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Colloidal Stability and Photophysical Characteristics of Luminesent Silica Nanoparticles Modified with Various Nitrogen/Oxygen-Containing Trialkoxysilanes

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Abstract—Surface modification of the luminescent silica nanoparticles doped with Tb(III)–*p*-sulfonatothiacalix[4]arene complex was carried out using a series of nitrogen/oxygen-containing trialkoxysilanes. It was found that groups capable of nonspecific interactions on the surface of the nanoparticles cause a significant decrease in their colloidal stability. The chromophore moieties in the modifiers were found to quench the luminescence of the nanoparticles. The surface modification of the nanoparticles is responsible for the change in the mechanism of luminescence quenching in the presence of copper(II) ions due to decreased accessibility of luminophores to the quencher.

Keywords: click reaction, azides, trialkoxysilanes, luminescence, silica nanoparticles, luminescence quenching

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Over the past decade researchers have paid increasing attention to luminescent silica nanoparticles primarily because they offer great opportunities for use in bioanalysis [1–3]. Sensor properties of nanoparticles are manifested in the fluorescence response to the interaction with substrates of a particular type. As luminescent labels serve both organic fluorescent dyes and lanthanide complexes, and the latter are advantageous in terms of high signal-to-noise ratio even in the presence of background luminescence signals from proteins, of large Stokes shift, long lifetimes of the excited state, narrow emission lines, and possibility of emission in different regions of the visible spectrum and in the near infrared region, depending on the metal center selected [4, 5]. Encapsulation of lanthanide complexes into silica matrix substantially increases the luminescence intensity and also significantly mitigates the toxic effects from lanthanide ions [6]. It is important to note that silica matrix is fairly loose, which leaves open the possibility of permeation of small ions and molecules inside it. Therefore, in the interaction with *d*-metals as quenchers both the dynamic (energy transfer) and static (degradation of the luminescent complex via ion/ ligand exchange) mechanisms of luminescence quenching can operate [7, 8]. The quenching mechanism that will dominate depends significantly on the distribution of the luminophore within the silica matrix. For example, luminophores located close to the nanoparticle shell undergo quenching by mixed dynamic/static mechanism, and those concentrated deep inside the matrix, predominantly by the static mechanism [9]. We have previously shown [10] that the nanoparticles doped by luminescent complex Tb(III)-*p*-sulfonatothiacalyx[4]arene (Tb-TCAS) with the surface modified by amino groups effectively bind d-metal ions and thus are suitable for fluorometric determination of copper(II) ions at concentrations down to 0.1 µM. However, the influence of the modifier structure on colloidal stability, photophysical





characteristics, and ability of nanoparticles to participate in metal ion binding still remains to be elucidated. Therefore, the aim of this study was to carry out modification of Tb–TCAS complex-doped silica nanoparticles by organosilicon modifiers containing donor atoms capable of coordination with *d*metal ions, as well as to examine the colloidal stability and photophysical characteristics of the resulting nanoparticles in the presence of some *d*-metals.

For modification of the nanoparticles we used derivatives prepared from commercially available 3aminopropyltriethoxysilane and 3-isocyanatopropyltriethoxysilane by the atom-economical reaction of copper-catalyzed azide-alkyne cycloaddition [11, 12] to give the corresponding triazole **2**, addition of isocyanates to amines and alcohols to produce the corresponding disubstituted urea **4** and urethane **5**, and the alkylation reaction to afford diester **3** (Scheme 1).

Silica nanoparticles doped with luminescent complex Tb–TCAS were synthesized by the reverse microemulsion procedure which has shown good results in introduction of water-soluble luminophores [6]. Covalent modification of the surface silanol groups of the resulting nanoparticles was carried out by the previously developed technique involving copolycondensation of trialkoxysilane with tetraethoxysilane in the presence of ammonia [10].

The modifier fixing on the nanoparticles surface was confirmed by IR spectroscopy. For example, in the case of modifier **3** comprising ester moieties the IR spectrum of the modified particles (Fig. 1, spectra *3* and *4*) contains intense bands of the C=O stretching vibrations of the ester moieties at 1741 cm⁻¹, as well as intense bands at 2976 cm⁻¹ and 2929 cm⁻¹ associated with the C–H asymmetric stretching vibrations of the CH₃ and CH₂ groups in the ester moieties, respectively, which were not observed for the unmodified nanoparticles (Fig. 1, spectrum *1*). Sample heating to 180°C improved the resolution due to the elimination of encapsulated water, so that the bands corresponding to vibrations of the C–H bond were more clearly distinguishable (Fig. 1, spectrum *4*).

