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Carbofunctional fluorine-containing triethoxysilanes: synthesis, film forming and properties

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Novel fluorine-containing carbofunctional organosilicon monomers were synthesized: 3-pentafluorobenzylideneaminopropylethoxysilane $(EtO)_3Si(CH_2)_3N{=}CH{-}C_6F_5$, *N*-3-methoxydiethoxysilylpropyltrifluoroacetamide $(EtO)_2(MeO)Si(CH_2)_3NHC(O)CF_3$, and 1,1,5-trihydrooctafluoroamyl *N*-3-triethoxysilylpropylaminopropanoate $(EtO)_3Si(CH_2)_3NH(CH_2)_2C(O)OCH_2(CF_2)_3CHF_2$. Compositions for the formation of transparent thermally stable films were prepared from these monomers. The films have low absorbance intensity near 1550 nm, *i.e.*, in the region of photosignal transmission of modern optical communication systems. The compositions can dissolve complexes with organofluorine ligands and produce transparent homogeneous films doped with rare-earth metals. The concentrations of the complexes in the matrices are 3.7—21.4 wt.% (metal concentrations are 0.6—3.7%). Fluorescence and fluorescence excitation spectra of the matrices and electronic absorption spectra of the doped films were studied.

Key words: 3-pentafluorobenzylideneaminopropyltriethoxysilane, *N*-3-methoxydiethoxysilylpropyltrifluoroacetamide, 1,1,5-trihydrooctafluoroamyl *N*-3-triethoxysilylpropylaminopropanoate, rare-earth metal complexes with fluorinated ligands, film preparation, near-IR spectroscopy, electronic absorption spectroscopy, fluorescence.

Adsorbents, heterogeneous catalysts,[1—7] aerogels,[8] cation-exchange resins,[9] and materials for photonics and laser optics[10] can be obtained from silicon alkoxides containing a functional organic substituent $(RO)_3Si(CH_2)_nZ$. Methods of sol—gel chemistry make it possible to introduce organic dye molecules and transition, rare-earth, and platinum metal cations into a hybrid organo-inorganic matrix. For instance, the sorption of rare-earth element (REE) cations by xerogels of functionalized organosilsesquioxanes $O_{1.5}Si(CH_2)_3{-}Z{-}(CH_2)_3SiO_{1.5}$ (Z = $NHC(O)C_6H_4C(O)NH$, $NHC(O)CH_2C(O)NH$, NHS(O)NH, and $NHS(O_2)NH$) has recently[11] been studied. Xerogels prepared by 3-acrylamidopropyltriethoxysilane hydrolysis were used as complexing agents for the uranyl cation.[12] Highly porous aerogels $SiO_2 \cdot O_{1.5}Si(CH_2)_3Z$ (Z = SH, $OC(O)C(Me){=}CH_2$, NCO, and NHC(O)OMe) were synthesized[13] by the co-hydrolysis of $Si(OMe)_4$ and $(MeO)_3Si(CH_2)_3Z$ followed by drying under supercritical conditions. REE complexes can also be incorporated into inorganic materials. For instance, erbium β-diketonates were incorporated into nanoporous glasses by supercritical impregnation.[14] Organo-inorganic glasses doped with Eu^{2+}/Eu^{3+} cations were obtained from a mixture of methyldiethoxysilane, methyltriethoxysilane, and tetrapropoxyzirconium or from a mixture of tetraethoxysilane, tin alkoxide, and titanium in the presence of europium chloride.[15,16] The preparation process is accompanied by the partial reduction of Eu^{3+} to Eu^{2+}. REE cations can also be incorporated into organic polymers. For instances, the lanthanide-containing organic polymers were prepared by the polymerization of the neodymium, europium, gadolinium, and terbium unsaturated acid derivatives.[17,18]

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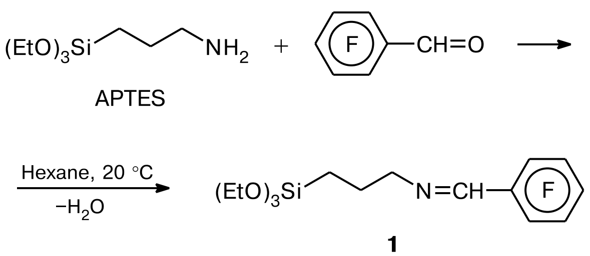
Coordination compounds of REE are capable of photo- and electroluminescence,[19,20] due to which they can be used in telecommunication devices and for the preparation of displays. REE cations are used as doping agents to quartz in photopulse amplifiers of optical communication systems.[21] Active research for the respective materials has been conducted recently to produce cheaper and more flexible plastic fibers.[19] The most part of the modern telecommunication systems operate at wavelengths near 1550 nm. This is the region of maximum transmission for quartz glass.[22] However, the same region for an organic polymer is characterized by intense absorbance caused by overtones of stretching vibrations of O—H, C—H, and N—H bonds.[23] The development of methods for syntheses of organic or organometallic monomers and polymers with the maximum transmission at ~1550 nm is an urgent problem. One of the methods is the use of organofluorine polymers with a minimum absorbance in the near-IR region. However, fluoroplastics poorly dissolve rare-earth metal compounds. The purpose of this work is to synthesize fluorine-containing organosilicon compounds capable of dissolving REE complexes and forming optically transparent sol—gel films.

