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β-Diketones and their derivatives in sol – gel processes

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Abstract. Published data on the use of β-diketones, metal β-diketonates and some structurally related compounds in sol – gel synthesis of new organic-inorganic hybrid materials are analyzed. Functionalization methods of β-diketones with carbofunctional organosilicon compounds are considered. Ways of insertion of a metal cation into the organic-inorganic hybrid matrix using non-functionalized β-diketonates are demonstrated. Particular attention is devoted to luminescent lanthanide derivatives, which is due to the prospects of practical application of materials obtained from them in photonics, integrated optics and medical diagnosis. The types and properties of most widely used sol – gel monomers and oligomers and the luminescence behaviour of lanthanide β-diketonates and metal-free silica matrices are considered. The bibliography includes 220 references.

I. Introduction

The last decade witnessed a considerable extension of the scope of application of sol – gel techniques for the production of modern materials having valuable optical, electronic and other properties. In particular, considerable attention has been paid to the development of diverse organic-inorganic hybrid materials in which organic particles of a particular sort are inserted in an inorganic, most often, silica matrix. Derivatives and complexes of β-diketones are used in many cases as organic components, owing to unique properties of these compounds.

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This review colligates the data on the application of β-diketones and their functional derivatives and complexes in a variety of sol – gel processes. The basic aspects of the sol – gel technique are briefly considered, including requirements to the starting reagents, methods of preparation of metal-containing gels and the key areas of application. Methods for the synthesis and functionalization of β-diketones are analyzed, particular attention being devoted to the introduction of organosilicon groups to prepare compounds that serve as monomers in hydrolytic polycondensation.

In the design of new functional materials, an important role belongs to coordination compounds with β-diketonate ligands, first of all, lanthanide complexes. These compounds have photoluminescence properties, which are even enhanced, in some cases, upon insertion of the complex into an inorganic matrix due to the transfer of absorbed energy from the matrix to the lanthanide cation.

The scope of practical applications of hybrid materials containing β-diketone derivatives is constantly extending. Currently, these materials are used in gas sensors, molecular thermometers, in the production of optical fibre and light-converting materials and so on. Target-directed search for new applications is impossible without understanding of the mechanisms of formation of hybrid materials and interaction of the organic and inorganic components.

II. Sol – gel processes in the synthesis of hybrid materials

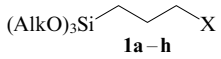
1. The starting reagents for sol – gel process

Silicon compounds, alkoxides $Si(OR)_4$ and $R'Si(OR)_3$, are the cheapest and most widely used starting compounds † for sol – gel processes.[1–5] The most readily available among them are ethoxy and methoxy derivatives with R = Et, Me; R′ = Me, Et, Ph, Vin: tetraethoxysilane (TEOS), tetramethoxysilane, methyl-, phenyl- and vinyltriethoxysilanes;

† In what follows, the starting reagents for the sol – gel process are called, for brevity sake, sol – gel monomers.

and methyl-, phenyl-, and vinyltrimethoxysilanes. Commercially available trialkoxy(propyl)silanes **1a–h** with a functional group in the 3-position of propyl are used as carbofunctional organosilicon monomers.

Structures **1**



1a–h

Alk = Et: X = NH_2 (**a**, APTES), NCO (**b**, IPTES), $OCH_2(CHCH_2O\text{-cyclo})$ (**c**); Alk = Me: X = $OC(O)C(Me)=CH_2$ (**d**), SH (**e**), $NH(CH_2)_2NH_2$ (**f**), $OC(O)CH=CH_2$ (**g**), Cl (**h**)

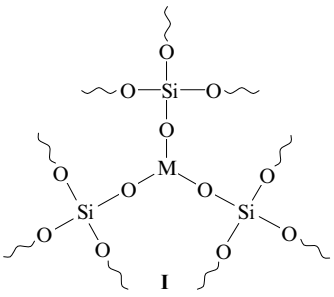
Fairly popular starting reagents are the alkoxides $R^FSi(OR)_3$ with perfluorinated organic substituents $R^F = CF_3(CF_2)_n(CH_2)_m$ ($n = 0-7$, $m = 1-3$) and $CF_3(CF_2)_nC(CF_3)_2(CH_2)_2$ ($n = 2-3$), which are suitable to form coatings with enhanced hydrophobic properties and low refractive indices.[6–8] Among all silicon alkoxides, tetraethoxysilane and ethyl silicate (partially hydrolyzed TEOS) are most readily available and least expensive. They are industrially produced on a large scale in the common synthesis from silicon tetrachloride and ethanol.[9] Dialkoxydiorganosilanes $(RO)_2SiR'_2$ are used in sol–gel processes as modifying additives.

Silicon chlorides, for example, $SiCl_4$, $RSiCl_3$, R_2SiCl_2, $Cl_3SiZSiCl_3$ [$Z = CH_2$, $(CH_2)_2$ and so on], are also sol–gel monomers. They are hydrolyzed at much higher rates than alkoxides[10,11] to give off a large amount of hydrogen chloride. The formation of a corrosive medium and limited possibility of controlling the hydrolytic polycondensation are mainly responsible for the rare use of silicon chlorides in the synthesis of organic-inorganic hybrids. Silicon hydrides $RSiH_3$, $H_3SiZSiH_3$ and so on are used even more rarely in sol–gel processes[12] as they are volatile, fire hazardous and expensive. Cleavage of the Si–H bonds occurs in the presence of bases or nucleophiles.

2. Preparation of metal-containing gels

Transition metal atoms can be inserted into the structure of organosilicates in different ways. Best studied are methods based on reactions of sodium alkyl(aryl)siliconates with metal chlorides and reactions of organochlorosilanes with metal acetates.[13–15] Co-hydrolysis of silicon and metal alkoxides gives rise to two phases, SiO_2 and MO_x.[16–18] Meanwhile, the non-hydrolytic procedure, namely, thermally initiated reactions of chlorides ($SiCl_4$, $AlCl_3$, $ZrCl_4$, $TiCl_4$, $H_2PtCl_6 \cdot 6H_2O$, $PdCl_2 \cdot 2H_2O$, $RuCl_3 \cdot 3H_2O$) with alkoxides [$Si(OEt)_4$, $Si(OPr^i)_4$, $Al(OPr^i)_3$, $Ti(OPr^i)_4$] produce single-phase metal siloxane gels[19–24] consisting of the Si–O–Si and Si–O–M structural fragments (structure **I**).[13–16]

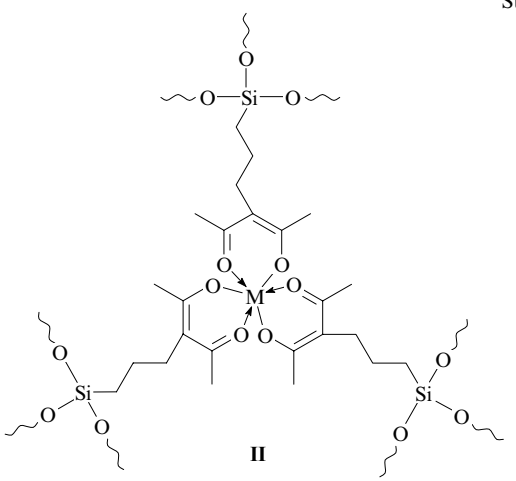
Structure **I**



I

Gels that differ considerably from metal siloxane gels are formed upon hydrolysis of complexes with peripheral trialkoxysilyl groups $[(RO)_3SiCH_2CH_2CH_2L]_nM$. The local environment of the metal atom is formed by organic groups (ligands L), which separate it from the silicate matrix. Gels of this class contain no Si–O–M bonds being composed of Si–O–Si and $Si-(CH_2)_n-L-M$ structural fragments (**II**).