The size of the nanoparticles synthesized was characterized by the dynamic light scattering method.

As seen from the data obtained (see table), all the modified nanoparticles, except for SiO₂&Tb–TCAS&Mod3, substantially exceed the unmodified particles in size and polydispersity index, reaching micrometer sizes in the case of SiO₂&Tb–TCAS&Mod4. The modification did not cause any significant reduction in the particle surface charge (see table), which allows the aggregation of the modified nanoparticles to be associated with nonspecific interactions.

The atomic force microscopic (AFM) data (Fig. 2) agree well with the dynamic light scattering results. In the case of the particles containing modifiers 2, 4, and 5, large particle sizes correspond to aggregates of small nanoparticles. Especially highly aggregated are the nanoparticles coated with modifier 4.



Fig. 1. IR spectra of (1) $SIO_2 \& Tb - TCAS$ nanoparticles, (2) compound **3**, and (3, 4) $SIO_2 \& Tb - TCAS \& Mod3$ nanoparticles, taken at (3) 25 and (4) 180°C.

Average hydrodynamic diameters (d), zeta potentials, and polydispersity indices of the nanoparticles in the presence of Fe(III) and Cu(II) ions^a

System	FeCl ₃ ·6H ₂ O			CuSO ₄ ·5H ₂ O		
	<i>d</i> , nm	PDI	ζ, mV	<i>d</i> , nm	PDI	ζ, mV
SiO ² &Tb-TCAS	80±1	0.154	-33.3			
$c(M) = 1 \times 10^{-6} M$	83±1	0.164	-32.7	95±5	0.276	-20.8
$c(M) = 1 \times 10^{-4} M$	1743±396	0.881	-16.4	110±19	0.509	-19.0
$c(M) = 5 \times 10^{-4} M$	713±189	0.960	36.9	209±12	0.470	-13.4
SiO ₂ &Tb-TCAS&Mod2	809±17	0.489	-30.6			
$c(M) = 1 \times 10^{-6} M$	915±17	0.683	-29.4	1005±22	0.474	-22.4
$c(M) = 1 \times 10^{-4} M$	$1424{\pm}111$	0.306	-2.1	1998±150	0.484	-15.0
$c(M) = 5 \times 10^{-4} M$	843±164	0.937	35.3	1342±86	0.325	-12.3
SiO ₂ &Tb-TCAS&Mod4	1715±584	0.945	-23.2			
$c(M) = 1 \times 10^{-6} M$	3536±1435	1.000	-23.3	787±196	0.847	-18.0
$c(M) = 1 \times 10^{-4} M$	2527±1041	1.000	-3.1	1541±561	0.975	-13.5
$c(M) = 5 \times 10^{-4} M$	699±494	0.857	37.9	623±251	0.543	-0.3
SiO ₂ &Tb-TCAS&Mod3	88±1	0.122	-24.9			
$c(M) = 1 \times 10^{-6} M$	71±1	0.190	-18.3	74±1	0.226	-15.0
$c(M) = 1 \times 10^{-4} M$	853±669	0.893	-2.7	80±4	0.268	-9.3
$c(M) = 5 \times 10^{-4} M$	147±31	0.595	36.5	715±26	0.575	-6.5
SiO ₂ &Tb-TCAS&Mod5	622±52	0.672	-29.6			
$c(M) = 1 \times 10^{-6} M$	653±23	0.537	-28.8	586±92	0.544	-26.6
$c(\mathbf{M}) = 1 \times 10^{-4} \mathbf{M}$	1420±665	0.790	-17.0	753±90	0.730	-20.1
$c(M) = 5 \times 10^{-4} M$	103±50	0.497	38.1	693±83	0.617	-12.8

^a $c_{\text{particles}} = 0.028 \text{ g/L}, c(\text{M}) = 0.001 - 0.5 \text{ mM}, \text{pH} = 7.4 \text{ (Tris)}.$



Fig. 2. AFM images of (a) SiO₂&Tb–TCAS, (b) SiO₂&Tb–TCAS&Mod2, (c) SiO₂&Tb–TCAS&Mod3, (d) SiO₂&Tb–TCAS&Mod4, and (e) SiO₂&Tb–TCAS&Mod5 samples.