3-Aminopropyltriethoxysilane (APTES) was used as the starting organosilicon compound.[24] It combines the properties of a film-forming agent and primary amine capable of participating in addition and substitution reactions. The target products were synthesized by the reactions of APTES with organofluorine compounds, which are reactive toward primary amines, *viz.*, perfluorobenzaldehyde, methyl trifluoroacetate, 1,1,5-trihydrooctafluoroamylacrylate.

The reaction of APTES with pentafluorobenzaldehyde affords 3-pentafluorobenzylideneaminopropyltriethoxysilane (**1**) (Scheme 1), which is a yellowish-green liquid.

Scheme 1

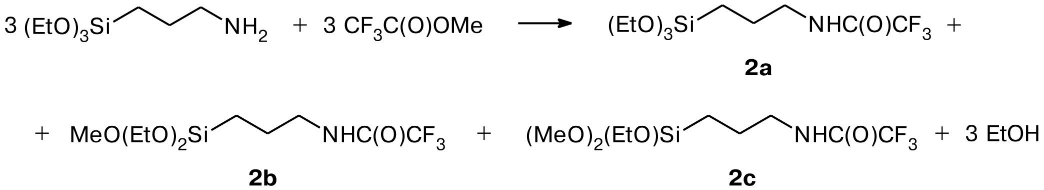


Anhydrous sodium sulfate was used to bind water formed in the reaction. After 2 h, the mixture became yellowish-green. According to the GLC data, the aldehyde has been consumed completely to this time. Although a drying agent was added to the system, APTES and the reaction product undergo partial hydrolysis by the water formed, which decreases the yield of compound **1** and produces an insoluble white precipitate: polyorganosilsesquioxane. Nevertheless, the main product is not oligomeric.

It should be expected that 3-triethoxysilylpropylamide $CF_3C(O)NH(CH_2)_3Si(OEt)_3$ is formed in the reaction of APTES with methyl trifluoroacetate. The reaction occurred rapidly with a small exothermic effect. However, according to the GLC data, the product isolated by rectification was a mixture of three compounds. The ^{1}H NMR spectrum of this mixture contains a signal of protons of the Me group bonded to the O atom along with signals of protons of the N—$(CH_2)_3$—Si, NH, and Si—O—Et groups. Thus, the ethoxyl radicals were partially replaced by methoxyls in the triethoxysilyl group during the reaction (Scheme 2).

Ester interchange seemed unexpected, because, as known from the literature,[25] the reaction of tetraethoxysilane with methanol requires more drastic conditions (210 °C). At the same time, the test showed that the alkoxy substituents can be exchanged between the Si and C atoms. The GLC method detected small quantities of triethoxymethoxysilane and diethoxydimethoxysilane appeared after 1 h in a mixture of tetraethoxysilane with methyl trifluoroacetate (1 : 1). Unlike the reaction with APTES, this process is slow. The fast ester interchange reaction can be explained by the catalytic effect of the base (the amine group of APTES) or by the fact that the triethoxysilyl substituent reacts not with methanol but with the methoxide anion, which is leaving upon nucleophilic substitution in ester and is a stronger nucleophile than a methanol molecule. In turn, the ethoxide ion evolved by ester interchange is a stronger base than methoxide and binds proton much more efficiently. The ratio of integral intensities of signals of protons of the methoxy and ethoxy groups in the ^{1}H NMR spectrum of the reaction product is 1 : 2. Therefore, the formula of the

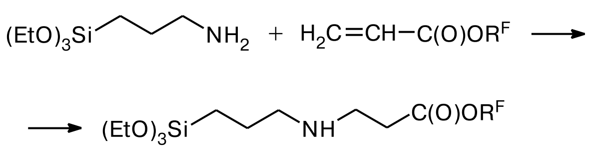
Scheme 2



isolated mixture of alkoxysilanes can be presented as $(EtO)_2(MeO)Si(CH_2)_3NHC(O)CF_3$ (**2**).

The reaction of APTES with 1,1,5-trihydrooctafluoroamylacrylate $H_2C=CH—C(O)O—CH_2—(CF_2)_3CHF_2$ proceeds mainly as amine addition to the C=C bond. The exchange of the EtO groups by R^FO occurs to a much less extent than that in the reaction with methyl trifluoroacetate. Mixing of equimolar quantities of the reactants produces 1,1,5-trihydrooctafluoroamyl *N*-3-triethoxysilylpropylaminopropanoate (**3**) (Scheme 3), which is a colorless liquid slowly hydrolyzed by air moisture in thin layer to form a transparent film.

