparent the CL-cell was charged with Eu^{3+} complex (0.02 mmol), purged with argon for 20 min for removal of O_2 from the gas space, and then 2 ml freshly distilled THF, saturated by air at stirring, was injected by syringe. After that, avoiding falling into the chemiluminescent chamber light of day, Bu^i_2AlH (0.2 mL, 0.8 mmol) was injected by syringe through the penicillin stopper with continuous stirring. In separate experiments, gaseous products (Bu^iH and H_2) contained in the reaction solution and the gaseous phase above that were analyzed by GLC according to ^{51,52}. To explore the possibility of CL generating under anaerobic conditions, the reaction was carried out in a quartz reactor made up with two

cylindrical ampoule-like parts where the solutions of $\text{Eu}(\text{fod})_3$ and Bu^i_2AlH were placed. The solutions were mixed after oxygen degassing by three freeze–evacuate–thaw cycles at 300 K in a CL chamber. Isolation of Eu^{2+} complex from the yellow-green reaction solution was effected according to the modified method of ⁵⁶ by removing excess THF solvent with vacuum (1 torr) and heating (75°C). At achievement of this temperature, THF was completely removed with formation of the orange precipitate and small volume of liquid (excess Bu^i_2AlH and its oxidation products). Then, reactor was cooled under argon and 2 ml of hexane was added to remove excess Bu^i_2AlH and its conversion products. This operation was performed 5 times. As a result, dark yellow Eu^{2+} complexes were isolated. The molecular formulas of the resulting Eu^{2+} complexes were determined using complexometric titration, elemental analysis, and IR spectroscopy. The UV-visible absorption spectra were recorded by spectrophotometer Perkin Elmer Lambda 750 instrument in argon atmosphere using 1 cm quartz cells fitted with hermetic stoppers.

IR spectra were recorded in solid state (KBr tablet) using «Bruker Vertex 70V» instrument. Elemental analysis of Eu^{2+} complexes were performed in the elemental analyzer CHNS with an error: $\pm 0.3\%$.

Spectral and other characteristics of the complexes obtained are presented below.

$\text{Eu}(\text{fod})_2 \cdot (\text{THF})_2$. Yield (19.2 mg, 44.8 %) Found (%): Eu, 17.7; F, 31.2; C, 37.8; H, 4.2; O, 9.1. Calculated for $\text{EuC}_{28}\text{H}_{36}\text{F}_{14}\text{O}_6$ (%): Eu, 17.2; F, 30.0; C, 37.9; H, 4.1; O, 10.80. IR absorptions (KBr), $\nu_{\text{max}}/\text{cm}^{-1}$: 840 (C-O, THF), 1034 (C-O, THF), 1228 (C-F), 1380-1425 ($-\text{C}(\text{CH}_3)_3$), 1460 ($-\text{CH}_2-$), 1702 ($-\text{CH}_2-$, $-\text{CH}_3$), 1735 (C=O), 1804 ($-\text{CF}_2-\text{CH}-\text{C}=\text{O}$).

$\text{Eu}(\text{dpm})_2 \cdot (\text{THF})_2$. Yield (15.3 mg, 31.3 %) Found (%): Eu, 22.9; C, 54.3; H, 8.7; O, 14.1. Calculated for $\text{EuC}_{30}\text{H}_{54}\text{O}_6$ (%): Eu, 23.0; C, 54.4; H, 8.1; O, 14.5. IR absorptions (KBr), $\nu_{\text{max}}/\text{cm}^{-1}$: 798 (C-O, THF), 1029 (C-O, THF), 1406 ($-\text{CH}_2-$), 1467 ($-\text{CH}_2-$), 1528 ($-\text{CH}=\text{}$), 1745 (C=O), 2873 ($-\text{CH}_2-$), 2929 ($-\text{CH}_2-$), 2959 ($-\text{CH}=\text{}$).

