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FLUORINE-CONTAINING β -DIKETONES IN THE PROCESS OF ORIGINATION OF LUMINESCENT NANOSCALE DISPERSION

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Abstract: The work is devoted to the study of methods for preparing actively fluorescent nanoscale dispersion. Fluorine-containing β -diketones such as 2-naphthoyl trifluoroacetone, 2-benzofuran oil trifluoroacetone form active luminescent complexes with europium, which are used for introduction of Aerosil based nanoscale dispersion in the ultrasonic disaggregation environment. The nanoscale dispersion prepared after dialysis purification are actively luminescent in the aqueous phase demonstrating high luminescence delay times

Keywords: fluorine-containing β -diketones, luminescent ultrafine particles, ultrasonic disaggregation, nanoscale dispersion, analysis

Introduction

Fluorine-containing β -diketones are among the best ligands in the formation of complexes with rare-earth elements. As a rule, fluorine-containing β -diketones complexes are of octadentate structure, with only three β -carbonyl moieties included in the metal coordination environment, and another two coordination vacancies are occupied by water or a ligand of another type [1, 2]. The regularity has been repeatedly confirmed by X-ray diffraction analysis, in particular, using the example of the hydrated tenoyltrifluoroacetone complex with europium of $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ composition [1]. Different versenes can act as soligands, in particular, trioctylphosphine oxide (TOPO) is a good water "displacer" [2, 3].

Complexes of fluorine-containing β -diketones with europium, as well as some other lanthanoid elements (samarium, terbium), exhibit photophysical properties (long-wavelength excitation $\approx 330\text{-}400$ nm, long-lived luminescence $\approx 40\text{-}60$ μs), which determine their use in immunofluorescence medical and biological analysis [2].

Such properties as hydrophobicity and excessive acidity of the fluorine-containing β -diketones determine the replaceability of the water molecules from the internal coordination sphere of a complex, which is a known luminescence killer [3]. The use of nanoscale dispersion, application of which in volumetric or solid-phase methods of analysis increases the sensitivity of immunodiagnosis of diseases and genetic deviations, is known as an advanced research direction of the time-resolved fluoroimmunoassay [3, 4].

Discussion of the research results.

The presented work is devoted to the development of methods for preparation of actively fluorescent nanoscale dispersion by means of sorptive doping with fluorine-containing β -diketones and europium (III) complexes under the conditions of Aerosil pyrogenic silica ultrasonication. The following fluorine-containing β -diketones were considered as ligands: 2-naphthoyl trifluoroacetone **1**, which is widely used in the DELFIA technology (dissociation-enhanced lanthanide fluorescent immunoassay [2]), and 2-benzofuran trifluoroacetone **2**, which is a prospective ligand [5].

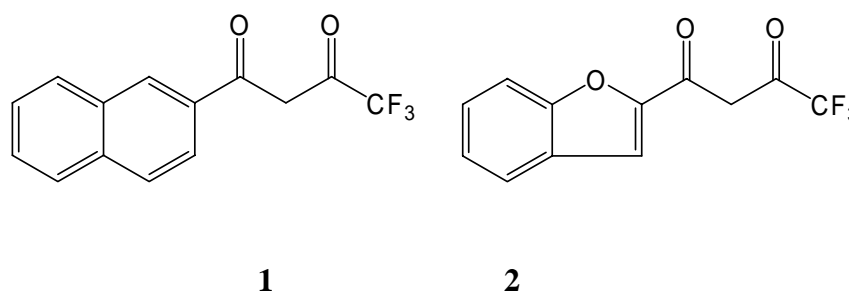


Figure 1. Fluorine-Containing 1,3-Diketones.

1 2-naphthoyl trifluoroacetone; **2** 2-benzofuran oil trifluoroacetone

Introduction of europium complexes of fluorine-containing diketones **1** and **2** in dispersions based on Aerosil 200, 300, 380, (manufactured by Orisil) under conditions of processing on ultrasonic devices of low and high capacity (Elmasonic S10/H and Labsonic 2000, at frequencies of 37 and 20 kHz and generator capacity of 60 and 170 W, respectively) has been investigated. The best disaggregation was achieved with the use of Aerosil 380, the dispersions based on which were studied further. 2% dispersion of Aerosil of grades (175, 300, 380) in water or micellar system - 0.3% solution of sodium dodecyl sulfate (SDS) in water was used for preparation of the dispersions. The following europium complexes were used for the sorptive doping: fluorine-containing β -diketones – Eu (III) – trioctylphosphine oxide (TOPO), of the composition 3:1:3.

In the process of ultrasonic disaggregation and “in situ” doping with fluorine-containing diketones complexes **1** and **2** particles of various sizes were formed (Table 1). The size of the

prepared nano particles was estimated by the turbidity spectra according to the procedure [6]. The resulting nanophases exhibit aggregate stability, at least for several weeks, after which they are partially sedimented with a decrease in luminescence in volume, however, they are quite easily resuspended with the exposure to sound for a short period of time (0.5-1 min), at that the luminescent properties are restored.

Table 1 presents experimental data on the study of the prepared nanoscale dispersion including their luminescent spectral properties. The dispersions were studied under excitation at wavelengths of 340 nm and 360 nm, for diketone complexes **1** and **2**, in accordance with the complexes absorption maxima. At that, the doping with fluorescent complexes of ultrafine particles was carried out in water and over the SDS (sodium dodecyl sulfate) with concentration of 0.3%, which provided formation of micelle.