Scheme 3

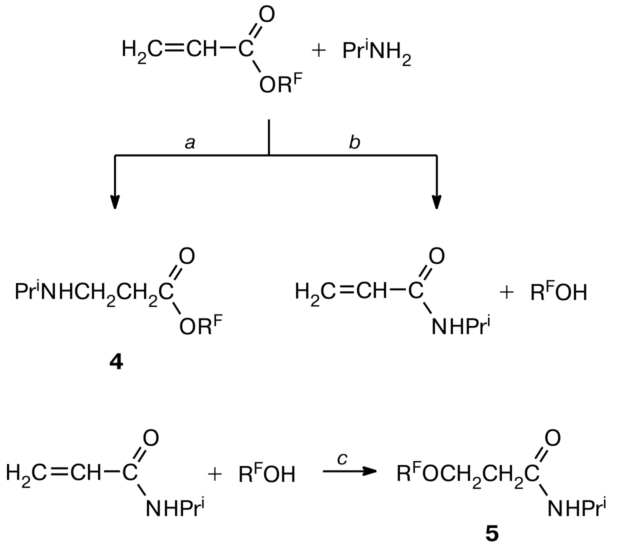


3

Compound **3** cannot be rectified because of the high molecular weight. The GLC analysis of **3** found admixtures (7—9%) being, according to the IR spectroscopy and ^{1}H NMR data, amides $R^FO—(CH_2)_2—C(O)NH—(CH_2)_3—Si(OEt)_3$ and $EtO—(CH_2)_2—C(O)NH—(CH_2)_3—Si(OEt)_2OR^F$. The formation of two different amides is confirmed by the ^{1}H NMR spectrum containing two signals of amidic protons (δ 7.41 and 7.56), a triplet at δ 4.00 assigned to protons of the $—CH_2—O—C\underline{H}_2CF_2—$ group, and a quadruplet at δ 3.21 corresponding to protons of the $CH_3C\underline{H}_2—O—CH_2—$ fragment. Ester interchange is indicated by the triplet at δ 4.19 attributed to the signal of methylenic protons of the $—Si—O—CH_2—CF_2—$ group. The formation of admixtures is explained by a series of consecutive reactions. First, the R^FO group at the carboxylic C atom is replaced by the amide group to form amide $H_2C=CH—C(O)NH—(CH_2)_3—Si(OEt)_3$ and alcohol R^FOH. The evolving fluorinated alcohol adds to the multiple bond of the unsaturated amide and is involved in the ester interchange of the alkoxysilyl fragment, and ethanol formed in the latter process adds to the C=C bond of the unsaturated amide.

To confirm this reaction route, we studied the reaction of fluoroacrylate with organic amine (Pr^iNH_2) of low molecular weight. Mixing of the reactants was accompanied by slight heating and an increase in the viscosity of the reaction mixture. The GLC method showed that the starting fluoroacrylate has reacted completely after 48 h to yield one main product (91%) containing the less amount of an admixture (9%). The data of IR and ^{1}H NMR spectroscopy indicate in favor of the formation of 1,1,5-trihydrooctafluoroamyl *N*-isopropylaminopropanoate (**4**) (Scheme 4). The IR spectra contain absorption bands corresponding to stretching and bending vibrations of the N—H, C—H, and C—F bonds (see Experimental) and a very intense absorption band at 1765 cm^{-1} belonging to stretching of the C=O bond in the ester group. The ^{1}H NMR spectrum exhibits signals of the protons of the isopropyl substituent, the NH proton of the amine group, and the protons of the methylene groups. These data confirm the formation of the addition product of amine to the C=C bond. However, the IR spectrum of the product contains, along with the above-listed bands, two medium-intensity absorption bands characteristic of amides (1660 (amide I) and 1570 cm^{-1} (amide II)), while the ^{1}H NMR spectrum exhibits a broadened signal at δ 7.53 and a triplet at 4.01 ppm corresponding to the proton of the amide group and $—OCH_2CF_2—$ group of amide **5**, respectively. The additional bands in the IR and ^{1}H NMR spectra are consistent with an admixture of fluorine-containing amide. Its formation can be due to the competing substitution of the fluoroalkoxy group at the carboxylic C atom (reaction *b*) followed by the interaction of the forming products (reaction *c*).

Scheme 4



$R^F = —CH_2CF_2CF_2CF_2CHF_2$

An attempt to decrease the admixture content in compound **4** by distillation was unsuccessful. According to the data of IR spectroscopy and GLC, the target compound **4** decomposes on heating because of intermolecular condensation to yield fluorinated alcohol and oligomeric amide.

Triethoxysilyl derivatives **1**—**3** are slowly hydrolyzed with air moisture in thin layers to form transparent films. The hydrolysis rate and film quality depend on the structure of the fluorine-containing organosilicon compound. The fluorinated organic substituent has a negative inductive effect compared to that of the $CH_2CH_2CH_2NH_2$ group in APTES (in the ^1H NMR spectra, the signals of the protons of the CH_2Si groups in compounds **1—3** exhibit downfield shift by 0.14 ppm compared to those of APTES). Therefore, the hydrolysis of the fluorine-containing derivatives (and, hence, film structuring) should be faster than in the case of APTES. Indeed, compounds **2** and **3** undergo structuring in air as a layer 50—170 μm thick on a glass support for 3 and 1 days, respectively. Amide **2** produces a transparent solid stable film. No cracking is observed. The solidification time can be shortened to 30 min, if the support is heated to 100 °C. The data of IR spectroscopy and elemental analysis indicate that the non-hydrolyzed ethoxy groups remain in the congealed film. The film composition corresponds to the formula $(CF_3C(O)NH(CH_2)_3SiO_{1.5})_n(CF_3C(O)NH(CH_2)_3\text{-}Si(OEt)O)_m$, $n : m \approx 1 : 1$. Heating to 250 °C for 30 min does not result in transparency loss and crack formation but the film darkens.

Under similar conditions, compound **3** undergoes structuring within 20—25 h. The resulting transparent solid film cracks on storage (2 weeks) or heating (100 °C). The addition of 25 wt.% oligomethylsiloxanediols $HO—(SiMe_2O)_n—H$ at n = 4—7 (**6**) enhances film elasticity. The appearance of cracks is observed only after heating to 150 °C for 30 min.

