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Synthesis of Europium(III) Phenanthroline-β-diketonate Silicon-containing Complex. Photoluminescence in Solution and in Sol–Gel Film

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Abstract—A phenanthroline benzoyltrifluoroacetonate europium complex showing a bright red photoluminescence at a wavelength 616 nm was synthesized by reacting 3-isocyanatopropyltriethoxysilane with anhydrous europium(III) tris(benzoyltrifluoroacetonate) and then with phenanthroline.

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Europium(III) β-diketonate complexes with red luminescence are used in immunofluorescent analysis [1, 2]. They are also of interest to photonics, laser optics, and technology of electroluminescent devices [3, 4]. For successful application in practice a material with a bright luminescence is required, which is provided in the case of a high quantum yields. We have shown previously [5] a possibility of obtaining a silicon-containing europium complex capable of forming transparent luminescent sol–gel films. The new ligand was synthesized from 3-isocyanatopropyltriethoxysilane and acetylacetone. The europium complex was obtained in two ways: (1) by interaction of the ligand with europium isopropoxide and (2) by interaction of tris(acetylacetonato)europium with 3-isocyanatopropyltriethoxysilane.

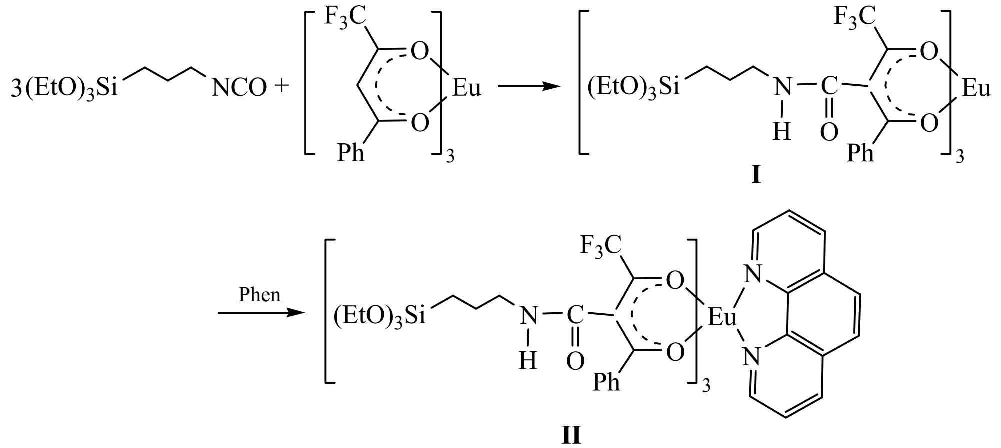
The product of these reactions readily forms transparent films, but the cationic luminescence is low [5]. The absorbed light energy is emitted rather as a broad band centered at 450 nm of silicon oxide matrix.

Now we report on the preparation of benzoyltrifluoroacetonate and phenanthrolinbenzoyltrifluoroacetonate silicon-containing europium complexes with bright red cationic photoluminescence both in film and in solution.

The cationic luminescence intensity depends on the structure of organic ligand, from which the absorbed energy is transferred to the resonant level of lanthanide and then emitted as a narrow band of *f*–*f*-transition. The benzoyltrifluoroacetonate ligand provides a more intense europium photoluminescence in comparison with acetylacetonate. To increase the luminosity of the complexes, neutral ligands are commonly used, phenanthroline in particular.

Our attempts to synthesize 3-benzoyltrifluoroacetonate derivatives of aminopropyltriethoxysilane and 3-isocyanatopropyltriethoxysilane and to obtain pure samples of the ligands failed. The interaction of benzoyltrifluoroacetone with aminopropyltriethoxysilane and 3-isocyanatopropyltriethoxysilane was accompanied by the formation of impurities, and the target compound could not be purified by vacuum distillation. At the same time, the reaction of anhydrous europium tris(benzoyltrifluoroacetonate) with 3-isocyanatopropyltriethoxysilane led to the expected complex **I**, which reacted with phenanthroline affording compound **II**. The reaction with 3-isocyanatopropyltriethoxysilane can be easily monitored by infrared spectroscopy, by observing decrease in the intensity of the very strong characteristic absorption band of NCO at 2274 cm^{-1}. After 7-h heating of europium tris(benzoyltrifluoroacetonate) with 3-isocyanatopropyltriethoxysilane almost all isocyanate was consumed. The addition of the phenanthroline solution caused precipitation of complex **II**.