Structure **II**



II

They can be described as coordination compounds encapsulated in an organosilicate matrix.[25–31] The type of the matrix and the metal content are easily adjusted by dilution of the complex by an appropriate alkoxide. Tetraethoxy- and tetramethoxysilanes are used more often than other compounds. Hydrolysis is usually performed by treating a solution of the coordination compound in $Si(OR)_4$ with hydrochloric acid. The dried heat-treated gels are used as heterogeneous catalysts. Their catalytic properties can be changed by carrying out the pyrolysis in argon, oxygen or hydrogen atmosphere.[25,26]

Most often, a monomer containing a stable complex linked to a trialkoxysilyl group is first synthesized and then hydrolytic polycondensation is carried out. The reverse order is also possible, *i.e.*, the metal cation can be introduced in the pre-formed gel by treating the gel with a metal salt.

The ligand-forming group at the silicon atom provides for the introduction of a specified amount of metal both into the initial monomer and into the resulting gel. The silicon : metal ratio is dictated only by the monomer structure and does not change during hydrolysis. Thus, it is possible to overcome a key difficulty faced in the preparation of metal-containing gels by co-precipitation, namely, large difference between the rates of hydrolysis of tetraalkoxysilane and metal alkoxide. High rates of hydrolytic polycondensation of the latter compared to $Si(OR)_4$ result in early precipitation of metal oxides not giving enough time for the mixed structures with Si–O–M bonds to form.

3. Practical applications of sol–gel technique

The substituent R in the sol–gel monomer $RSi(OEt)_3$ determines the organic component of the hybrid material.[3,5,16,25,27] By hydrolysis and co-hydrolysis with TEOS, it is possible to introduce most, if not any, known organic groups into the xerogel. The crucial factors in this case are the possibility to prepare trialkoxyorganosilane and the stability of the silicon–carbon bond against water in the

presence of electrophilic or nucleophilic catalysts. The scope of the method is markedly extended when two or more trialkoxysilyl groups are introduced into the organic molecule, *i.e.*, when, for example, derivatives $(EtO)_3Si-Z-Si(OEt)_3$ are used. Since the overall functionality of the compound increases, it becomes possible to obtain spatially cross-linked structures from monomers of the type $(EtO)_2MeSiZSi(OEt)_3$, $(EtO)_2MeSiZSiMe(OEt)_2$ or $(EtO)_2MeSiZSiMe_2(OEt)$ [Z = CH_2, $(CH_2)_2$, CH=CH, *p*-phenylene, *p*-biphenylene]. The selection of the organic groups is determined by the target properties of the final product. If the substituent R is a part of the organic monomer, two sequences for the process are possible: hydrolysis–polymerization and polymerization–hydrolysis. These methods were used to prepare many hybrids of organic and inorganic polymers.

Sol–gel processes can be conventionally divided into three types: (i) large-scale, well-mastered processes used in industry for a rather long time with high consumptions of industrial monomers and oligomers; (ii) relatively new processes that require little amounts of monomers or oligomers; (iii) processes under development (research dealing with the preparation of new starting compounds for sol–gel processes and new promising materials).

The scale of using sol–gel processes in industry can be demonstrated by considering the hot investment casting process [32,33] widely employed in metallurgy and mechanical engineering. The formulations used to fabricate the ceramic investment moulds are based on ethyl silicate, fine quartz powder and coarser silicon dioxide dispersions (river sand). The consumption of ethyl silicate in the foundry production reaches hundreds of thousand tons annually. A modification of this process uses aqueous solutions of stabilized silicon dioxide sols instead of ethyl silicate.[34] These solutions are also consumed [34] by textile industry and by manufacture of paper, heat insulating materials and heterogeneous catalysts.

Some types of industrially produced organosilicon varnishes [35] represent mixtures of silicon-containing sol–gel oligomers cured in thin layer under the action of air moisture to give solid transparent photo and thermally stable coatings.

Large amounts of sol–gel oligomers are consumed in oil production industry [36,37] to prevent well water-flooding and to enhance oil recovery.

Medium-scale processes are, for example, the processes developed in the USSR for the synthesis of high-purity silicon dioxide TEOS for fibre optics,[38] numerous high-temperature ceramic articles,[39] reagents for adsorption refining of arsenic [40] and production of silica gels for medicine, in particular:

— hydrogels with recovery and healing properties obtained from silicon alkoxides and polyols;[41]

— silicon dioxide for clinical applications [42] in the complex therapy of infectious diseases, in surgery, dentistry, tocology and gynaecology.

Functionalized hybrids [43] are used in extraction and separation of rare metals, gas cleaning from hazardous organic impurities and waste water treatment to remove toxic metals.

The current studies deal with the search for new sol–gel methods for the design of hybrid nanocomposites containing various polysaccharides and enzymes [44] and materials with enhanced high-temperature conductivity [45] or photo- and electroluminescence,[46,47] light-reflecting,[48,49] light-converting,[50,51] sensor,[52] non-linear optical,[53–55] photorefractive,[56] photochromic [57] and laser properties.[58]

The possibilities of using hybrid materials in the development of new heterogeneous catalysts are under vigorous research,[59] in particular, this refers to materials based on metal nanoparticles incorporated in organosilicate matrices.[60] Sol–gel methods are employed to produce photonic crystals,[61] ion-conducting membranes for fuel cells,[62] new thermo- and photostable dyes and varnishes.[35]

Luminophores can be incorporated in sol–gel matrices without preliminary functionalization or by introduction of trialkoxysilyl groups into the molecule.[46,47]

The fabrication of light-reflecting coatings (*e.g.*, on laser crystals) is based on the use of fluorinated organosilicon sol–gel monomers,[48] which are cured in thin layer to give a transparent film with a low refractive index (below 1.302). One more method [49] utilizes the TEOS–surfactant sol, which gives a mesoporous coating after curing and burning-out of the organic material. Low refractive index (below 1.20) is achieved due to high dilution of the material with air, which fills fine pores with sizes smaller than the visible light wavelength. Since the annealing stage is required, these coatings can be applied only on high-temperature materials.

Solar power production utilizes light-converting materials — europium- and terbium-containing ormosils (organically modified silicates) — as coatings [50,51] for photovoltaic cells where they serve for conversion of solar UV radiation to the visible light to which a silicon solar cell has higher sensitivity.

III. Preparation and functionalization of β-diketones

β-Diketones (1,3-diketones, pentane-2,4-diones) [63–67] are used as analytical reagents for determination of a number of elements,[63] and metal β-diketonates [68–70] find wide use in various fields of science and technology. Some are highly volatile and highly thermally stable; they are used to prepare metal-containing coatings and films by chemical vapour deposition. Lanthanide β-diketonates have attractive optical properties and can be used in medical diagnosis, integral optics and laser technology.[71] β-Diketones having long-chain alkyl groups (> 10 carbon atoms) in the side chain present practical interest, as they are diphilic and can form Langmuir layers at the interface between the aqueous and gas phases. Under certain conditions, these layers can bind metal ions, which makes them suitable for the design of thin-film catalytic, optical and light emitting systems.[72]

1. Methods for the synthesis of β-diketones

Claisen condensation is the most popular method for the synthesis of β-diketones.[73,74] β-Diketones may also be prepared in good yields by acylation of ketones with acid anhydrides in the presence of boron trifluoride etherate [75] or with acid chlorides with the use of $ZnCl_2$, $TiCl_4$ or $SnCl_4$.[76] Acylation of lithium enolates and enol silyl ethers with acyl halides results in regioselective synthesis of 1,3-diketones.[77] Aromatic 1,3-diketones can be obtained by Baker–Venkatamaran rearrangement.[78]

During the last decade, new preparative methods were developed including the synthesis of 1,3-diketones from

aromatic α-bromo ketones and the Furukawa's reagent ($EtZnCH_2I$),[79] by the reaction of organic lithium derivatives with BF_2 complex of 3-oxopropanoates,[80] by the reaction of γ-acyloxy-α,β-unsaturated ketones with $CH_2(ZnO)_2$,[81] and by the reactions of α,β-unsaturated ketones with acyl chlorides and diethylzinc in the presence of $RhCl(PPh_3)_3$.[82]

1,3-Diketones are highly reactive compounds. They tend to react both with nucleophilic and electrophilic reagents. Proceeding from this fact, they are functionalized at the central carbon atom and at the side hydrocarbon moiety.