Compound **1** has the highest hydrolytic stability. Being a thin layer on a glass support, it remains liquid in air for a fortnight. At the same time, its synthesis included hydrolysis with water involved in the reaction and the formation of cross-linked insoluble siloxanes. So explicit discrepancy in the behavior of this compound in the pure state and as a reaction mixture can be due to the presence of a base (APTES) that catalyzes the hydrolysis process. It turned out that the addition of 20 wt.% APTES to compound **1** increases sharply the structuring rate, and the film solidifies for 1 h but becomes brittle and strongly opalescent. The elastic transparent film was formed from a composition consisting of compounds **1**, **6**, and APTES taken in a weight ratio of 1 : 1 : 0.3. This film endures heating to 200 °C for 30 min without transparency loss.

No absorbance in the telecommunication frequency region is one of the main requirements imposed on photonics materials. The most promising is the optical signal transmission with a wavelength of 1550 nm.[21,22] The near-IR spectra of the solid films obtained from compounds **1—3** are presented in Fig. 1. In the spectrum of the film formed of imine **1**, APTES, and siloxanediols (see Fig. 1, *a*), the most intense absorption bands are observed at 1383, 1695, 1703, 1750, 2213, 2295, 2372, 2401, and 2469 nm. They are the first overtones and composite vibrations of the C—H bonds of the methylene bridges in the imine group and methyl groups of the Me_2Si fragments. The absorption bands corresponding to the first overtones of vibrations of the N—H bond do not appear in a wavelength interval of 1400—1700 nm during detection at an absorbance sensitivity of 0—0.1. This can be caused by a low concentration of a component with the $—NH_2$ group in the composition (the APTES content is 15 wt.%). The spectrum contains no absorption bands corresponding to overtones of the O—H bonds of adsorbed water, which can indicate that the film material is hydrophobic.

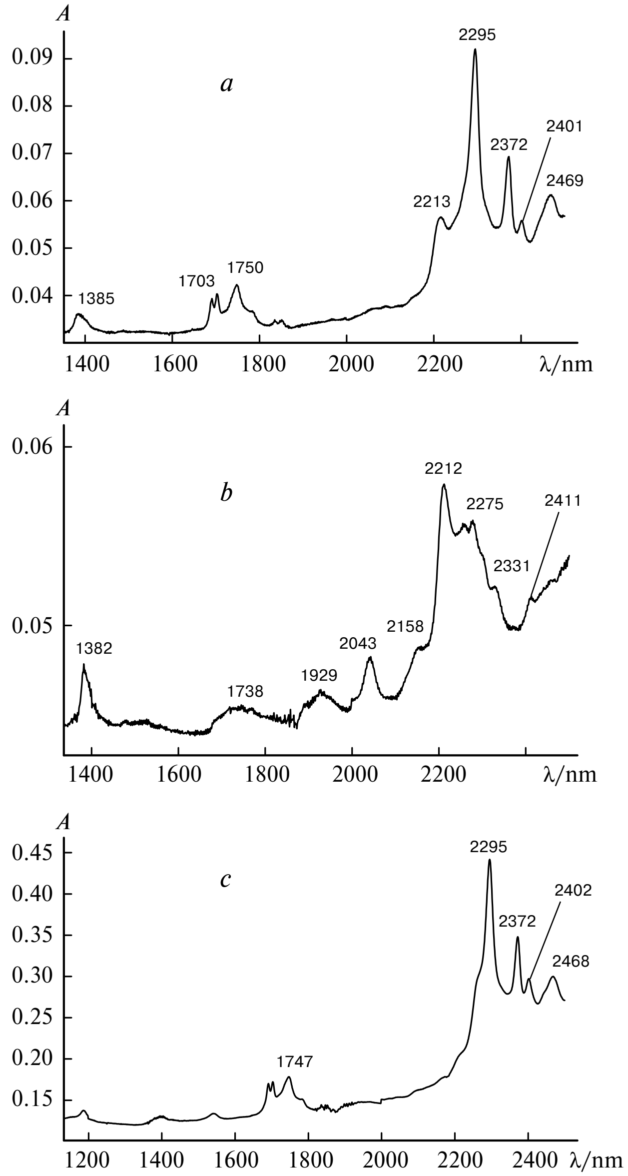


Fig. 1. Near-IR absorption spectra of the solid films based on compounds **1—3**: compound **1** + APTES + $HO(SiMe_2O)_nH$ (*a*), compound **2** (*b*), and compound **3** + $HO(SiMe_2O)_nH$ (*c*).

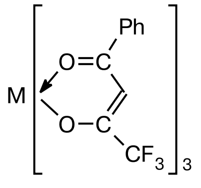
The spectrum of the film obtained from amide **2** (see Fig. 1, *b*) contains medium-intensity absorption bands corresponding to composite vibrations of the C—H bonds of the methyl and methylene groups (1382, 2158, 2212, 2275, 2331, and 2411 nm). The medium-intensity band at

2043 nm is assigned to composite vibrations of the N—H bond in amides. The low-intensity bands at 1738 and 1929 nm are the first overtones of the C—H bond of the methylene and carbonyl groups, respectively, in amides. The presence of an insignificant amount of water in the film is indicated by shoulders at 1400 and 1890 nm of the medium- and low-intensity absorption bands. Absorption bands of the first overtones of vibrations of the N—H bond do not appear in a wavelength interval of 1400—1700 nm even when the spectrum is recorded at the high absorbance sensitivity (0—0.06), probably, because the CF_3 group is close to the amide fragment.