IR spectra of compounds **I** and **II** are of complex structure due to diversity of their fragments. The most intense are the bands of β-dicarbonyl group bound with the europium cation (1692, 1624 cm^{-1}), and



I

II

triethoxysilyl group (1140 , 1076, 944, 792 cm^{-1}). The stretching NH vibrations in the amide group appear as a broad band of moderate intensity at 3340 cm^{-1}. Two peaks, at 1716 and 1540 cm^{-1} (amide **I**, amide **II**) should be assigned to the amide group. In the low-frequency region between 850 and 650 cm^{-1} two narrow lines (764, 704 cm^{-1}) are observed related to the out-of-plane C–H bending vibrations of aryl group. The bands of the in-plane vibrations at 1100, 1188, and 1292 cm^{-1} are overlapped by the absorption of triethoxysilyl and trifluoromethyl fragments. Stretching vibrations of C–H bonds in the groups C_2H_5O and $(CH_2)_3$ appear as strong bands at 2975, 2927, and 2890 cm^{-1}, and those in the aromatic fragments, as less intense absorption at 3150–3000 cm^{-1}.

^{1}H NMR spectrum of compound **I** is poorly resolved because of the presence of the paramagnetic europium cation, but virtually all fragments can be identified. Two of the most intense multiplets at 1.23 and 3.85 ppm belong to the protons of CH_3CH_2O fragment, three multiplets at 0.8, 1.7, and 3.1 ppm belong to the trimethylene bridge $SiCH_2CH_2CH_2N$, and a multiplet at 7.1 ppm, to the phenyl group protons. In the electronic spectrum of complex **II** there are three absorption bands, at 222, 268, and 322 nm, with high extinction coefficients (10^4 to 10^5 l mol^{-1} cm^{-1}).

Compound **I**, which is a viscous liquid, readily forms a transparent thick (100–200 μm) sol–gel film at the deposition onto a substrate by pouring. The dilution with ethanol makes it possible to adjust the thickness of the coating. The curing time is 5 to 20 h depending on the thickness of the layer. Thick films suffer cracking at storage, while thin films (5–20 μm) are stable.

Figure 1 shows the excitation and emission spectra of the complex **I** taken as a film on a quartz substrate. The excitation spectrum of photoluminescence regis,-tered at a wavelength 615 nm has four bands with poorly resolved maxima at 305, 340, 370, and 470 nm. Structure of the emission spectra somewhat changed depending on the wavelength of the exciting light, due to the complexity of the composite film. At λ_{exc} = 340 nm the spectrum contains five narrow bands, of which four (582, 594, 616, 654, 704 nm) belong to the transitions from the excited level $^5D_0$ of Eu^{3+} cation on the levels of the ground-state multiplet ^7F_i (i = 0–4) and one (540 nm) band corresponds to $^5D_1 \rightarrow {}^7F_1$ transition. Initiation with the light of longer wavelength (λ_{exc} = 370 nm) causes appearance of an additional short-wave maximum with λ = 500 nm, due to the $^5D_2 \rightarrow {}^7F_3$ transition. In both cases the most intense transition is $^5D_0 \rightarrow {}^7F_2$ with λ = 616 nm. The fluorescence of the silicon oxide matrix is expressed as a low-intensity broad band in the range from 390 to 550 nm.

