Synthesis and photophysical properties of silica nanoparticles based on europium(III) complexes*

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Monodisperse 280—480 nm silica particles doped with europium complexes with thenoyltrifluoroacetylacetone and adducts with some phosphine oxides as luminophores were prepared for the first time by the optimized Stober procedure using surfactants. The size and the polydispersity of the obtained particles depend on the luminophore incorporated in the polymer template. The photophysical properties of aqueous dispersions of the europium(III)-doped silica particles were studied by the luminescence method.

Key words: silica nanoparticles, europium(III) complexes, phosphine oxides, antenna, luminescence.

Currently, the luminescent silica nanoparticles form the most promising basis for the further development of nanotechnological approaches in bioanalysis and medicine.[1—3] A promising procedure for the preparation of luminescent silica nanoparticles is the introduction of luminophores inside silica nanoparticles followed by biomodification of their surface.[4—12] The choice of europium complexes as luminophores is due to their long lifetimes

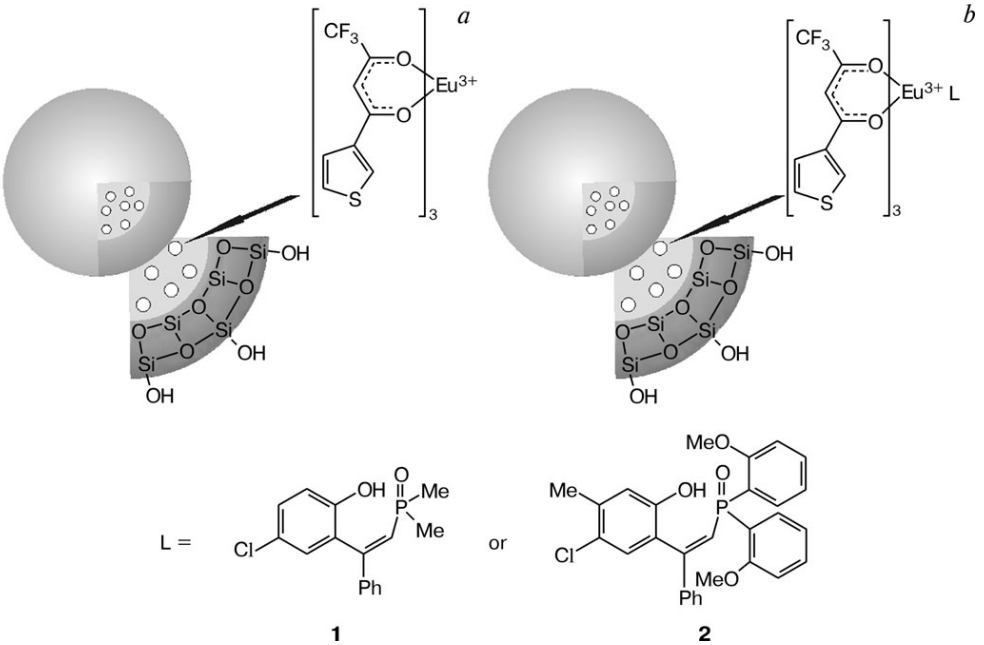

Fig. 1. Europium(III) thenoyltrifluoroacetylacetonate (*a*) and its mixed-ligand complexes **1** and **2** (*b*) doped into silica nanoparticles.

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(0.2—0.8 ms), considerably exceeding the lifetimes of organic luminophores, narrow lines, and great Stokes shifts.[13,14] These features almost rule out the overlap of the emission of the marker based on a europium complex with intrinsic luminescence of living tissues and provide good signal-to-noise ratio. The nature of the ligand is of enormous importance for the luminescence of lanthanide complexes, since the ligand functions as a peculiar "antenna", which feeds the excited level of the europium ion, the radiative deactivation of which is responsible for luminescence. As the basic luminophore, we chose europium(III) thenoyltrifluoroacetylacetonate ($Eu(TTA)_3$), which emits in the visible spectral range (the most intense emission occurs at 612 nm).[15,16] The luminophores used for doping of silica nanoparticles (Fig. 1) included, apart from $Eu(TTA)_3$, also mixed-ligand complexes, so-called adducts with phosphine oxides **1** and **2**. The interest in the mixed-ligand complexes is caused by the possibility of modifying the solubility and luminescence properties of Eu^{III} complexes.