$\text{Eu}(\text{acac})_2 \cdot (\text{THF})_2$. Yield (4.1 mg, 16.4 %) Found (%): Eu, 30.7; C, 43.6; H, 6.5; O - 19.2. Calculated for $\text{EuC}_{18}\text{H}_{30}\text{O}_6$ (%): Eu, 30.8; C, 43.7; H, 6.1; O, 19.4. IR absorptions (KBr), $\nu_{\text{max}}/\text{cm}^{-1}$: 797 (C-O, THF), 1026 (C-O, THF), 1386 ($-\text{CH}_2-$), 1461 ($-\text{CH}_3$), 1528 ($-\text{CH}$), 1745 (C=O), 2855 ($-\text{CH}_2-$), 2925 (CH_3), 2956 ($-\text{CH}=\text{}$).

$\text{Eu}(\text{CH}_3\text{COO})_2 \cdot (\text{THF})_2$. Yield (6.3 mg, 39.9 %) Found (%): Eu, 36.9; C, 35.1; H, 5.6; O, 22.4. Calculated for $\text{EuC}_{12}\text{H}_{22}\text{O}_6$ (%): Eu, 36.7; C, 34.8; H, 5.3; O, 23.2. IR absorptions (KBr), $\nu_{\text{max}}/\text{cm}^{-1}$: 789 (C-O, THF), 1030 (C-O, THF), 1386 ($-\text{CH}_2-$), 1423 (CH_2), 1745 (C=O), 2855 ($-\text{CH}_2-$), 2925 ($-\text{CH}_3$).

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- S4. R. G. Bulgakov, V. P. Kazakov, G. A. Tolstikov, *Chemiluminescence of Organometallic Compounds*, Nauka, Moscow, 1989.
- S5. R.G. Bulgakov, S.M. Eliseeva, D.I. Galimov, *J. Lumin.*, 2013, **136**, 95-99.

- S6. R. G. Bulgakov, S. M. Eliseeva, D.I. Galimov, *Russ. Chem. Bull., Int. Ed.*, 2013, **62**, 2345-2348.

Figure S1. PL spectra of isolated complexes $\text{EuL}_2 \cdot (\text{THF})_2$ in $\text{CHCl}_3\text{-CDCl}_3$ (after NMR measurements). 1 – $\text{Eu}(\text{acac})_2 \cdot (\text{THF})_2$, $4.84 \cdot 10^{-4}$ M; 2 – $\text{Eu}(\text{CH}_3\text{COO})_2 \cdot (\text{THF})_2$, $2.64 \cdot 10^{-4}$ M; 3 – $\text{Eu}(\text{dpm})_2 \cdot (\text{THF})_2$, $3.5 \cdot 10^{-5}$ M.