2. Methods of functionalization of 1,3-diketones

a. Introduction of unsaturated groups

Unsaturated β-diketones occupy a special position in organic, polymer and coordination chemistry. They serve as monomers for the synthesis of metal-containing polymers, which are of interest as functional materials with valuable electrical, magnetic, optical or semiconductor properties. Also, they can be employed in heterogeneous catalysis, in particular, as the starting compounds for the preparation of polymer-immobilized nanoparticles of transition metals.[60] In this case, unsaturated 1,3-diketones are chosen due to the necessity to obtain thermodynamically stable monomeric complexes and uniform distribution of the metal in the macromolecule after polymerization.[60, 83] Owing to the unsaturated group, a trialkoxysilyl substituent can be introduced in the molecule by means of hydrosilylation.[84]

There are two principal approaches to the synthesis of unsaturated diketones. One is based on the reaction of the sodium derivative of diketone with haloalkene. In this case, an unsaturated group can be introduced only into the methylene group.[85] The other approach is based on the Claisen condensation and its modifications.[86–88] A new method based on the Heck reaction has recently appeared.[89]

γ,δ-Unsaturated β-diketones can be prepared by acylation of ketones by *N*-acylbenzotriazoles containing moieties of unsaturated aliphatic or aromatic acids. This method ensures the regioselective formation of the C–C bond in relatively high yields.[90]

b. Functionalization of the central carbon atom

The synthetic routes to 3-substituted pentane-2,4-diones include alkylation and arylation by various methods.[91] In essence, all these reactions utilize the nucleophilicity of β-diketones. By alkylation, various functional groups can be introduced in the diketone molecule.[92–94] The reactions are accompanied by the formation of large amounts of bulky precipitates of sodium, potassium, lithium or ammonium halides. This can be avoided by using catalytic alkylation of β-diketones with alcohols, which gives water. The latest studies[95] demonstrated that reactions occur in the presence of Lewis acids [$InCl_3$, $InBr_3$, $FeCl_3$, $Bi(OTf)_3$]. Heteropoly acids such as phosphotungstic and phosphomolybdic acids are used as effective, environmentally safe and moisture- and air-stable catalysts for nucleophilic substitution, giving rise to monoalkylated diketones.[96] Arylation is carried out by classical synthesis of β-diketones,[97] rearrangement of phosphoranes,[98] cross-coupling of aryl halides with β-diketones[99] and so on.

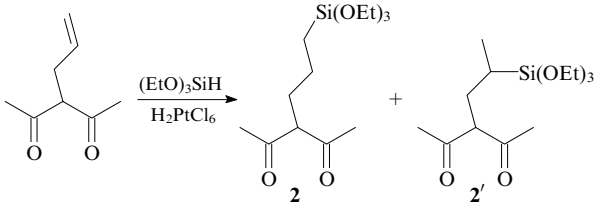
3. Functionalization of β-diketones with organosilicon compounds

Four types of reactions are used to prepare sol–gel monomers containing a β-diketone or enamino ketone group in the organic moiety. The first type — hydrosilylation — requires the presence of an unsaturated group in the β-diketone and the Si–H bond in alkoxysilane; the second one is the replacement of the hydrogen atom in the 3-position of the diketone by a trialkoxysilylpropyl group using a halogen-containing carbofunctional organosilicon compound; the third one implies the reaction with organosilicon isocyanate **1b**, while the fourth one comprises the reaction with organic and/or organosilicon primary amine (APTES) to give enamino ketone.

a. Hydrosilylation of 3-allylpentane-2,4-dione with triethoxysilane

3-(3-Triethoxysilylpropyl)pentane-2,4-dione (**2**) was prepared[100, 101] by hydrosilylation of 3-allylpentane-2,4-dione with triethoxysilane in the presence of the Speier's catalyst (a solution of H_2PtCl_6 in isopropyl alcohol). The reaction mainly involves the terminal carbon atom of the allyl group (Scheme 1).

Scheme 1



When performing reactions of this sort, it should be borne in mind that the ethoxy group and the hydrogen atom in triethoxysilane may be replaced by the OH group of the diketone existing in the enol form. However, 3-allylpentane-2,4-dione does not react with triethoxysilane at 80–100 °C unless H_2PtCl_6 is added. This reaction does not occur with tetraethoxysilane and hexamethyldisilazane either.

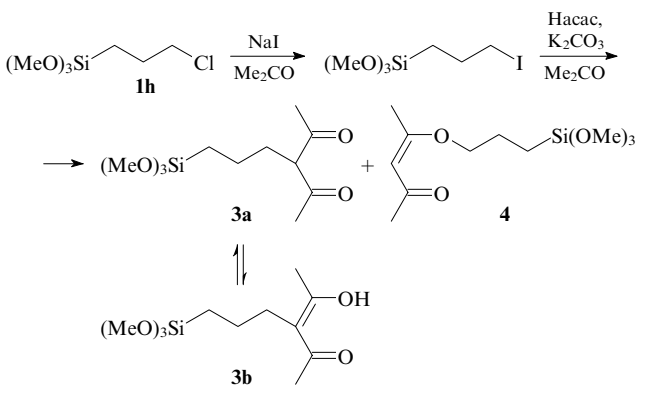
Pentane-2,4-dione silylated at the allyl group exists mainly as the diketone with a minor amount of the enol. Silylated β-diketones **2** and **2′** are hydrolyzed by air moisture to give viscous oligomers and, after 24 h, a transparent sticky layer.

Reactions of organohydrosilanes with metal β-diketonates both involving the double bond of the acetylacetone enol form and involving the carbonyl oxygen atom were reported.[102] Processes of this type should result in destruction of the β-diketonate to give hydrolytically unstable metal alkoxides. The derivatives thus obtained were used[102] as heat stabilizers of polyorganosiloxanes.

b. Reaction of acetylacetone with 1-iodo-3-trimethoxysilylpropane

A 3-trimethoxysilylpropyl substituent is introduced into the 3-position of acetylacetone (to give compound **3**) *via* the sequence of reactions of 1-chloro-3-trimethoxysilylpropane (**1h**) with sodium iodide in acetone and then with acetylacetone (Hacac) and potassium bicarbonate.[103] The reaction is accompanied by the formation of acetylacetone 3-trimethoxysilylpropyl ether (**4**) as a by-product, which cannot be separated from the major product by distillation (Scheme 2).[104]

Scheme 2

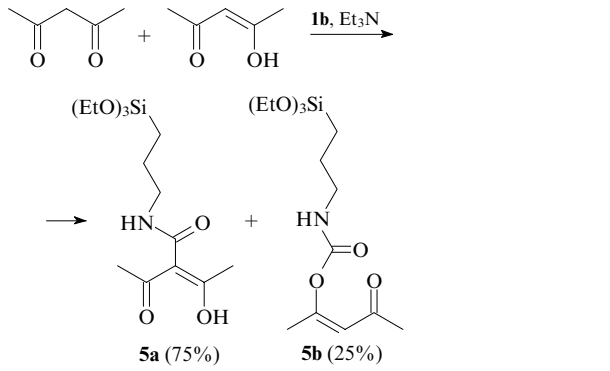


3a : **3b** : **4** = 13 : 5 : 1

c. Reactions of acetylacetone with organosilicon isocyanates

The reaction of acetylacetone with IPTES (**1b**) [105] proceeds up to high degrees of conversion only on heating in the presence of catalytic amounts of triethylamine and gives a mixture of addition products at the C–H (**5a**) and O–H (**5b**) bonds (Scheme 3).

Scheme 3

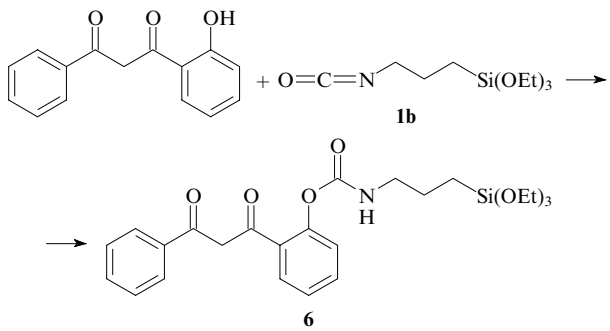


4-Hydroxy-3-(3-triethoxysilylpropylcarbamoyl)pent-3-en-2-one (**5a**) formed upon addition to the C–H bond is an organic amide, while 4-(3-triethoxysilylpropylcarbamoyloxy)pent-3-en-2-one (**5b**) resulting from addition to the O–H-group is a carbamic acid ester (urethane).

d. Reactions of *ortho*-hydroxydibenzoylmethane with organosilicon isocyanates

Isocyanate **1b** reacts with 2-hydroxydibenzoylmethane [106] as with phenol, the reaction being catalyzed by triethylamine, to give 2-(3-triethoxysilylpropylaminocarbonyloxy)dibenzoylmethane **6** (Scheme 4).