The modification significantly affects the photophysical properties of the nanoparticles (Fig. 3). For all samples, excluding the SiO₂&Tb–TCAS&Mod3 dispersions, no less than twofold decrease in the luminescence intensity was observed. This is due both to aggregation of the nanoparticles (the most highly aggregated SiO₂&Tb–TCAS&Mod4 and SiO₂&Tb– TCAS&Mod2 nanoparticles exhibited the lowest luminescence intensity) and absorption of aromatic chromophores of the modifiers near 330 nm, which is the wavelength of excitation of the Tb–TCAS complex.

As mentioned above, the addition of Cu(II) and Fe(III) ions to aqueous dispersions of the Tb–TCAS complex-doped nanoparticles results in luminescence quenching, and this may be useful in fluorometric determination of the metals as well as of substrates

which induce the fluorescence response in nanoparticles via metal binding [10]. To study in more detail the luminescence quenching mechanism for functionalized nanoparticles in the presence of Fe(III) and Cu(II) ions, we carried out fluorescence titration and measured the lifetimes of excited states.

For the unmodified particles in the presence of the Fe(III) ions (Fig. 4a, spectra 5 and 5') the static mechanism of the luminescence quenching dominates, since the addition of excess Fe(III) ions cause only insignificant changes in the lifetime of the excited state. However, the dynamic mechanism also makes a small contribution. Coating the nanoparticles with the modifiers does not produce substantial changes, except for a slight reduction of quenching in the case of modifiers 2, 3, and 4. Study of the nanoparticles size and surface charge in the presence of Fe(III) ions (see

table) showed that the addition of Fe(III) ions substantially affects both the colloidal stability and surface charge of the nanoparticles. For example, in the case of unmodified particles the addition of Fe(III) ions at c 10⁻⁴ M leads to a significant decrease in the surface charge of the nanoparticles and to a formation of micron-sized aggregates, with an increase in the amount of Fe(III) ions to c 5×10^{-4} M resulting in surface recharging accompanied by a decrease in the aggregate size. Thus, for the unmodified nanoparticles both the ion exchange and aggregation of nanoparticles are the key mechanisms of the luminescence quenching. A similar trend is exhibited by the modified nanoparticles. Specifically, the addition of Fe(III) ions causes surface recharging, and when the isoelectric point is attained the size of the aggregates is at a maximum. In the case of the nanoparticles coated with modifiers 2, 4, and 5 the aggregate size after surface recharging is substantially smaller than that observed initially.

In the presence of copper(II) ions the situation significantly differs from that for the systems with iron(III) ions. For example, for the unmodified nanoparticles the dynamic quenching mechanism dominates, with the titration curves for the luminescence intensity and lifetime exhibiting similar trends (Fig. 4b, curves 5 and 5'). This is possibly due to the luminophore distribution both inside the nanoparticles and close to the shell. Specifically, luminophores located near the nanoparticle shell undergo quenching primarily via energy transfer due to proximity to the quencher, and luminophores located deeper inside the



Fig. 3. Emission spectra of the solutions of (1) SiO₂&Tb–TCAS, (2) SiO₂&Tb–TCAS&Mod3, (3) SiO₂&Tb–TCAS&Mod5, (4) SiO₂&Tb–TCAS&Mod4, and (5) SiO₂&Tb–TCAS&Mod2. $c_{\text{particles}} = 0.028 \text{ g/L}, \text{ pH} = 7.4 (0.001 \text{ M} \text{Tris}), \lambda_{\text{exc}} = 330 \text{ nm}.$

nanoparticles, only via ion exchange by the static mechanism at a quencher ion concentration sufficiently high for diffusion. The modified particles exhibit higher I/I_0 ratios (Fig. 4b, curves I-4), while the t/t_0 ratios change insignificantly, which indicates a large contribution from the static mechanism. A good reason thereto is an increase in the shell thickness via modification of the nanoparticles, whereby the latter take the form of a core with the luminophore



Fig. 4. Variation in the I/I_0 and t/t_0 (apostrophized) ratios at 547 nm for the dispersions of (1) SiO₂&Tb–TCAS&Mod2, (2) SiO₂&Tb–TCAS&Mod4, (3) SiO₂&Tb–TCAS&Mod3, (4) SiO₂&Tb–TCAS&Mod5, and (5) SiO₂&Tb–TCAS nanoparticles with (a) Cu(II) and (b) Fe(III) ion concentration.

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concentrated deep inside the nanoparticles, surrounded by a thick outer shell which contains no luminophore. As a result, quenching occurs only via permeation of the copper ions which replace the terbium ions, and the energy transfer to the quencher ions is not so significant.