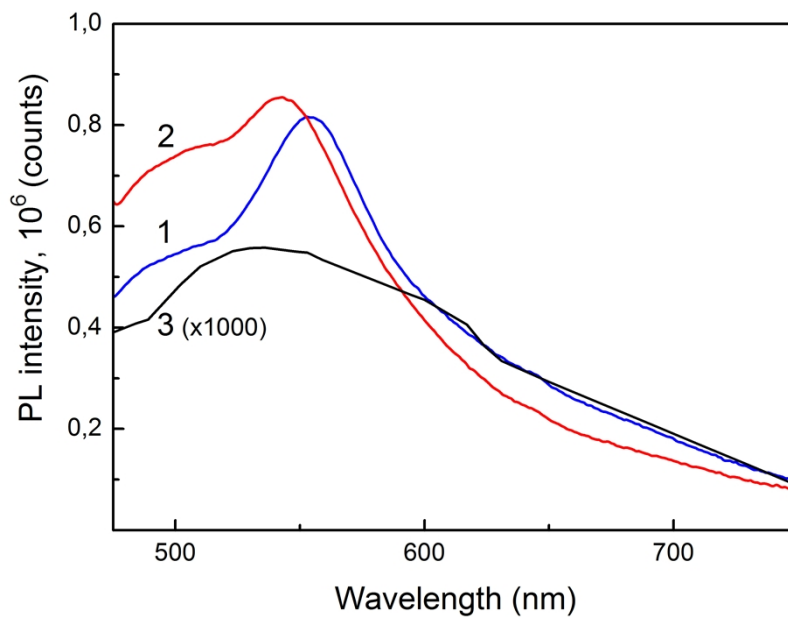


Figure S2. CL kinetics of BGCL (1) and at interaction in system $\text{Eu}(\text{acac})_3 \cdot \text{H}_2\text{O} \cdot \text{THF} \cdot \text{Bu}_3\text{Al} \cdot \text{O}_2$ at 300 K (2). CL were measured with chemiluminometer. $[\text{Eu}^{3+}]_0 = 1 \cdot 10^{-2}$ M, $[\text{Bu}_3\text{Al}]_0 = 4 \cdot 10^{-1}$ M, $V(\text{THF}) = 2.0$ mL.

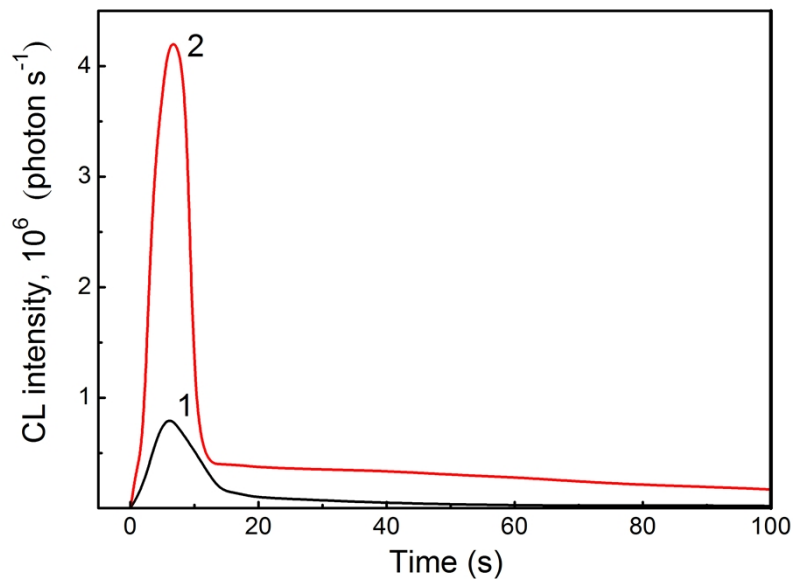


Figure S3. PL(1) and CL (2) spectra of solutions in reaction of the $\text{Eu}(\text{acac})_3 \cdot \text{H}_2\text{O}$ and Bu^i_3Al in THF at 300 K. $[\text{Eu}(\text{acac})_3 \cdot \text{H}_2\text{O}]_0 = 10^{-2}$ M, $[\text{Bu}^i_3\text{Al}]_0 = 4 \cdot 10^{-1}$ M, $V(\text{THF}) = 2$ ml.