The nanoparticles were prepared by the optimized Stober procedure,[17] which is based on the polymerization of tetraethoxysilane (TEOS) in aqueous ethanol. This basic procedure was chosen, first of all, due to good solubility of europium complexes in aqueous ethanol and poor solubility in water. A peculiar feature of this procedure is layer-by-layer polymerization, which allows variation of the size of silica nanoparticles over a broad range by using various additives. This considerably differs from the microemulsion procedure in which the particle size is dictated by the reverse micelle size.[18] The purpose of this stage was to optimize the Stober procedure for preparing the silica nanoparticles of variable size doped with highly luminescent europium(III) complexes.

Experimental

The work was performed using commercial TEOS (98%), sodium dodecyl sulfate (SDS, 99%), NH_3 (28—30% aqueous solution, Acros), $Eu(NO_3)_3 \cdot 6H_2O$ (Adrich), and $Eu(TTA)_3 \cdot 2H_2O$. Phosphine oxides **1** and **2** were synthesized by standard procedures.[19—21]

Adducts $(EuTTA)_3$-**1** and $Eu(TTA)_3$-**2** were isolated from chloroform solutions obtained by mixing the components in 1 : 1 molar ratio. The adducts were characterized in a previous study.[20]

Synthesis of silica particles. Two solutions of equal volumes (12.5 mL) were prepared, one by mixing 11.36 mL of an ethanol solution of luminophore of variable concentration ($2 \cdot 10^{-3}$ to 10^{-2} mol L^{-1}) and 1.14 mL of TEOS and the other by mixing 4.05 mL of an aqueous solution of SDS (10^{-3} mol L^{-1}), 0.4 mL of NH_3, and 8.05 mL of EtOH. The solutions were stirred for 15 min and poured together. The concentrations of all components in the final solution were as follows, mol L^{-1}: luminophore, $(1—5) \cdot 10^{-3}$; TEOS, 0.2; H_2O, 9; SDS, $1 \cdot 10^{-3}$; NH_3, 0.12. The synthesis was performed for 6 h with continuous stirring. The silica nanoparticles without luminophore were synthesized by a reported procedure.[17] The concentrations of the luminophores added during the synthesis and the designations of the nanoparticles are summarized in Table 1.

Table 1. Designations of the particles depending on the concentration of the luminophore (C) introduced during the synthesis

Nanoparticles	Luminophore	C/mol · L^{-1}
SiO_2	—	0
SiO_2-Eu1	$Eu(TTA)_3$	$1 \cdot 10^{-3}$
SiO_2-Eu2	$Eu(TTA)_3$	$2 \cdot 10^{-3}$
SiO_2-Eu3	$Eu(TTA)_3$	$5 \cdot 10^{-3}$
SiO_2-Eu4	$Eu(TTA)_3$-**1**	$1 \cdot 10^{-3}$
SiO_2-Eu5	$Eu(TTA)_3$-**1**	$2 \cdot 10^{-3}$
SiO_2-Eu6	$Eu(TTA)_3$-**1**	$5 \cdot 10^{-3}$
SiO_2-Eu7	$Eu(TTA)_3$-**2**	$1 \cdot 10^{-3}$
SiO_2-Eu8	$Eu(TTA)_3$-**2**	$2 \cdot 10^{-3}$
SiO_2-Eu9	$Eu(TTA)_3$-**2**	$5 \cdot 10^{-3}$

The photomicrographs of the silica nanoparticles were obtained on a JEM 100 C JEO transmission electron microscope (Japan) at the Institute of Macromolecular Compounds of the RAS (St.-Petersburg).

The europium content in the synthesized samples of nanoparticles was determined by inductively coupled plasma atomic emission spectroscopy on an iCAP 6300 DUO instrument (Thermo Scientific, USA).

The fluorescence spectra of aqueous suspensions of the synthesized silica nanoparticles doped with europium(III) complexes were recorded on an FL-221-NIR spectrofluorimeter (Jobin Yvon) at excitation wavelength of 350 nm.