Figure 2 shows the photoluminescence and the photoluminescence excitation spectra of a solution of the complex **II** in acetonitrile. A large dilution (to $C = 2\times10^{-6}$ M) was necessary to obtain a spectrum that fits to the scale of the registrar with a minimum of the monochromator slit (2.5 nm) that showed a high luminosity of the complex. The relative quantum yield of luminescence calculated by comparison with a standard dye rhodamine 6G is 66%. Measurements with dilute solutions indicate the absence of luminescence of silicon component of the complex and the correspondence between the electron absorption spectrum and the excitation spectrum.

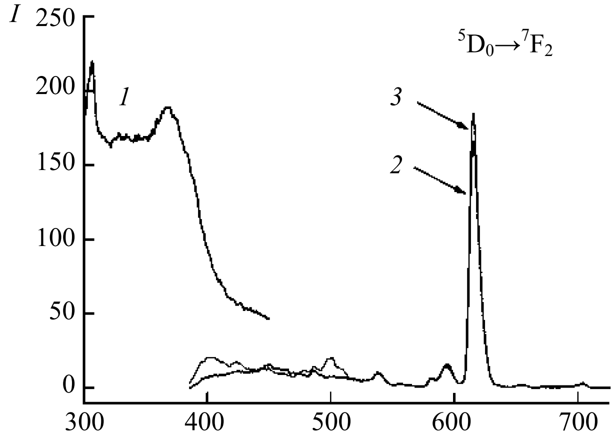


Fig. 1. Excitation (*1*, l_{reg} = 615 nm) and emission (*2*, l_{exc} = 340 nm; *3*, l_{exc} = 370 nm) spectra of the complex **I** film. The film thickness was 134 microns, slit 5 nm.

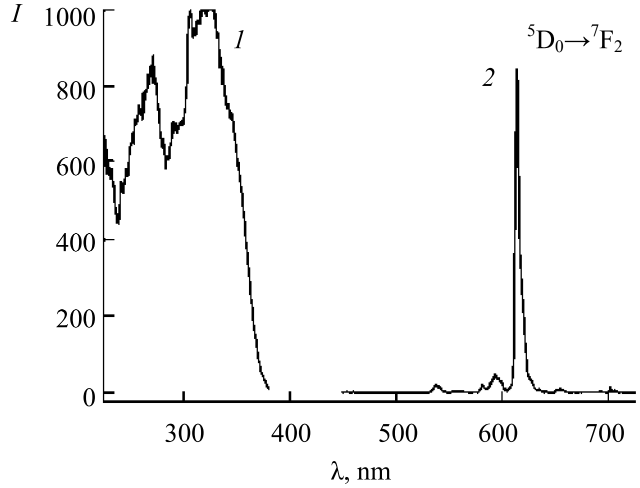


Fig. 2. Excitation (*1*, l_{reg} = 615 nm) and emission (*2*, l_{exc} = 340 nm) spectra of complex **II** in acetonitrile, $C = 2\times10^{-6}$ M, slit 2.5 nm.

EXPERIMENTAL

The IR spectra were taken from the compounds as liquid film between KBr or CaF_2 plates, or as suspensions in mineral oil, and recorded on an FSM 1201 IR-Fourier spectrometer. Electron absorption spectra were measured on a Perkin-Elmer Lambda 25 spectrophotometer, fluorescence and fluorescence excitation spectra, on a Perkin-Elmer LS-55 spectrofluorimeter. The spectral width of the slit of excitation and recording monochromators was 2.5 to 5.0 nm. The film was set at an angle to the exciting light, and fluorescence emission was collected from its surface. In addition, before the monochromator of registering unit a correcting built-in filter was placed blocking the scattered and reflected exciting radiation. The spectra obtained were corrected for spectral sensitivity of the photomultiplier and the spectral transmittance curve of the filter. The ^1H NMR spectra of solutions in $CDCl_3$ were recorded on a Bruker Avance DPX-200 instrument (200 MHz) at 25ºC, internal reference Me_4Si.