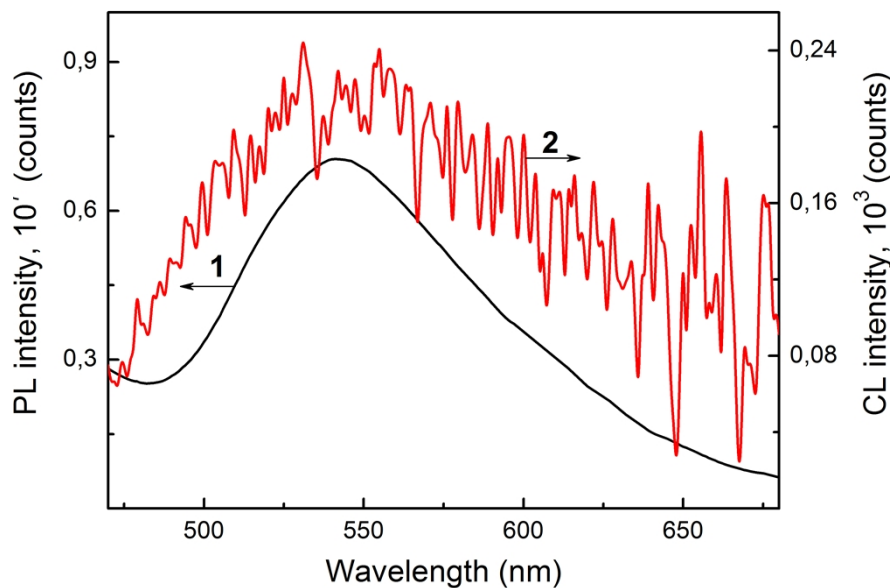


Figure S4. Reduction kinetics of Eu^{3+} to Eu^{2+} in the reaction $\text{Eu}(\text{acac})_3 \cdot \text{H}_2\text{O}$ and Bu^i_3Al in THF. $[\text{Eu}(\text{acac})_3 \cdot \text{H}_2\text{O}]_0 = 10^{-2}$ M, $[\text{Bu}^i_3\text{Al}]_0 = 4 \cdot 10^{-1}$ M, $V(\text{THF}) = 2$ ml.

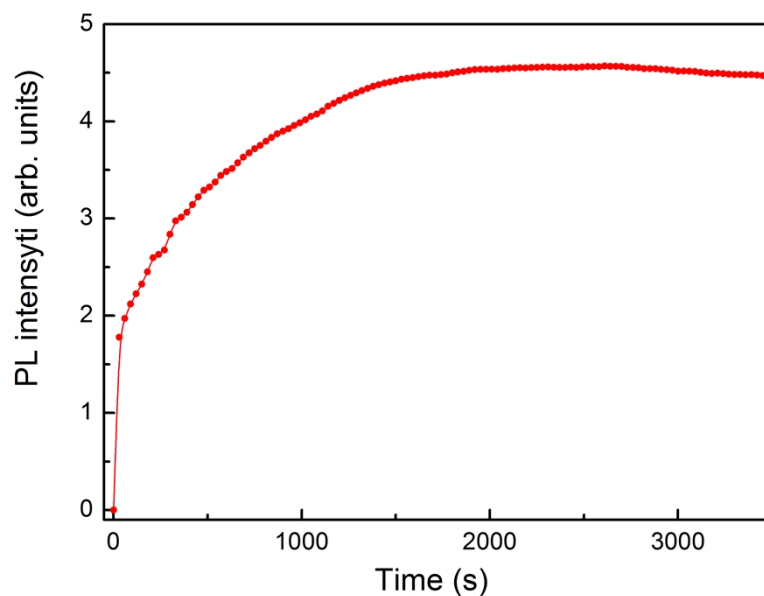


Figure S5. Spectral overlap of the absorption spectra (red line) of the Eu^{2+} ion (10^{-2} M) and phosphorescence spectrum (black line) of isobutyric aldehyde $^3\text{Pr}^i\text{C}(\text{H})=\text{O}^*$ ($5 \cdot 10^{-4}$ M). 1-4 – absorption spectra of the reaction solutions, obtained after interaction of Bu^i_2AlH with $\text{Eu}(\text{CH}_3\text{COO})_3 \cdot 6\text{H}_2\text{O}$ (1), $\text{Eu}(\text{acac})_3 \cdot \text{H}_2\text{O}$ (2), $\text{Eu}(\text{dpm})_3$ (3), and $\text{Eu}(\text{fod})_3$ (4) in THF; 5 – phosphorescence spectrum of isobutyric aldehyde $^3\text{Pr}^i\text{C}(\text{H})=\text{O}^*$ ($5 \cdot 10^{-4}$ M) in THF at 77 K. 6 – BGCL spectrum. $[\text{Bu}^i_2\text{AlH}]_0 = 4 \cdot 10^{-1}$ M, $V(\text{THF}) = 2.0$ mL, $T = 300$ K.