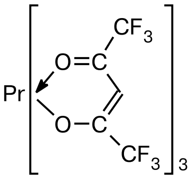
The spectrum of the film formed from compound **3** (see Fig. 1, *c*) exhibits low-intensity absorption bands at 1195, 1400, 1547, and 1930 nm. They correspond to the second overtone of the >C=O bond of the ester (1195 nm), first overtone of the N—H bond of the secondary amine (1547 nm), and to the first and second overtones of the O—H bonds of adsorbed water (1930 and 1400 nm). The bands at 1703, 1747, 2295, 2372, 2402, and 2468 nm are of much higher intensity: 1703 and 1747 nm are the first overtones of vibrations of the C—H bonds of CH_3— and —CH_2— groups, respectively, and the others belong to the region of composite vibrations of the same groups (CH_3—, 2372 nm; —CH_2—, 2295, 2402, and 2468 nm).

Thus, the films formed from compounds **1** and **2** are transparent in a region of 1400—1700 nm, due to which they are promising as materials for optical communication systems.

Compounds **1—3** and related compositions were used as transparent matrices for the incorporation of REE complexes. The derivatives with partially or completely fluorinated ligands should be most compatible with the fluorinated matrices. The solubility of the complexes was tested for europium(III) (**7**) and erbium(III) benzoyltrifluoroacetonates (**8**), praseodymium(III) hexafluoroacetylacetonate (**9**), and erbium(III) (**10**) and samarium(III) perfluorononanoates (**11**). The two latter were obtained from erbium(III) carbonate and samarium(III) oxide by the reaction with heptafluorononanoic acid.



7, **8**



9

M = Eu (**7**), Er (**8**)

Imine **1** and amide **2** dissolve satisfactorily only perfluorinated β-diketonate **9**. The maximum concentrations calculated per complex (praseodymium cation) reach 6.2% (C_{Pr} = 1.1%) and 18.1% (C_{Pr} = 3.1%), respectively. Both β-diketonates **7** and **8** and perfluorononanoate salts **10** and **11** are well dissolved in compound **3**. The maximum concentrations are 8.3 (C_{Eu} = 1.6%), 6.3 (C_{Er} = 1.3%), 17.5 (C_{Er} = 1.9%), and 17.2 (C_{Sm} = 1.9%), respectively. An interesting feature was observed for salts **10** and **11**: they are poorly dissolved in imine **1** and amide **2**, but the addition of one water droplet to a mixture of salt **10** and a solution of amide **2** in THF results in the instant disappearance of the precipitate.

The solidification of the thin composition layer in air induces no precipitation of the complexes and no blooming. It should be kept in mind that APTES and siloxanediols **6** were added to a saturated solution of the complex in the pure fluorine-containing organosilicon compound before supporting to obtain qualitative films. This resulted in some dilution and a decrease in the complex concentration. However, the subsequent film structuring is accompanied by a decrease in its weight due to the removal of ethanol and water evolved upon the formation of a silicone matrix. Due to this, the concentration of the complexes somewhat increases. For instance, the primary concentration of praseodymium complex **9** in imine **1** was 6.2% (C_{Pr} = 1.1%), whereas in the liquid composition based on this complex the concentration decreased to 3.0% (C_{Pr} = 0.5%). For film structuring, the weight decrease for this composition was 20%, and the complex concentration increased to 3.7% (C_{Pr} = 0.6%). The changes in the concentration of erbium complex **8** upon dilution of compound **3** with oligosiloxanediols are not so significant: 6.3% (C_{Er} = 1.3%) in pure compound **3** and 5.1% (C_{Er} = 1.0%) in the liquid composition. However, the structuring of this composition is accompanied by a more significant decrease in the film weight (by 28%) and, hence, the concentration of complex **8** in the congealed matrix was already 7.4% (C_{Er} = 1.5%). No addition of other components was required to form films of pure amide **2**. Structuring is accompanied by the film weight decrease by 19% and, therefore, the concentration of complex **9** in the solid matrix was 21.4% (C_{Pr} = 3.7%), which is somewhat higher than that in liquid amide **2** (C_{compl} = 18.1%, C_{Pr} = 3.1%).

The films containing the incorporated REE complexes were studied by electronic absorption spectroscopy (EAS). The pure fluorine-containing organosilicon matrices intensely absorb UV radiation up to 370—420 nm (**1**, up to 420 nm; **2** and **3**, up to 370 nm). It is known[26] that the frontier absorbance of peralkylated silicones lies at 180—200 nm. The substantial shift to the long-wave region for compounds **2** and **3** (to 370 nm) is due to the chromophoric groups >C=O or >C=N— in their composition.