Scheme 4

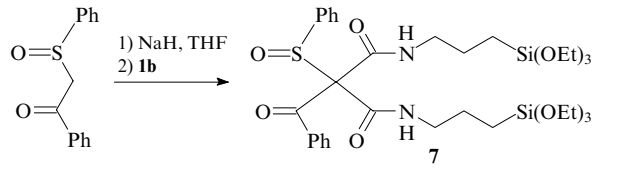


The reactivity of isocyanates towards phenols is known [107] to be higher than the reactivity towards CH-acids. Probably, this is why no reaction occurs at the methylene C–H bond of β-diketone. It is also known that dibenzoylmethane mainly exists in the β-diketone form and, hence, the reaction with the enol hydroxyl group is not observed either.

e. Reactions of sodium salts of thenoyltrifluoroacetone and phenyl phenacyl sulfoxide with organosilicon isocyanates

It is considered [108] that IPTES reacts with the sodium salt of 2-thenoyltrifluoroacetone in 2 : 1 ratio on heating in THF to afford β-diketone doubly substituted with 3-triethoxysilylpropylaminocarbonyl groups in the 3-position. Note that this compound was obtained *in situ* to be used in the co-hydrolysis with TEOS and its structure was not proven by spectroscopy. Under similar conditions, the sodium salt of phenyl phenacyl sulfoxide, the sulfur analogue of dibenzoylmethane, reacts with IPTES yielding disubstituted product 7 (Scheme 5).[109]

Scheme 5

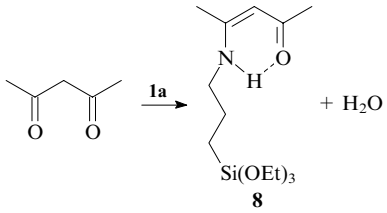


f. Reactions of acetylacetone with organosilicon amines

In the general case, the condensation of β-diketones with ammonia and amines serves as the traditional method for the synthesis of enaminoketones (β-aminovinyl ketones).[110–118] They constitute an extensive class of ligands and are versatile precursors of pharmacologically active compounds and important intermediates in organic synthesis.[119, 120]

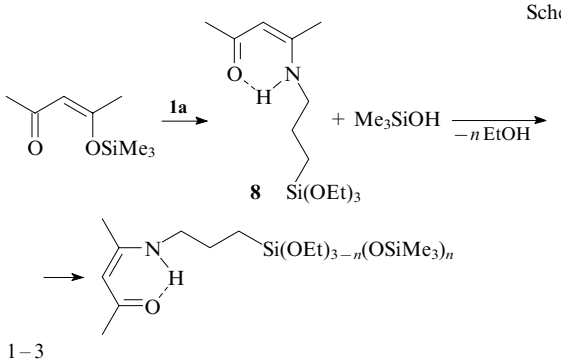
4-(3-Triethoxysilylpropyl)aminopent-3-en-2-one (**8**) was obtained by the reaction of acetylacetone with APTES (Scheme 6).[121–123]

Scheme 6



Water liberated in the reaction then reacts with the starting amine and product **8**, thus decreasing the product yield (to 40%) and increasing the yield of oligomers. The

Scheme 7

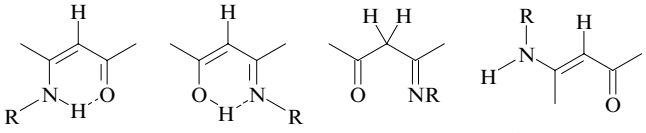


n = 1–3

second route *via* the trimethylsilyl ether of acetylacetone [122] gives a higher yield (50%) of products distillable *in vacuo* (Scheme 7).

However, by this method, it is more difficult to prepare a pure sample of **8**, because it reacts with trimethylsilanol formed in the reaction to give replacement products of the ethoxy group at the silicon atom by Me_3SiO. The IR and NMR spectroscopy data indicate that compound **8** exists mainly as the *cis*-enamino ketone (structure **III**) with some *trans*-isomer impurity (**III′**). No iminoenol (**IV**) and ketone imine (**V**) forms were detected.

Structures **III**–**V**



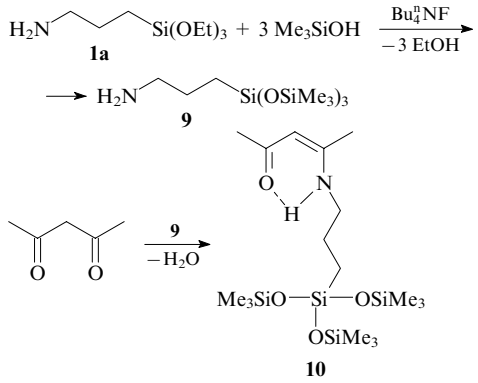
III (*cis*) **IV** **V** **III′** (*trans*-s-*cis*)

R = $(CH_2)_3Si(OEt)_3$

Compound **8** is relatively stable to atmospheric moisture. No formation of solid films was detected after 48 h in thin layer on a glass substrate.

(3-Aminopropyl)tris(trimethylsiloxy)silane (**9**) obtained by etherification of amine **1a** with trimethylsilanol in the presence of a catalytic amount of tetrabutylammonium fluoride reacts with acetylacetone on heating to 100 °C to give 4-[3-tris(trimethylsiloxy)silylpropyl]aminopent-3-en-2-one (**10**). After vacuum distillation, the product is air-stable transparent liquid (Scheme 8).

Scheme 8



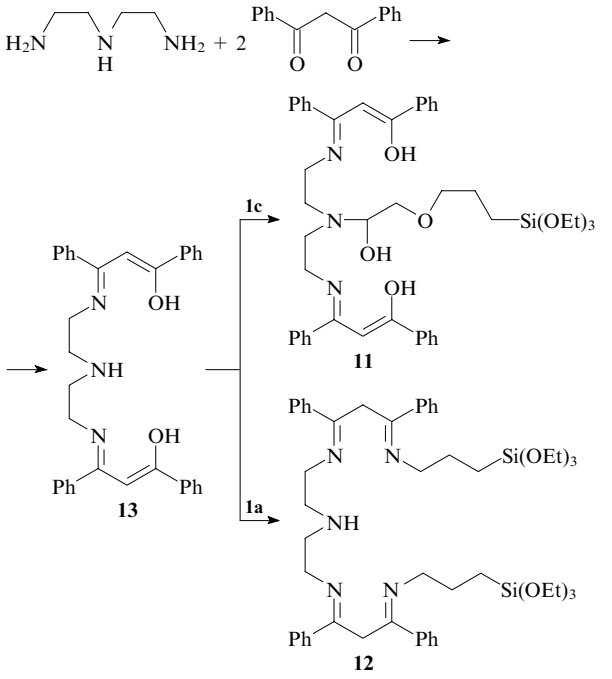
1a **9** **10**

Product **10**, like compound **8**, is enamino ketone. The trimethylsiloxane group is introduced in the ligand to increase the thermal stability and the solubility of complexes formed by this ligand in polyorganosiloxane rubbers.

g. Reactions of dibenzoylmethane with diethylenetriamine, 3-(glycidyloxypropyl)trimethoxysilane and organosilicon amines