The particle size and zeta-potentials in the aqueous dispersions were measured on a Malvern Mastersize 2000 particle analyzer.

The effective hydrodynamic radius (R_H) was calculated by the Einstein—Stokes equation for the first cumulant: $D = k_B T/6\pi\eta R_{H,}$, where D is the diffusion coefficient, k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity.

All samples were prepared using doubly distilled water filtered through a PVDF membrane (0.45 μm).

All of the measurements were performed at least twice.

Results and Discussion

Silica particles were prepared by alkaline hydrolysis of TEOS followed by polymerization in the presence of SDS (see Ref. 17) and luminophores ($Eu(TTA)_3$, $Eu(TTA)_3$-**1**, $Eu(TTA)_3$-**2**), the concentration of the latter being varied (see Table 1). The nanoparticle size in the synthesized samples (see Table 1) was estimated based on transmission electron microscopic images (Fig. 2, *a—d*). Table 2 presents the nanoparticle diameters and the maximum deviations of the measured diameters obtained in the size analysis. It follows from the presented data that the size and the polydispersity of the formed silica particles depend on the structure of the luminophore (see Table 2). In particular, the particle polydispersity increases upon the luminophore incorporation into the silica template.

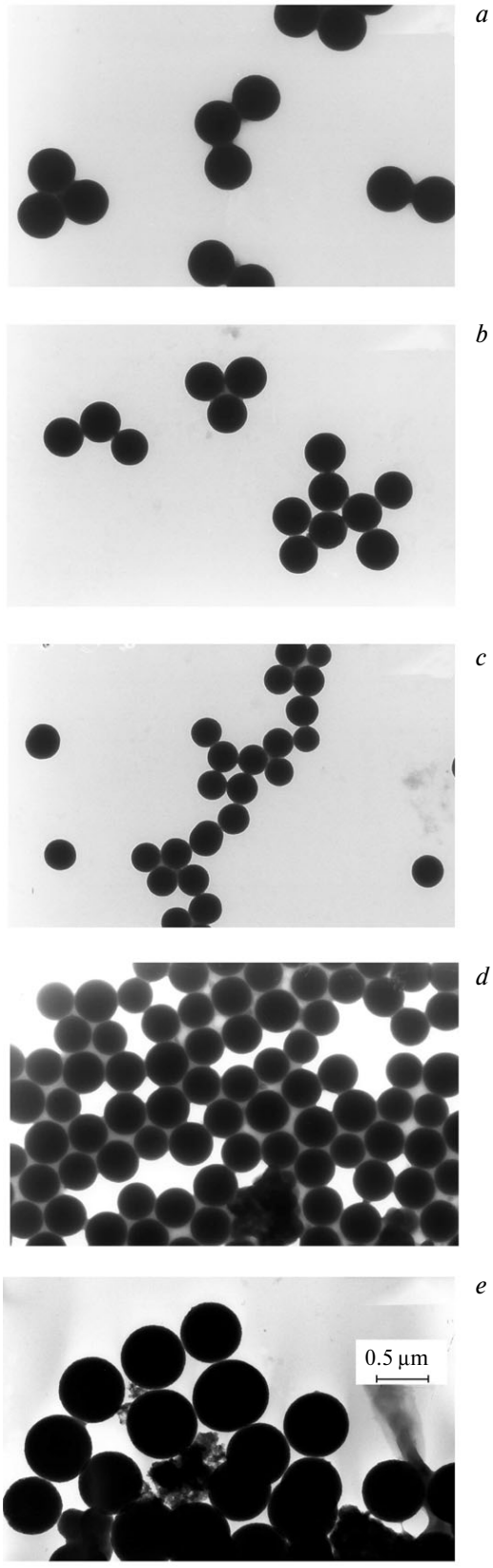

Fig. 2. Photomicrographs of dispersions of SiO_2 (*a*), SiO_2-Eu1 (*b*), SiO_2-Eu4 (*c*), SiO_2-Eu7 (*d*), and SiO_2-Eu2 (*e*).