3-Isotcyanatopropyltriethoxysilane (Aldrich) was distilled in a vacuum before use, rhodamine 6G (LC 5900) (Lambda Physik) was used without further purification. Europium isopropylate was synthesized from anhydrous europium chloride and sodium isopropylate by the procedure in [6]. Quartz substrate (3×12×40) for the formation of films was processed for 10 h with a saturated solution of NaOH in isopropyl alcohol, then 10 h with a mixture of potassium bichromate with sulfuric acid, and then was washed with water and dried at 150–170°C.

Europium(III) tris[2-(3'-triethoxysilylpropylaminocarbonyl)-1,1,1-trifluoro-4-phenylbut-2-en-2-ol-4-onate](1,10-phenanthroline) (II). To a solution of 1.21 g (0.006 mol) of benzoyltrifluoroacetone in 5 ml of THF was added in a vacuum 0.61 g (0.002 mol) of europium isopropoxide. The reaction mixture was heated for 4 h at 80°C in a sealed evacuated ampule, and then the volatile products were removed. 1.11 g (70%) of europium tris(benzoyltrifluoroacetonate) was obtained as a white powder. To a dispersion of 1.00 g (0.001 mol) of europium tris(benzoyltrifluoroacetonate) in 5 ml of toluene was added 0.74 g (0.003 mol) of 3-isocyanatopropyltriethoxysilane. The mixture was heated at 110°C for 8 h in an evacuated ampule. A small amount of precipitate was separated in a centrifuge, the liquid was decanted, the volatile substances were removed in a vacuum. 1.08 g (70%) of compound **I** was obtained as a yellow-orange oily liquid. IR spectrum (ν, cm^{-1}): 3340 m (NH), 3063 v.w (HC=C), 2975 v.s (CH), 2927 s (CH), 2890 s (CH), 2734 v.w (CH_2N), 1716 s (C=O, amide **I**), 1692 m (Eu–O–C=C–C=O), 1624 v.s (Eu–O–C=C–C=O), 1540 s (NH, amide **II**), 1445 m (CH), 1387 m (CH), 1292 v.s (CH, CF), 1188 s (CH-aryl, CF), 1140 v.s (SiOEt), 1100 s (CH-aryl, CF), 1076 v.s (SiOEt), 944 s (SiOEt), 792 s (SiOEt), 764 (CH-aryl), 704 s (CH-aryl).

To a solution of 0.90 g (0.0006 mol) of compound **I** in ethanol was added 0.16 g (0.0009 mol) of 1,10-phenanthroline. A few minutes later a dense finely dispersed precipitate separated, which was filtered off, washed with ethanol, and dried in a vacuum. 0.90 g

(87%) of compound **II** was obtained as a white-pink powder. IR spectrum (ν, cm^{-1}): 3345 m (NH), 3060 v.w (HC=C), 2724 v.w (CH_2N), 1722 m (C=O, amide **I**), 1611 m (Eu–O–C=C–C= O), 1577 v.s (Eu–O–C=C–C=O), 1529 s (NH, amide **II**), 1320 m (CH), 1289 v.s (CH, CF), 1245 m (CH), 1184 s (CH-aryl, CF), 1140 v.s (SiOEt), 1103 v.s (CH-aryl, CF), 1079 m (SiOEt), 940 m (SiOEt), 798 s (SiOEt), 768 s (CH-aryl), 700 m (CH-aryl). Electron spectrum (λ, nm; ε, $l\ mol^{-1}\ cm^{-1}$): 222, 6.5×10^4, 268, 1.3×10^5, 322, 1.1×10^5; Found, %: C 50.83, H 5.11. $C_{72}H_{89}Eu\cdot F_9N_5O_{18}Si_3$. Calculated, %: C 50.20, H 5.22.

Preparation of films. Complex **I** was applied to the fused quartz substrate and kept in air at room temperature for 20 h. The thickness of the formed solid film was 134 μm.

Complex **I** was diluted with ethyl alcohol 1:5 (by volume), the solution was kept for 1 day at room temperature and applied to a substrate. The formation of transparent solid film 14 μm thick was observed after 3–5 h.

Analyses were performed in the Analytical center of the Institute of Organometallic Chemistry, Russian Academy of Sciences.

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