The electronic absorption spectrum of compound **10** in THF contains four absorption bands (378, 488, 522, and 652 nm) corresponding to the f—f-transitions in the Er^{3+} cation: $^4I_{15/2} \rightarrow {}^4G_{11/2}$, $^4I_{15/2} \rightarrow {}^4F_{7/2}$, $^4I_{15/2} \rightarrow {}^2H_{11/2}$, and $^4I_{15/2} \rightarrow {}^4F_{9/2}$. The two most intense bands also ap-

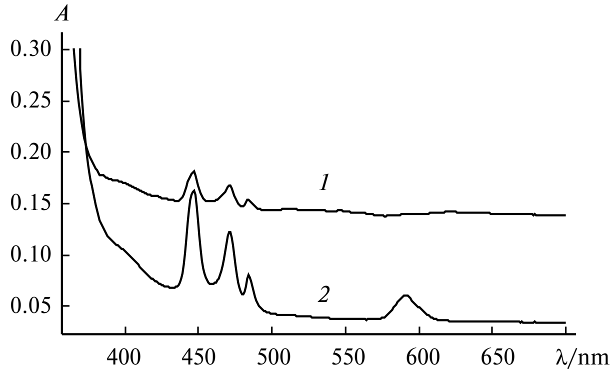


Fig. 2. Electronic absorption spectra of complex **9**: *1*, in the film of amide **2**, content of complex **9** 21 wt.%, layer thickness 200 μm; *2*, in acetonitrile, $C = 3.27 \cdot 10^{-2}$ mol L^{-1}.

pear in the spectrum of the film containing the incorporated salt (14 wt.%). The electronic absorption spectra of praseodymium β-diketonate complex **9** in acetonitrile and in the film are presented in Fig. 2. The spectrum of the solution exhibits four absorption bands at 446, 471, 484, and 590 nm attributed to the transitions $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$, and $^3H_4 \rightarrow {}^1D_2$. Only the three most intense bands at 446, 471, and 484 nm are manifested in the spectrum of the film formed of amide **2** and containing 21 wt.% complex **9**.

Two absorption bands at 400 and 1089 nm (transitions $^6H_{5/2} \rightarrow {}^6P_{3/2}$ and $^6H_{5/2} \rightarrow {}^6F_{9/2}$) correspond to samarium perfluoronanonoate (**11**) with a concentration of 22 wt.% in the film based on compound **3**. The same bands are observed in the spectrum of a solution of this compound in THF. For all complexes under study, no noticeable shifts of absorption bands relatively to solutions in THF or acetonitrile were observed when they were incorporated into the fluorocontaining organosilicon matrices.

The absorption bands corresponding to the f—f-transitions in the REE cations are known[27] to be low-intensity in nature. The study of the EAS of the films with the incorporated praseodymium, europium, erbium, and samarium complexes showed that high intensities of these bands cannot be achieved for a layer thickness of 70—170 μm even at high concentrations of the complex (up to 22 wt.%). Thicker films (up to 400 μm) can be formed but they possess lower stability and undergo cracking upon storage or heating.

Hexafluoroacetylacetonate complexes are the most volatile of all the known REE coordination compounds.[28] The prolong exploitation of the film at room and, the more so, elevated temperature can induce the removal of the complex from the thin layer. To check volatility, we measured the EAS of praseodymium hexafluoroacetylacetonate incorporated into the matrix of compound **3**. The support coated with the film was heated for 30 min at 100 °C. No substantial spectral changes were found. The position and intensity of the absorption bands corresponding to the praseodymium cation remain the same, and only the background absorbance of the film increases. This is a consequence of an increase in the reflecting ability of its surface due to heating. Thus, the fluorocontaining organosilicon matrix strongly retains the incorporated complex.

The fluorescence spectra of the films contain an emission band at 430 nm, and the fluorescence excitation spectra consist of two absorption bands at 250—274 and 357—370 nm (Table 1). The nature of the organofluorine chromophore exerts virtually no effect on the emission position. For instance, the maximum of the emission band of compound **1** with the chromophore emitting in the longest-wave region (—N=CH—C_6F_5, 430 nm) is shifted by 3 nm to the short-wave region relatively to the less efficient chromophore C(O)OR^F (compound **3**, 433 nm). Such a close arrangement of the maxima and a slight difference in emission band intensities are explained by the same nature of the emitting centers. The emission at 420—430 nm of the organo-inorganic hybrids obtained by the methods of colloid chemistry is caused by cross-linked siloxane structures ("domains") ~5 Å in size.[29] We have

Table 1. Fluorescence and fluorescence excitation spectra of the fluorine-containing organosilicon films

Film	Fluorescence spectrum			Fluorescence excitation spectrum		
	λ_{ex}*	λ	*I* (rel. units)	λ_{mon}**	λ	*I* (rel. units)
	nm			nm		
1 + APTES + HO$(SiMe_2O)_n$H	360	430	110	480	274	24
					370	36
2	370	426	43	490	250	12
					357	11
3 + HO$(SiMe_2O)_n$H	360	433	130	550	255	7
					362	13

* Wavelength of fluorescence excitation.

** Wavelength at which the fluorescence excitation spectrum was detected.

recently[30] obtained similar data for the phosphorus-containing organosilicon sol—gel films.

Experimental

IR spectra of compounds as liquid films between KBr plates or suspensions in Nujol were recorded on a Specord IR-75 spectrophotometer. Electronic absorption spectra of solutions and films were measured on a Specord M-40 spectrophotometer, using quartz cells 5 mm thick for solutions. Near-IR spectra of films on quartz supports were recorded on a Cary-500 Scan spectrophotometer. Fluorescence and fluorescence excitation spectra were obtained on an SFL-1211A spectrofluorimeter (SOLAR TII). ^{1}H NMR spectra were recorded on a Bruker Avance DPX-200 instrument (200 MHz) at 25 °C using Me_4Si as internal standard. Trifluoroacetamide (**2**) and the reaction products of 1,1,5-trihydrooctafluoroamylacrylate with APTES (**3**) and with isopropylamine (**4**, **5**) were analyzed on a Tsvet-530 chromatograph on a stainless steel column 0.30×200 cm packed with 5% SE-30 on the Chromaton N-Super solid support.