Table 2. Nanoparticle diameters from transmission electron microscopy data

Nanoparticles	*d*/nm
SiO_2	432±8 (2%)
SiO_2-Eu1	378±15 (4%)
SiO_2-Eu2	690±50 (7%)
SiO_2-Eu4	280±38 (14%)
SiO_2-Eu7	488±50 (10%)

The atomic emission analysis of the obtained nanoparticles confirms the presence of europium complexes. However, for the concentrations of Eu^{III} complexes being equal, the least effective doping in the synthesis is observed for the $Eu(TTA)_3$-**1** adduct, which is in line with its lower solubility in aqueous ethanol as compared with $Eu(TTA)_3$-**2** or $Eu(TTA)_3$ (Table 3).

The colloid stability and the sizes of the obtained nanoparticles in aqueous solutions were estimated by dynamic light scattering. The results are summarized in Table 4. The colloidal dispersions of SiO_2-Eu1, SiO_2-Eu2, SiO_2-Eu4, and SiO_2-Eu7 show good correspondence between

Table 3. Eu content (*C*) in nanoparticle dispersion (1 g L^{-1}) from atomic emission spectroscopy data

Nanoparticles	*C* (%)±10%	Nanoparticles	*C* (%)±10%
SiO_2-Eu1	0.30	SiO_2-Eu4	0.15
SiO_2-Eu3	0.48	SiO_2-Eu7	0.28

Table 4. Average hydrodynamic diameter (*d*) and polydispersity index (PDI) for silica particles in water from dynamic light scattering data

Dispersion	*C*/g L^{-1}	*d*/nm	PDI	ζ±10%/mV
SiO_2-Eu1	2.50	434±4	0.064	–56
	0.50	441±6	0.059	—
SiO_2-Eu2	0.13	619±15	0.274	–53
	0.01	493±34	0.364	—
SiO_2-Eu3	2.66	848±35	0.241	–48
	0.53	1197±53	0.986	—
SiO_2-Eu4	2.27	424±34	0.262	–57
	0.45	519±14	0.442	—
SiO_2-Eu5	0.09	466±64	0.396	–48
	0.01	507±34	0.522	—
SiO_2-Eu6	2.60	731±40	0.209	–37
	0.52	1004±26	0.301	—
SiO_2-Eu7	1.87	467±8	0.092	—
	0.37	519±10	0.218	—
SiO_2-Eu8	0.08	743±17	0.245	–39
	0.01	661±15	0.493	—
SiO_2-Eu9	2.60	720±46	0.085	–53
	0.52	961±30	0.273	—

the particle size from the transmission electron microscopy and dynamic light scattering data; note that dynamic light scattering, unlike the electron microscopy, reflects the presence of the hydration layer at the nanoparticle surface and partial aggregation of nanoparticles in aqueous solutions.[22] Dilution of dispersions (five- and ten-fold) has almost no effect on the aggregative behavior of nanoparticles.

The emission for all of the obtained dispersions was excited by irradiation at 350 nm, because the excitation spectra of aqueous solutions of all the obtained dispersions show one band at 350 nm, which is demonstrated in Fig. 3 for a colloidal dispersion of SiO_2-Eu1. The emission spectra of the obtained dispersions exhibit a band at 612 nm ($^5D_0 \rightarrow {}^7F_2$) characteristic of Eu^{III} and less intense bands at 580 and 596 nm ($^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$).[15,16] Figure 3 shows a typical emission spectrum of an aqueous dispersion of SiO_2-$Eu(TTA)_3$. As an example for the complex $Eu(TTA)_3$ most soluble in aqueous ethanol, it was found that an increase in the initial luminophore concentration from $1 \cdot 10^{-3}$ to $5 \cdot 10^{-3}$ mol L^{-1} results in the formation of particles with more intense Eu^{III} luminescence (see Fig. 3). The introduction of $1 \cdot 10^{-3}$ mol L^{-1} of adducts, instead of the basic luminophore, into the silica particles entails a buildup of Eu^{III} luminescence intensity (Fig. 4). For this initial luminophore concentration, the complexes $Eu(TTA)_3$ and $Eu(TTA)_3$-**2** are incorporated into silica particles in approximately equal amounts (see Table 2), the particles SiO_2-Eu7 producing more intense luminescence than SiO_2-Eu1. The luminescence intensity of SiO_2-Eu4 particles doped with $Eu(TTA)_3$-**1** is similar to or even somewhat exceeds the corresponding value for SiO_2-Eu1, despite the much lower content of Eu^{III} in SiO_2-Eu4 than in SiO_2-Eu1. Thus, under these concentration conditions, the nature of the luminophore has a crucial influence on the luminescence of nanoparticles. Indeed, according to our early publication,[20] the luminescence of complex $Eu(TTA)_3$-**2** is much more intense