Ligands **11** and **12** meant for deposition onto hydroxylated silicon dioxide were prepared from dibenzoylmethane, diethylenetriamine and carbofunctional alkoxysilanes. Two dibenzoylmethane molecules react with diethylenetriamine to furnish bis(iminoenol) derivative **13**. The subsequent functionalization by the reaction of the secondary amino group with the oxirane ring of 3-(glycidyloxypropyl)trimethoxysilane (**1c**) yields ligand **11** (Scheme 9).[124] Ligand **12** containing five donor nitrogen atoms was obtained from derivative **13** and IPTES. The chemical binding to a SiO_2 surface was achieved [124, 125] by heating solutions of these compounds in ethanol with dispersed silica. From these ligands, copper complexes immobilized on silica gel were obtained; these complexes were tested as catalysts for the oxidation of 3,5-di-*tert*-butylcatechol with molecular oxygen giving rise to 3,5-di-*tert*-butylquinone.[124, 125]

Scheme 9



13 **11** **12**

IV. Sol–gel processes involving β-diketones

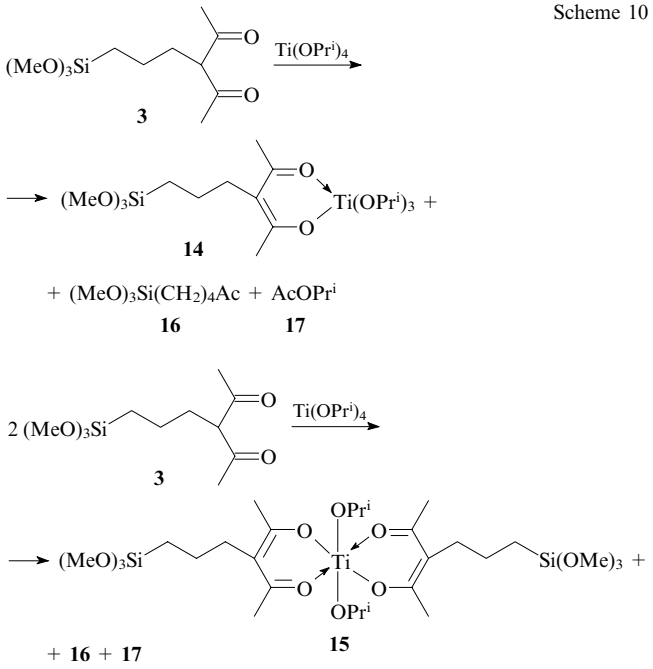
1. Transition metal β-diketonates in organosilicate matrices

a. Titanium complexes with silicon-containing β-diketones. Titanium-containing xerogels and aerogels

3-(3-Trimethoxysilylpropyl)pentane-2,4-dione (**3**) was used to produce anatase and the mixed phase rutile–cristobalite from titanium–silicon precursors.[103] Titanium complexes **14** and **15** were synthesized by the reaction of diketone **3** with titanium tetra(isopropoxide) in 1 : 1 and 2 : 1 molar ratios (Scheme 10). Hydrolysis of complexes **14** and **15** with equimolar amounts of water in methanol in the presence of a basic catalyst ($NH_3 \cdot H_2O$) induces gel formation in 30 min. Drying under usual conditions affords xerogels as powders, long-term treatment in a plastic container produces yellow transparent monolithic glasses, and supercritical drying furnishes opalescent aerogels with a specific surface area (S_{sp}) of 230 $m^2\ g^{-1}$ (from compound **14**) and 90 $m^2\ g^{-1}$ (from compound **15**). The burning-out of the organic component of powdered xerogels in air at 550 °C (calcination) affords amorphous phases $TiO_2 \cdot SiO_2$ (from compound **14**, S_{sp} = 208 $m^2\ g^{-1}$) and $TiO_2 \cdot 2\,SiO_2$ (from compound **15**, S_{sp} = 361 $m^2\ g^{-1}$). Heating of calcined xerogels to 1200 °C gives the mixed phase rutile–cristobalite (from compound **14**) and virtually pure rutile in amorphous silica (from compound **15**).

A substantial advantage of the titanium–silicon monomers is the possibility of preparing gels with a homogeneous element distribution. Hydrolysis of a $Ti(OPr^i)_4$ and $Si(OEt)_4$ mixture does not provide this option due to the large difference between the rates of hydrolysis and condensation of the two alkoxides. The titanium derivative reacts with

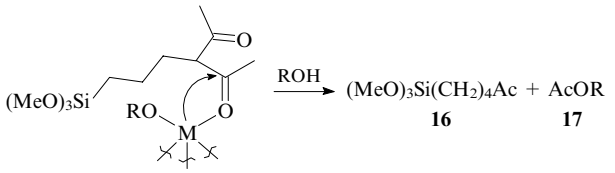
Scheme 10



water much faster than tetraethoxysilane, which results in fast precipitation of TiO_2, whereas $Si(OEt)_4$ still remains in solution for a rather long period.

A detailed study of the reactions of diketone **3** with titanium, zirconium and aluminium alkoxides demonstrated[104] that the reactions are accompanied by side hydrodeacylation of β-diketone, the formation of 4-trimethoxysilylbutyl methyl ketone (**16**) and alkyl acetates **17** (Scheme 11).

Scheme 11



M = Ti, Zr, Al; R = Pr^i, Pr^n, Bu^s

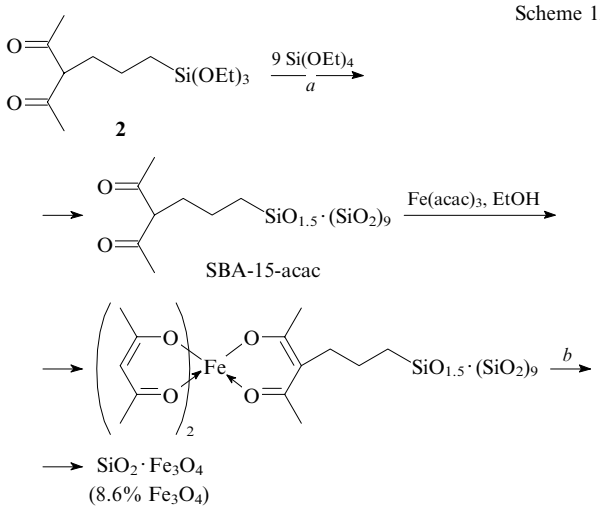
For titanium tetraisopropoxide and zirconium tetra-n-propoxide, this process occurs to only approximately 15%, whereas for a stronger Lewis acid — tri(*sec*-butoxy)aluminium — it becomes predominant. By using an excess of $Ti(OPr^i)_4$ or $Zr(OPr^n)_4$, this side process can be minimized.

b. Iron β-diketonate in mesoporous silica. Preparation of magnetic nanocomposite

Mesoporous silica of the SBA-15 type containing nano-sized magnetite Fe_3O_4 particles was obtained[126] from an organic-inorganic hybrid functionalized by acetylacetonate groups and iron(III) tris(acetylacetonate) (Scheme 12).

Mesoporous silica was prepared by co-hydrolysis of 3-(3-triethoxysilylpropyl)pentane-2,4-dione with TEOS (1 : 9 mol) in the presence of triblock copolymer Pluronic-123 (P-123). Chemically bound iron acetylacetonate groups were inserted into mesopores by exchange reaction with an ethanol solution of $Fe(acac)_3$. The subsequent heating to 265 °C of a suspension of iron-containing xerogel in a mixture of high-boiling organic solvents and $Fe(acac)_3$

Scheme 12



(*a*) P-123, H_2O, HCl, NaF; (*b*) $Fe(acac)_3$, Ph_2O, hexadecane-1,2-diol, oleic acid, oleic acid amide, 265 °C

resulted in the formation of mesoporous silica containing 8.6 mass % of nano-sized magnetite particles with an average diameter of 3.8 nm. As a result of similar operations carried out for SBA-15 without β-diketonate groups, magnetite was formed on the surface of colloidal particles rather than inside the mesopores.

2. Lanthanide β-diketonates in organosilicate matrices

Analysis of the currently available data about β-diketonate metal-containing gels demonstrates that most of publications are devoted to lanthanide derivatives, first of all, those having luminescence properties. This is caused by the prospects of the practical use of materials based on them for photonics, integrated optics and medical diagnostic procedures. Since luminescence properties play a crucial role, studies of this type concentrate on the photoluminescence spectra of lanthanide-containing glasses, films and colloidal solutions.

a. Methods for the preparation of gels doped with lanthanide β-diketonates

Luminescent sol–gel materials are usually prepared in two ways:

— dissolution of lanthanide β-diketonate in the initial composition consisting of the monomer, the solvent and the catalyst;

— dissolution of lanthanide β-diketonate in the already formed sol.