Thus, silica nanoparticles modified with nitrogen/ oxygen-containing moieties were obtained. It was shown that the introduction of modifiers comprising chromophore groups, in particular triazole moieties, absorbing in the near UV region results in substantial reduction of the luminescence intensity of the nanoparticles. At covalent modification of the nanoparticles, due to an increase in the outer shell thickness, the luminescence quenching in the presence of Cu(II) ions occurs by predominantly static mechanism.

EXPERIMENTAL

The solvents were purified before use by the procedures described in [13]. Known techniques were employed for the syntheses of compounds 1 [14], 2 [14], 4 [15], 5 [16], and *p*-sulfonatothiacalix[4]arene [17]. The chemicals used were commercially available from "Alfa Aesar," "Acros," and "Lancaster." All physicochemical measurements were performed using bidistilled water. All samples were preliminarily maintained for 30 min in an ultrasonic bath at 25°C.

Elemental analysis was carried out on a Perkin Elmer PE 2400 series II CHNS/O analyzer. The NMR spectra were recorded on a Bruker Avance 400 Nanobay spectrometer in CDCl₃. Mass spectra were obtained on a Shimadzu GCMS 2010 Ultra gas chromatograph-mass spectrometer with an HP-5MS column. The IR spectra of the samples (suspensions in mineral oil or KBr pellets) were recorded on a Bruker Vector-22 spectrometer. Dynamic light scattering and zeta potential measurements were performed on a Malvern Zetasizer instrument at 25°C using polystyrene cells (l = 10 mm). Luminescence spectra were recorded on a Fluorolog FL-221 (HORIBA Jobin Yvon) spectrofluorometer in the 450–650 nm range at the excitation wavelength of 330 nm.

The excited-state lifetimes were measured on an FL-1042 accessory for the spectrofluorometer using a xenon flash lamp with the following parameters: time per flash 50.00 ms, flash count 200 ms, initial delay 0.05 ms, and sample window 2 ms. Excitation of the sample was performed at 330 nm, and emission was detected at 546 nm.

The atomic force microscopy measurements were conducted on a Multimode V (Veeco, USA) microscope in the contact mode with an RTESP (Veeco) cantilever. Mica surface was coated by 20 μ L of an aqueous dispersion of the nanoparticles with the concentration of 0.0028 g/L and then dried at 80°C for 3 h. The AFM images were obtained in the Laboratory of Spectroscopy, Microscopy, and Thermal Analysis, Kazan National Research Technological University.

Silica nanoparticles doped with Tb(III)–*p*-sulfonatothiacalyx[4]arene complex were synthesized by the method of reverse microemulsion [6]. Covalent modification of the nanoparticles surface was performed by the known procedure from [10].

N,N-Bis(2-ethoxy-2-oxoethyl)-N-[3-(triethoxysilyl)propylamine (3). To a solution of 25.7 g (154 mmol) of ethyl bromoacetate in 35 mL of benzene a mixture of 9.5 g (43 mmol) of 3-aminopropyltriethoxysilane and 15.6 g (154 mmol) of triethylamine in 50 mL of benzene was added dropwise at stirring. The reaction mixture was refluxed using a Dimroth condenser for 5 h under an inert atmosphere. After cooling the precipitated ammonium salt was filtered off on a frit glass filter and washed with benzene. The resulting filtrate was concentrated. Yield 11.9 g (71%), yellow viscous oily substance. IR spectrum, v, cm⁻¹: 1080 s (Si-O), 1741 s (C=O), 2929 m (CH₂), 2976 s (CH₃). ¹H NMR spectrum (400 MHz, 25°C), δ , ppm: 0.55– 0.64 m [2H, (SiCH₂CH₂CH₂NH)], 1.18 t (9H, OCH_2CH_3 , ${}^{3}J_{HH} = 7.0$ Hz), 1.21–1.26 m (6H, COOCH₂CH₃), 1.51–1.62 m (2H, SiCH₂CH₂CH₂NH), 2.65-2.70 m (2H, SiCH₂CH₂CH₂NH), 3.51 s (4H, NHCH₂), 3.74–3.81 m (6H, OCH₂CH₃), 4.09–4.17 m (4H, COOCH₂CH₃). Mass-spectrum, m/z 394 $[M]^+$. Found, %: C 50.51; H 8.85; N 3.38; Si 7.33. C₁₇H₃₅NO₇Si. Calculated, %: C 50.64; H 8.76; N 3.69; Si 7.40.

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