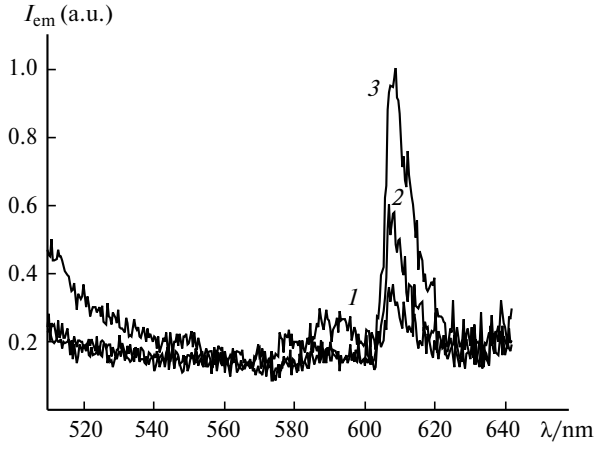

Fig. 4. Emission spectra of aqueous dispersions of SiO_2-Eu1 (2.5 g L^{-1}) (*1*), SiO_2-Eu4 (2.27 g L^{-1}) (*2*), and SiO_2-Eu7 (1.87 g L^{-1}) (*3*).

than the luminescence of $Eu(TTA)_3$-**1** or $Eu(TTA)_3$. As the initial luminophore concentration is increased to $2 \cdot 10^{-3}$ mol L^{-1}, as in the case of 10^{-3} mol L^{-1} concentration, the most intense luminescence is observed for the silica particles SiO_2-Eu8 containing the complex $Eu(TTA)_3$-**2** (Fig. 5, see Table 1). For the aqueous dispersions of SiO_2-Eu2 doped with $Eu(TTA)_3$ and SiO_2-Eu5 doped with $Eu(TTA)_3$-**1**, the luminescence intensities coincide. However, upon further increase in the initial concentrations of the adducts ($Eu(TTA)_3$-**1** and $Eu(TTA)_3$-**2**) and $Eu(TTA)_3$ to $5 \cdot 10^{-3}$ mol L^{-1}, the most intense luminescence is observed for the silica nanoparticles SiO_2-Eu3 doped with $Eu(TTA)_3$ (Fig. 6, see Table 1). This is attributable to lower solubility of complexes $Eu(TTA)_3$-**1** and $Eu(TTA)_3$-**2** in aqueous ethanol compared to $Eu(TTA)_3$, which results in a smaller amount of luminophore being incorporated in the silica particles during the synthesis. Thus, the luminescence intensity of the aqueous dispersion of nanoparticles doped with $Eu(TTA)_3$ can be in-

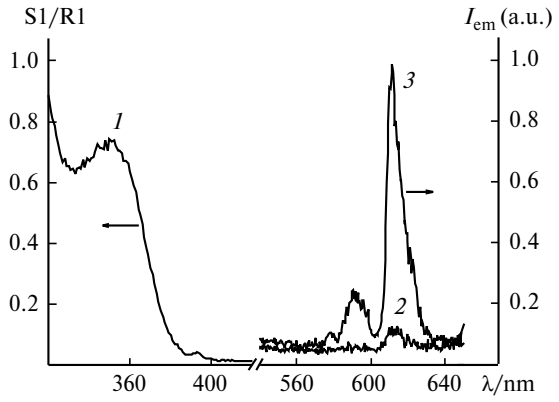

Fig. 3. Excitation spectrum of aqueous dispersion of SiO_2-Eu1 (4.07 g L^{-1}) (*1*) and emission spectra of aqueous dispersions of SiO_2-Eu1 (2.5 g L^{-1}) (*2*) and SiO_2-Eu3 (2.66 g L^{-1}) (*3*).