Hexane was distilled over metallic sodium.[31] Isopropylamine was purified by distillation above CaH_2. 1,1,5-Trihydrooctafluoroamylacrylate (Research Institute of Polymers, Dzerzhinsk, Russia) and 3-aminopropyltriethoxysilane (Slavgorod Production Union "Altaikhimprom," Russia) were distilled under reduced pressure. Methyl trifluoroacetate (Aldrich), pentafluorobenzaldehyde (Aldrich), erbium carbonate and samarium oxide (Novosibirsk Plant of Rare Metals, Russia), and heptadecafluorononanoic acid (Aldrich) were used as received. Oligosiloxanediols **6** were prepared[32] by the hydrolysis of α,ω-dichlorooligodimethylsiloxanes $ClMe_2Si(OSiMe_2)_nCl$ (n = 2—6).[25]

3-Pentafluorobenzylideneaminopropyltriethoxysilane (1). Anhydrous Na_2SO_4 (3 g) was added to a solution of pentafluorobenzaldehyde (1.50 g, 6.78 mmol) in hexane (15 mL). A solution of APTES (1.33 g, 6.78 mmol) in hexane (15 mL) was added dropwise with stirring to the resulting mixture for 30 min. After 1 h, a hydrolyzed reaction product was precipitated. Twenty min after the end of the reaction, the solution was decanted, and hexane was removed *in vacuo*. Compound **1** was isolated in 81% yield (2.5 g) as a yellowish-green liquid, n_D^{20} 1.4517. Found (%): C, 49.39; H, 5.60. $C_{16}H_{22}F_5NO_3Si$. Calculated (%): C, 48.11; H, 5.55. EAS ($CHCl_3$), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 243 (6011), 284 (1640), 383 (47). IR, ν/cm^{-1}: 1660 (C=N); 1640, 1500, 1070, 1000, 960 (C_6F_5); 1100 (Si—O—C); 1180, 960, 780 (EtO). ^{1}H NMR ($CDCl_3$), δ: 0.65 (t, 2 H, CH_2Si, J = 8.4 Hz); 1.20 (t, 9 H, 3 $C\underline{H}_3CH_2O$, J = 7.0 Hz); 1.85 (m, 2 H, CH_2); 3.68 (t, 2 H, CH_2N, J = 6.7 Hz); 3.8 (q, 6 H, 3 $OC\underline{H}_2CH_3$); 8.35 (s, 1 H, CH=N).

Reaction of methyl trifluoroacetate with APTES. Methyl trifluoroacetate (9.27 g, 0.072 mol) was poured dropwise with water cooling to APTES (16.03 g, 0.072 mol), which was accompanied by heating of the reaction mixture. The reaction course was monitored by GLC. The reaction mixture was distilled *in vacuo*, and a fraction (14.73 g) boiling at 94 °C (1 Torr) was collected. According to the GLC data, the reaction product is not an individual compound but a mixture of three substances. The overall formula of the resulting mixture of alkoxysilanes was $CF_3C(O)NHCH_2CH_2CH_2Si(OEt)_2(OMe)$ (**2**), n_D^{20} 1.4059. Found (%): C, 39.79; H, 6.66. $C_{10}H_{20}F_3NO_4Si$. Calculated (%): C, 39.59; H, 6.65. EAS ($CHCl_3$), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 270 (3.4), 295 (1.7). IR, ν/cm^{-1}: 3300, 3100, 800 (N—H); 1700 (amide I); 1550 (amide II); 1200, 1180 (CF_3). ^{1}H NMR ($CDCl_3$), δ: 0.65 (t, 2 H, CH_2Si, J = 7.8 Hz); 1.21 (m, 6 H, 2 $OCH_2C\underline{H}_3$); 1.75 (m, 2 H, CH_2); 3.40 (q, 2 H, NCH_2); 3.56 (s, 3 H, OMe); 3.85 (m, 4 H, 2 $OC\underline{H}_2Me$); 7.21 (br.s, NH).

Reaction of APTES with 1,1,5-trihydrooctafluoroamylacrylate. APTES (2.21 g, 9.99 mmol) was added to 1,1,5-trihydrooctafluoroamylacrylate (2.86 g, 9.99 mmol), and a slight heating of the reaction mixture was observed. After the reaction mixture was stored at room temperature for 1 day and evacuated *in vacuo* for 1 h, the GLC analysis showed that the reaction mixture consisted by 91% of 1,1,5-trihydrooctafluoroamyl *N*-3-triethoxysilylpropylaminopropanoate (**3**), n_D^{20} 1.4034. Found (%): C, 38.68; H, 4.76. $C_{17}H_{29}F_8NO_5Si$. Calculated (%): C, 40.23; H, 5.76. EAS ($CHCl_3$), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 280 (23.5), 330 sh. IR, ν/cm^{-1}: 3320, 3180, 1540 (N—H); 1765 (C=O); 1370, 1300, 1250 (C—F); 1180, 960, 780 (EtO); 1650 (amide I); 1570 (amide II). ^{1}H NMR ($CDCl_3$), δ: 0.61 (m, 2 H, $SiCH_2$); 1.21 (t, 9 H, 3 CH_3, J = 7.0 Hz); 1.58 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 2.32 (m, 1 H, NH); 2.60 (m, 4 H, $C\underline{H}_2NC\underline{H}_2$); 2.85 (m, 2 H, $CH_2C(O)O$); 3.80 (q, 6 H, $Si(OC\underline{H}_2CH_3)_3$); 4.61 (t, 2 H, $C(O)OCH_2CF_2$—, $^3J_{H,F}$ = 13.8 Hz); 6.06 (tt, 1 H, CF_2CHF_2, $^2J_{H,F}$ = 51.8 Hz, $^3J_{H,F}$ = 5.3 Hz); 7.41 and 7.56 (both br.s, 1 H each, C(O)NH).