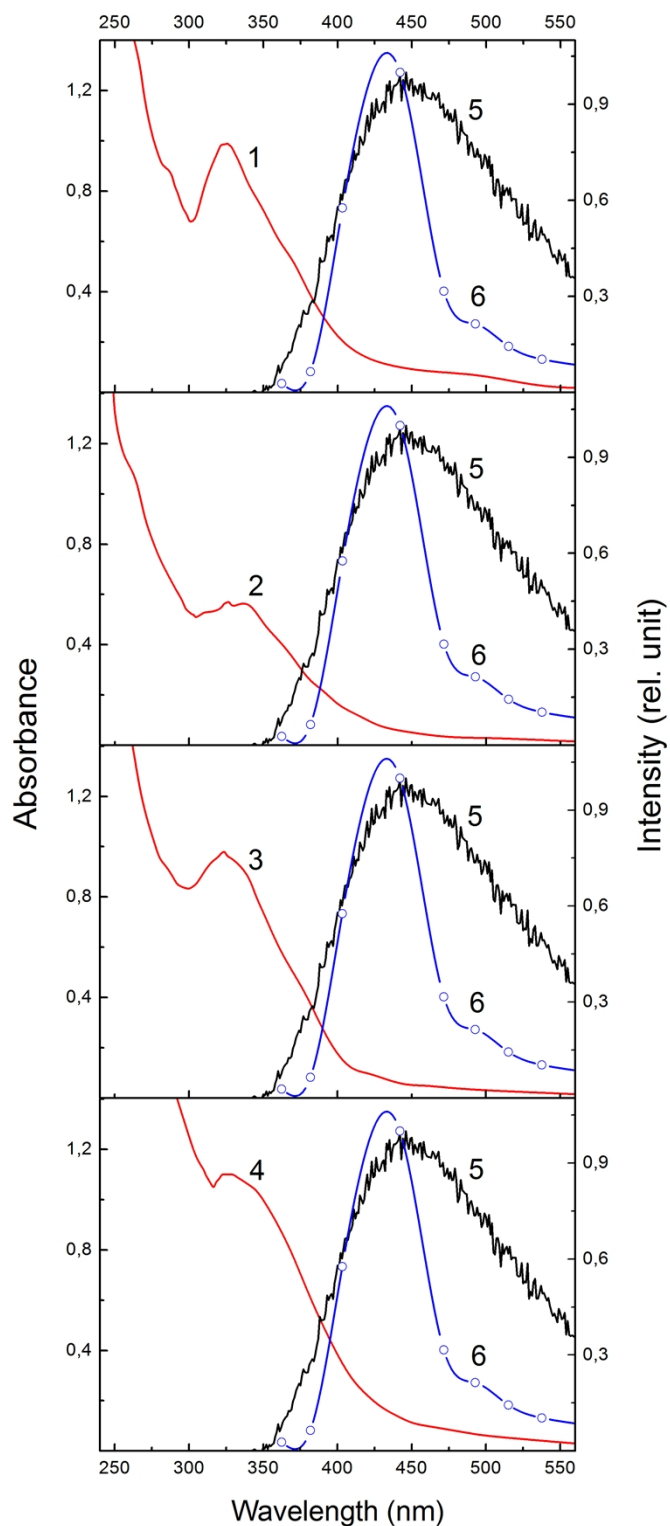


Figure S6. Energy level diagram of enhanced green CL due to energy transfer from triplet excited isobutyric aldehyde ${}^3\text{Pr}^i\text{C}(\text{H})=\text{O}^*$ to the Eu^{2+} ion.