Hydrochloric acid is used most often as the catalyst, considering rather high volatility of HCl. The subsequent polycondensation of a thin layer of the sol on a substrate affords a film. By conducting the reaction under specially selected conditions, it is possible to obtain transparent glasses. This is often done in fluoroplastic reactors with a small orifice for removal of volatile products. The process is carried out for long periods under temperature-controlled conditions (40–80 °C). For preventing crack formation, special reagents such as DMF are added to the composition.

There is a process modification where the lanthanide β-diketonate is prepared *in situ* by adding, first, metal chloride or nitrate and then, separately, the ligand to the sol. In the vicinity of room temperature, the complex is not

formed because β-diketone is not deprotonated due to low basicity of the medium. However, during drying of the gel and the subsequent heat treatment, the formation of β-diketonate becomes possible. Process of this type is accompanied by considerable enhancement of photoluminescence, indicating accumulation of the coordination compound. Indeed, the fluorescence intensity increased more than 1000-fold upon heating of a gel containing europium chloride, thenoyltrifluoroacetone and triphenylphosphine oxide at 100 °C for 24 h.[127]

During the formation of films, the hydrolytic polycondensation in thin layer occurs fairly efficiently due to atmospheric moisture; therefore, for some sol–gel monomers the preliminary preparation of the sol is not necessary. The initial liquid composition is deposited on a substrate by means of a centrifuge or by casting. The hardening time is controlled by selecting the type and concentration of the catalyst. The organosilicon amine APTES is a very convenient basic catalyst. The mechanisms of action of APTES and some organic amines were studied[128] in relation to the hydrolytic polycondensation of methyl(trimethoxy)silane and three monomers with organofluorine substituents.

Lanthanide β-diketonate incorporated into the sol–gel matrix exists under the influence of the local environment of constituent fragments. By analogy with solutions, this influence can be considered as solvation. In the case where functionalized metal β-diketonate is added to the sol–gel monomer, its segregation into a separate phase during gel formation appears unlikely if the rates of hydrolysis of the main monomer and the added complex are commensurable. However, when a coordination compound with purely organic ligands is used, the effect of solvation processes that prevent microphase separation becomes crucial. Many metal β-diketonates that are moderately or readily soluble in the initial alcohol–tetra(tri)alkoxysilane compositions precipitate during the gel formation or form a turbid final product. The introduction of polar groups — amino, amide, ester, urea and urethane groups — into the monomer promotes solvation of the complex, prevents its segregation into a separate phase, and allows the preparation of homogeneous transparent glasses and films. Ladilina *et al.*[129, 130] demonstrated the efficiency of solvation of europium and erbium benzoyltrifluoroacetonates and praseodymium hexafluoroacetonate with the fluorinated sol–gel monomers $(EtO)_3Si(CH_2)_3R^F$ [$R^F = N{=}CHC_6F_5$, $NHC(O)CF_3$, $NH(CH_2)_2CO_2CH_2(CF_2)_4H$] and $(EtO)_3Si(CH_2)_3NHC(O)(CF_2)_4C(O)NH(CH_2)_3Si(OEt)_3$.

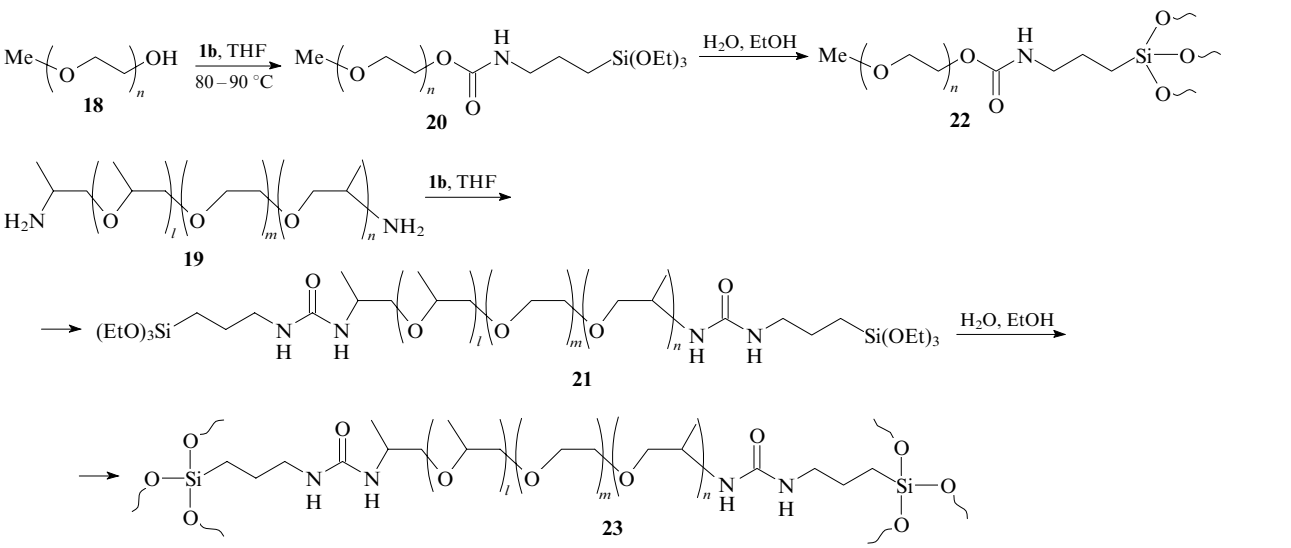
The ligand environment of the cation, the concentration of the complex in the solution and the nature of the solvent have a pronounced effect on the intensity of the cation-centred photoluminescence of lanthanide β-diketonate. Similar dependences were observed in solid-phase objects prepared by sol–gel processes. As regards luminescence properties, important are the effects of electron excitation from the matrix to the ligand and then to the metal cation and the probability of photoexcitation and emission of the proper sol–gel matrix.

b. The nature of the emission band of silicon-containing sol–gel matrices

Transparent organosilicon sol–gel films and glasses often exhibit an emission band at 300–500 nm. It was first found[131] in the spectra of gels obtained by solvolysis of TEOS with acetic acid. The most intense fluorescence is observed for organic-inorganic hybrids containing amino and amide groups. The nature of this band was studied[132–156] by fluorescence, UV/Vis and IR spectroscopy, small-angle X-ray scattering, and ^{13}C and ^{29}Si NMR spectroscopy. The luminescence probes used included terbium nitrate and bipyridine,[134] europium triflate,[138, 142, 143, 145, 146] bipyridine-tris(thenoyltrifluoroacetonato)europium[135] and bipyridine-tris(naphthoyltrifluoroacetonato)europium[149, 151] incorporated in the sol–gel matrices, which were formed by hydrolysis or solvolysis of the reaction products of IPTES with two types of oligomers: polyethylene glycol methyl ethers **18** and poly(ethylene propylene) glycols **19** containing primary amino groups at chain ends (Scheme 13).

Liquid oligomers **20** and **21** thus formed were converted to solid organic-inorganic hybrids **22** and **23**, respectively, which were called by the authors mono-urethanesils and di-ureasils, because they contain triethoxysilane and urethane

Scheme 13



or urea groups.[140, 141, 145] Hydrolysis with atmospheric moisture in layer allows the formation of transparent films of high optical quality.[140–143, 145, 146] The solid framework of these materials is composed of a silicon-and-oxygen network linked to polyethylene oxide chains *via* urea or urethane moieties. Liquid oligomers and the gels and xerogels formed upon hydrolysis efficiently solvate lanthanide salts and β-diketonates. The hydrolytic condensation does not induce their deposition as a separate phase. The set of spectroscopy data indicates that the films resulting from the sol–gel process are not ideal amorphous glassy solids. De Zea Bermudez and co-workers[143, 145, 146] proposed the formation of a two-level hierarchical structure. The first level is formed by siloxane particles of diameter 5–7 Å; in lanthanide-containing hybrids, they form relatively ordered clusters with sizes of 50–70 Å. Within the clusters, the polymer chains occur in the coiled conformation, while between the clusters, they are in essentially stretched. It is assumed that this structure is responsible for concentrating the incident light energy and its emission. The authors concluded that emission of mono-urethanesil and di-ureasil films at 300–500 nm comes from two sources: recombination of donor–acceptor pairs in the urea NH groups and in oxygen defects of the type $^{\bullet}O-O-Si(\equiv O_2C)$, which arise in silica nanodomains.[147, 148] The asymmetrical emission band actually consists of two components. The short-wavelength component is due to recombination and the long-wavelength one is related to emission of silica nanodomains. The mechanism responsible for the NH component is associated with the photoinduced proton transfer between the NH_2^-- and N^--defects.