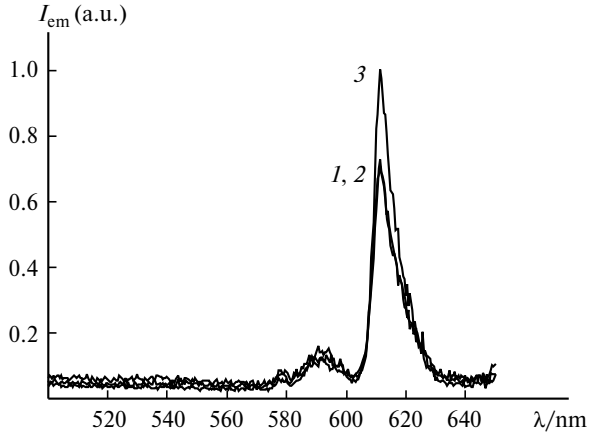

Fig. 5. Emission spectra of aqueous dispersions of SiO_2-Eu2 (*1*), SiO_2-Eu5 (*2*), and SiO_2-Eu8 (*3*); concentration 12.67 g L^{-1}.

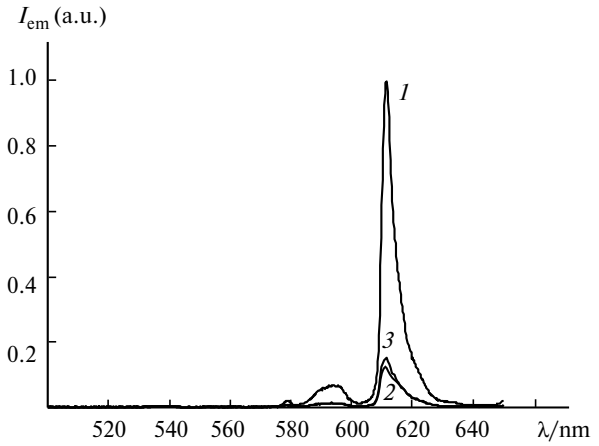

Fig. 6. Emission spectra of aqueous dispersions of SiO_2-Eu3 (*1*), SiO_2-Eu6 (*2*), and SiO_2-Eu9 (*3*); concentration 2.6 g L^{-1}.

creased over a broad range by increasing the initial concentration of the introduced luminophore. However, when analyzing the luminescence signal intensity of silica nanoparticles, it should be borne in mind that this value is caused by not only the amount of luminophore dopants but also by their distribution in the silica matrix. The mere presence of the silica environment increases the quantum yield (by changing the refractive index) and often contributes to elongation of the excited state lifetime.[23] Thus, the thickness of the silica shell affects the luminescence signal intensity. Meanwhile, the accumulation of luminophores in nanoparticles may be accompanied by luminescence quenching (so-called accumulation effect).[24] Therefore, there cannot be a linear correlation between the luminescence signal intensity and the luminophore content in the nanoparticle. The photophysical properties of the initial luminophore represent one more factor that affects the luminescence intensity of colloidal dispersions of silica nanoparticles, as follows from comparison of the luminescence properties of silica nanoparticles doped with complexes $Eu(TTA)_3$, $Eu(TTA)_3$-**2**, and $Eu(TTA)_3$-**1**. However, the incorporation of more intensely luminescent complexes can be limited by their insufficient solubility.

Thus, on the basis of the Stober procedure we synthesized silica nanoparticles doped with new luminescent adducts, $Eu(TTA)_3$-**2** and $Eu(TTA)_3$-**1**. The nanoparticle size was determined from transmission electron microscopy data in dried samples and from dynamic light scattering data in solutions. The effect of the structure of the doping complex on the nanoparticle size and polydispersity was demonstrated. Correlations between the photophysical properties of nanoparticles and the nature and concentration of the introduced luminophore were revealed. In particular, the effect of photophysical properties and the solubility of the lanthanide complex on the luminescence of silica nanoparticles doped with lanthanide complexes was demonstrated.

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