Reaction of isopropylamine with 1,1,5-trihydrooctafluoroamylacrylate. Isopropylamine (0.53 g, 9.01 mmol) was added to 1,1,5-trihydrooctafluoroamylacrylate (2.58 g, 9 mmol), which was accompanied by a slight heating of the reaction mixture. After the reaction mixture was stored at room temperature for 3 days and evacuated for 1 h, the GLC analysis showed that the reaction mixture consisted by 90% of 1,1,5-trihydrooctafluoroamyl *N*-isopropylaminopropanoate (**4**), n_D^{20} 1.3822. Found (%): C, 40.90; H, 6.29. $C_{11}H_{15}F_8NO_2$. Calculated (%): C, 38.27; H, 4.38. IR, ν/cm^{-1}: 3320, 3180, 1550 (N—H); 2960, 2940, 2870, 2830, 1470, 1440 (C—H); 1765 (C=O); 1370, 1300, 1250 (C—F); 1660 (amide I); 1570 (amide II). ^{1}H NMR ($CDCl_3$), δ: 1.07 (d, 6 H, $CH(C\underline{H}_3)_2$, J = 6.3 Hz); 2.10 (br.s, 1 H, NH); 2.63 (t, 2 H, NCH_2, J = 6.5 Hz); 2.82 (m, 1 H, $C\underline{H}(CH_3)_2$); 2.92 (t, 2 H, $CH_2C(O)O$, J = 6.5 Hz); 4.61 (t, 2 H, $C(O)OCH_2CF_2$, $^3J_{H,F}$ = 13.8 Hz); 6.06 (tt, 1 H, CF_2CHF_2, $^2J_{H,F}$ = 51.9 Hz, $^3J_{H,F}$ = 5.3 Hz). Amide **5**, ^{1}H NMR, δ: 1.14 (d, 6 H, $CH(C\underline{H}_3)_2$, J = 6.3 Hz); 2.53 (t, 2 H, $OC\underline{H}_2CH_2$, J = 6.5 Hz); 2.78 (m, 1 H, $C\underline{H}(CH_3)_2$); 2.92 (t, 2 H, $CH_2C(O)O$, J = 6.3 Hz); 4.01 (t, 2 H, $CH_2OC\underline{H}_2CF_2$, $^3J_{H,F}$ = 14.7 Hz); 7.53 (br.s, 1 H, C(O)NH).

Erbium(III) perfluorononanoate (10). Distilled water (3 mL) and erbium(III) carbonate (0.10 g, 0.19 mmol) were added to a solution of heptadecafluorononanoic acid (0.60 g, 1.29 mmol) in THF (7 mL). The reaction mixture was heated at 50 °C until the carbonate was completely consumed. The solvent was removed *in vacuo* (to a volume of ~1 mL), the solution was decanted from the precipitate formed, and the precipitate was dried *in vacuo* and purified by sublimation. Compound $(C_8F_{17}C(O)O)_3Er \cdot nH_2O$ (n = 5—7) (**10**) was isolated (0.41 g, 68%) as a white powder. Found (%): C, 20.56; Er, 10.3. $C_{24}ErF_{51}O_6$. Calculated (%): C, 20.84; Er, 10.8. IR (Nujol), ν/cm^{-1}: 3640, 3420 (O—H); 1750, 1710, 1660, 1630 ($C(=O)_2$); 1230, 1200, 1140 (C—F).

Samarium(III) perfluorononanoate (11). A solution of heptadecafluorononanoic acid (0.45 g, 0.97 mmol) in THF (7 mL), distilled water (2 mL), and samarium(III) oxide (0.05 g, 0.14 mmol) were placed in an ampule. The sealed ampule was heated at 100 °C until the samarium oxide powder dissolved completely (~20 min). The further treatment of the reaction mixture was similar to that described for compound **10**. Compound $(C_8F_{17}C(O)O)_3Sm \cdot nH_2O$ (n = 5—7) (**11**) was isolated (0.28 g, 63%) as a white powder. Found (%): C, 21.31; Sm, 8.8. $C_{24}F_{51}O_6Sm$. Calculated (%): C, 21.06; Sm, 9.8. IR (Nujol), ν/cm^{-1}: 3640, 3420 (O—H); 1730, 1650, 1630 (C(=O)$_2$); 1230, 1200, 1150 (C—F).

Determination of solubility of REE compounds. Fluorocontaining organosilicon compound **1**, **2**, or **3** to be tested was added by small portions (0.02—0.05 g) to a weighed sample of the REE complex or salt (0.01—0.02 g), and the resulting mixture was weighed and stirred. The addition was continued until the weighed sample dissolved completely.

Preparation of films. Compositions formed of compounds **1**, **3**, APTES, oligodimethylsiloxanediols, and amide **2**, which contained an REE compound (or without this compound) were coated on glass or quartz supports, and they were left to stand at room temperature to complete solidification. Films of amide **2** were also solidified by heating for 30 min at 100 °C. The film thickness was 80—200 μm.

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