It is known[157] that the microstructure of some purely organic polymers, for example, polyurethanes, is also determined by two types of domains: hard (crystalline) and soft (amorphous). The effect of silicon dioxide inserted in the hard polyurethane domains on the temperature range of crystallization was explored.[157] Organic-inorganic hybrids of this type consist of chemically (*i.e.*, covalently) nonbonded polyurethane and silica blocks. They were prepared by hydrolysis of a polyurethane and TEOS solution in DMF catalyzed by formic acid. The presence of the silica component in polyurethane was found to strongly hinder the phase transition in hard domains. *N*-(Triethoxysilylpropyl)dansylamide [dansyl is 5-(dimethylamino)-1-naphthalenesulfonyl] was used as the luminescence probe.

Bekiari *et al.*[132, 133, 137] observed intense photoluminescence of gels obtained by solvolysis of APTES and di-ureasil by organic acids in the absence of moisture and oxygen. The water molecules come from esterification reaction between the acid and ethanol. The process in general is described by Scheme 14.

Scheme 14

$$\equiv SiOEt + AcOH \longrightarrow \equiv SiOAc + EtOH$$

$$AcOH + EtOH \longrightarrow AcOEt + H_2O$$

$$\equiv SiOEt + H_2O \longrightarrow \equiv SiOH + EtOH$$

$$\equiv SiOAc + H_2O \longrightarrow \equiv SiOH + AcOH$$

$$\equiv SiOH + HOSi\equiv \longrightarrow \equiv Si-O-Si\equiv + H_2O$$

Finally, this affords gels containing nanoclusters with attached organic groups. A characteristic feature of this process is trapping of the liberated ethanol, which prevents the formation of nanoclusters. Therefore, the products of the reaction with acetic and valeric acids have higher degrees of structuring and more intense photoluminescence compared with the products of hydrolysis in the absence of acids. The maximum quantum yields were 27%–35%, and, therefore, urea- and urethanosil sol–gel films were proposed[144, 147, 148] as white light emitters. Thick di-ureasil xerogel films doped with monoisotopic lithium-6 salicylate proved to be effective scintillators[156] suitable as large-size neutron detectors.

The position of the emission band in the photoluminescence spectra of sols, gels and films depends on the excitation wavelength. It shifts to longer wavelengths upon the decrease in the exciting light energy. A proposed[137] explanation to the red shift is as follows. The formed nanoclusters and domains have different size. High-energy light quanta excite, first of all, the smallest domains. Their subsequent relaxation by the electron–hole recombination mechanism results in UV light emission. As the energy decreases, more and more coarse domains are excited and, hence, the emission occurs in longer-wavelength (visible) region. This is confirmed by the observed[137] red shift of the photoluminescence maximum depending on the gel ageing time (aged gel emits at longer wavelengths, because it consists of coarser nanoclusters).

Blue photoluminescence shifts to longer wavelengths as films are heated.[153] Simultaneously, the photoluminescence intensity increases. A comparative investigation[154] of the luminescence properties of polysiloxane $(RMeSiO)_n$ and silsesquioxane $(RSiO_{1.5})_n$ (R = n-$C_{18}H_{37}$) polymers demonstrated that the latter show higher emission characteristics.

c. Europium β-diketonates in urea- and urethanosil matrices

Europium β-diketonates — bipyridine-tris(thenoyltrifluoroacetonato)europium[135] and bipyridine-tris(naphthoyltrifluoroacetonato)europium[149, 151] — are readily soluble in di-ureasils. The subsequent curing produces transparent films. Upon UV irradiation, the energy absorbed by the matrix can be transferred through the ligand to the europium cation and emitted as narrow $^5D_0 \rightarrow {}^7F_{0-4}$ bands. The emission intensity of di-ureasil decreases and can be completely or partially degenerated. The efficiency of this type of transfer depends on both the chain length (n) of the starting oligomer and the nature of the inserted complex. It was found that efficient energy transfer occurs to europium β-diketonates,[135] whereas for europium triflate[142, 143, 145, 146] it is of low efficiency. The intensity of cation-centred emission for bipyridine-tris(naphthoyltrifluoroacetonato)europium-doped di-ureasil is 60% of the rhodamine B luminescence intensity.[147] The observed low-intensity emission at 470 nm is related to transitions from the ligand excited level. A distinctive feature of the emission of monourethano- and di-ureasil films is the above-mentioned dependence of the position of the emission band on the exciting light energy (red shift upon increase in the excitation wavelength). Conversely, position of the ligand emission band almost does not depend on the excitation energy. This circumstance is utilized to establish the nature of the emission in the spectral range typical of both the matrix and the ligands that belong to the inserted complexes.

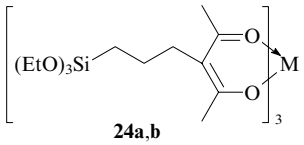
Europium triflate molecules were found[145, 146] to be solvated by either nitrogen atoms or carbonyl oxygen atoms, depending on the length of the polyoxyethylene

chain of the sol–gel monomer. The prospects of using luminophore-doped di-urea- and mono-urethanosils in the lighting technology, solar power production, integral optics and biomedicine were considered.[158] The nature of fluorescence of sol–gel matrices has apparently much in common with the luminescence of inorganic silicon and germanium oxide glasses,[159] which is caused by structure defects.

d. Sol–gel glasses and films based on europium and terbium complexes with 3-(3-triethoxysilylpropyl)pentane-2,4-dione

Anhydrous europium and terbium tris(β-diketonates) **24a**,**b** were synthesized[100, 101] by the reaction of ligand **2** with europium and terbium isopropoxides.

Structures **24**



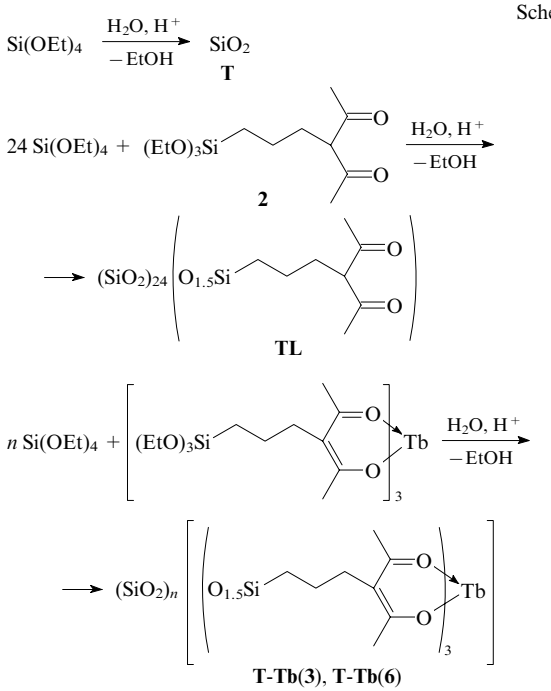
24a,**b**

M = Eu (**a**), Tb (**b**)

These complexes were used to obtain luminescent films and glasses. The europium chelate forms a transparent yellow film within 20–30 min from a solution in diethyl ether. For the formation of a high-quality film from the terbium complex, ~30 mass % of amine **1a** should be added.