Table 1. Characteristics of Nanoscale Dispersion (NSD) Prepared by Ultrasonic Doping of Aerosil 380 Complexes of Europium with Fluorine-Containing Diketones **1** and **2** (10-fold dilution) in Comparison with Solutions of these Complexes.

	NSD-1	Complex	NSD-2 (SDS 0.3%)	Complex (SDS 0.3%)	NSD-3	Complex	NSD-4 (SDS 0.3%)	Complex (SDS 0.3%)
Diketone	1	1	1	1	2	2	2	2
ω (aerosil) %	0.02	-	0.02	-	0.02	-	0.02	-
C(Eu ³⁺), mole/l	$1.02 \cdot 10^{-4}$	$1.04 \cdot 10^{-4}$	$1.01 \cdot 10^{-4}$	$1.06 \cdot 10^{-4}$	$1.04 \cdot 10^{-4}$	$1.02 \cdot 10^{-4}$	$1.05 \cdot 10^{-4}$	$1.01 \cdot 10^{-4}$
D, nm	111	-	803	-	270	-	366	-
λ exc.(nm)	340	340	340	340	356	356	356	356
I _{lum.} rel. units	8.74	2.35	70.74	10.61	12.11	8.92	35.74	8.06
I _{lum} /C _{Eu}	$8.56 \cdot 10^4$	$2.25 \cdot 10^4$	$7.00 \cdot 10^5$	$1.00 \cdot 10^5$	$1.16 \cdot 10^5$	$8.74 \cdot 10^4$	$3.40 \cdot 10^5$	$7.98 \cdot 10^4$
I _{lum.} (rel. units) Per a particle	$7.53 \cdot 10^{-11}$	-	$5.70 \cdot 10^{-9}$	-	$1.19 \cdot 10^{-11}$	-	$3.57 \cdot 10^{-11}$	-

The luminescence levels of the prepared dispersions are rather high and exceed the luminescence of the corresponding complexes of fluorine-containing diketones **1,2**, not containing nanophase and studied for comparison in the same concentrations. The given fact indicates the

complexes inhibition due to their sorption in the extensive pore system of the disaggregated Aerosil. Luminescence is significantly higher in micellar environment in the presence of sodium dodecyl sulfate, in which the complexes are additionally inhibited from the quenching effect of water, but at that the resulting particles are larger in size. Complexes of fluorine-containing diketones complexes are strongly retained mainly in the interstitial volume of the ultrafine particles rather than their surface, which is confirmed by experiments in dialysis of dispersions against water carried out for several days. As a result of this dialysis luminescence of nanoscale dispersion is maintained at ≈ 70 -90% of the original.

Thus, despite the inorganic nature of the surface of the initial silicate matrix, a high sorbent property of europium complexes with fluorinated diketones in the pores of ultrafine particles have been recorded. The data obtained allow to conclude the prospects for the further research of luminescent reagents for immunoassay based on silicate ultrafine particles disaggregated and doped under ultrasonication environment.

Experimental procedure.

Reagents and solutions

Aerosil 200, 300, 380, manufactured by Orisil, were studied in the processes of disaggregation. 0.2% suspension of aerosil in water (bidistilled water) or in solution of sodium dodecyl sulphate (0.3%) (SDS) (Acros) were exposed to disaggregation. Nitrate of europium (III) hexahydrate ("CP" grade, Novosibirsk Plant of Chemical Reagents), 2-naphthoyl trifluoroacetone **1** – NTA (Aldrich), 2-benzofuran oil trifluoroacetone **2** prepared by the method [5], trioctylphosphine – TOPO (Aldrich, 99%), DMF ("CP" grade, GOST 20289-74) were used for the synthesis and introduction of fluorescent labels.

Equipment

Disaggregation and sorptive doping were performed in Elmasonic S10/H (Germany) and Labsonic 2000 (Germany) ultrasonic baths at frequencies of 37 and 20 kHz and generator capacity of 60 and 170 W, respectively. Luminescence of nanoscale dispersion and complexes containing europium ion were recorded on Fluorat-02 "Panorama" spectrofluorometer manufactured by Lumex (time delay 100 μ s and integration time 1000 μ s).

Typical procedure for the synthesis of NSD 1-4 doped nanoscale dispersions

Ligand complex + Eu^{3+} + TOPO in the ratio of 3:1:3 while stirring the mixture in 0.1 ml of dimethylformamide at a concentration of Eu^{3+} - $1.61 \cdot 10^{-2}$ mol/l was pre-prepared.

A weighed quantity of 0.2 g of aerosil was placed in a round-bottom flask, distilled water or a solution of 0.3% dodecylsulfate Na (10 ml) was introduced, mechanical stirring on a magnetic stir bar was carried out for 10 minutes, then a solution of the complex was introduced slowly into the dispersion at intensive stirring. Then the dispersion was placed in an ultrasonic device and subjected to disaggregation at low power (60 W) for 4 hours, and at ultrasound of high power (170 W) for 10 minutes.

Measurement of luminescent spectral properties was carried out by 10 times dilution of the dispersion.

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