Using silylated complex **24b** and the sol–gel technique, terbium-containing silicon oxide glasses were prepared[160] and studied for their photoluminescence. Among all lanthanides, terbium appears to be most convenient for evaluation of the energy transfer from the silicon oxide matrix to the ligand and then to the cation, because terbium shows strong luminescence and its transitions are most proximate to the UV region in which one should expect absorption and emission of colourless tetraethoxysilane-based sol–gel glasses. The luminescence excitation (LE) and photoluminescence (PL) spectra were studied for glasses of four types designated in Scheme 15 by **T**, **TL**, **T-Tb(3)** and **T-Tb(6)**.

Scheme 15



T-Tb(3): n = 68, [Tb^{3+}] = 3.30 mass %;
T-Tb(6): n = 30, [Tb^{3+}] = 6.27 mass %

Glass **T** is amorphous silicon dioxide, **TL** is silicon dioxide with inserted fragments of ligand **2**. Glasses **T-Tb(3)** and **T-Tb(6)** are silicon dioxide glasses containing 3.30 mass % and 6.27 mass % Tb^{3+}, respectively. The LE spectrum of glass **T** shows a broad band at 338 nm (λ_{det} = 433 nm), which shifts to 376 nm as the detection wavelength increased to 515 nm. Excitation in this region (λ_{excit} = 360 nm) gives rise to a compound band with a maximum at 433 nm and a shoulder at 520 nm in the PL spectrum. Thus, to generate emission of silicon dioxide obtained by hydrolysis of TEOS, excitation at λ = 340–380 nm is required. Transition to the glass **TL** is accompanied by the appearance of silsesquioxane structural fragments $O_{1.5}Si(CH_2)_3CHAc_2$ in SiO_2. At the same excitation wavelength of 360 nm, this leads to overall shift of the emission to longer wavelengths and to an increase in the intensity of the 510–515 nm band. Both effects are enhanced with increase in λ_{excit} to 420 nm.

The emission spectra of glasses containing the terbium complex at λ_{excit} = 360 nm look differently depending on the lanthanide concentration. When the terbium concentration is 3.30 mass.%, a narrow line at 546 nm due to the most intense $^5D_4 \rightarrow {}^7F_5$ transition in the Tb^{3+} cation appears against the background of the broad emission band of the matrix with a maximum at 560 nm. The other three transitions (584, 620 and 649 nm) occur as shoulders at the slope of the matrix emission band (Fig. 1). The displacement of λ_{excit} to 420 nm induces the disappearance of the cation luminescence of glass **T-Tb(3)**. The increase in the terbium content to 6.27% seems to cause the concentration quenching and the Tb^{3+} luminescence is not manifested. Thus, the obtained data indicate that there exists a transfer channel of the light energy absorbed by the sol–gel matrix to the cation. The relatively low intensity of the cation luminescence implies relatively low probability of implementation of this mechanism.

The LE spectra of terbium glasses exhibit a short-wavelength band at λ = 275 nm, the position of this band remaining invariable on both the variation of the terbium complex concentration and the change in the detection wavelength (543 or 621 nm). This band has a common

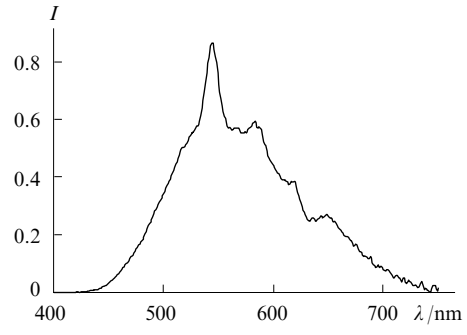


Figure 1. Photoluminescence spectrum of glass **T-Tb(3)** (λ_{excit} = 360 nm).[160]
Here and below: I is the relative intensity in arbitrary unions.

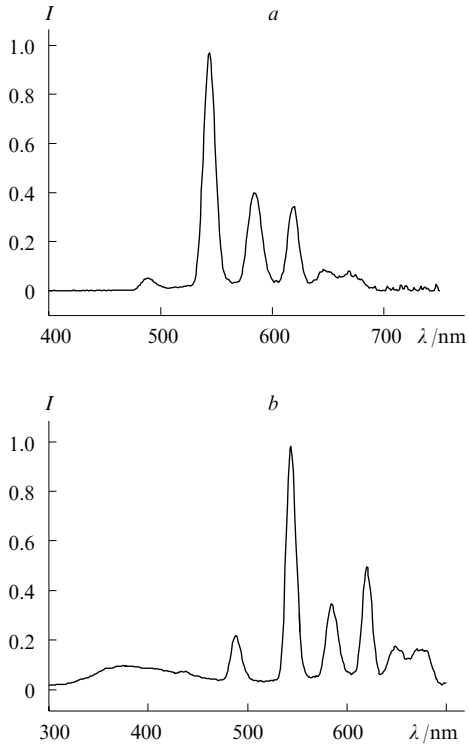


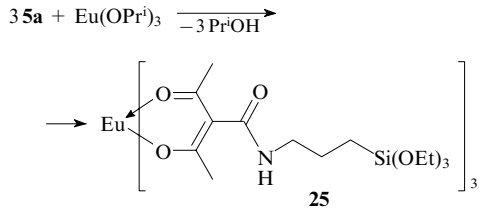
Figure 2. Photoluminescence spectra of glasses **T-Tb(3)** (λ_{excit} = 275 nm) (*a*) and **T-Tb(6)** (λ_{excit} = 280 nm) (*b*).[160]

nature with the band at 298 nm in the electronic absorption spectrum and is due to the $n \rightarrow \pi^*$ transition in the chelating ligand. The irradiation at 275–280 nm induces green luminescence of terbium glasses. The spectra display only narrow emission lines of the Tb^{3+} cation, whereas luminescence of the matrix either does not occur or has a very low intensity (Fig. 2).

e. Europium complexes with triethoxysilylpropylcarbamoyl-substituted β-diketones

Acetylacetone derivatives. Europium complex **25** was prepared[105] by the reaction of a mixture of compounds **5a**,**b** with europium isopropoxide (Scheme 16).

Scheme 16

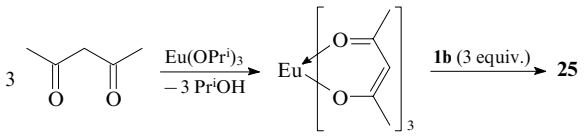


25

Of the two components of the mixture, only the enol form **5a** can participate in the reaction. Triethoxysilyl urethane **5b**, which does not react, is removed on heating *in vacuo*. An alternative synthesis of complex **25** is the reaction of anhydrous europium tris(acetylacetonate) with IPTES (Scheme 17).

Infrared spectra, data of elemental analysis and data of spectrofluorimetry confirmed that samples of Eu complex synthesized in different ways are fully identical.

Scheme 17



Transparent solid films were obtained from compound **25** by adding APTES or by dissolving the compound in 96% ethanol (1 : 2 by volume) and keeping the solution for 2–3 days.

The LE spectra of europium-containing films exhibit three broad overlapping bands with maxima at 387, 440 and 512 nm (λ_{det} = 615 nm). The PL spectra were measured upon excitation at 285 and 340 nm (Fig. 3).

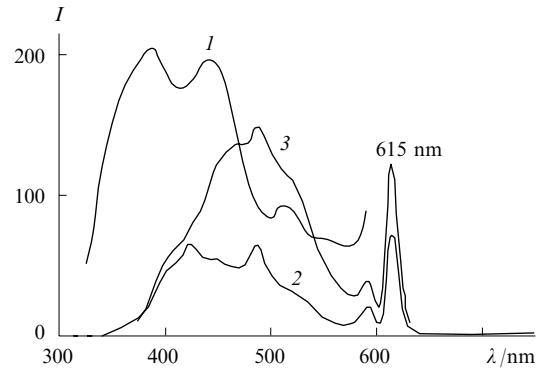


Figure 3. Fluorescence excitation (*1*, λ_{det} = 615 nm) and emission spectra (*2*, λ_{excit} = 285 nm; *3*, λ_{excit} = 340 nm) of the film containing complex **25**.[105]
[Eu^{3+}] = 15.4 mass %.

Excitation of the short-wavelength spectral range (λ_{excit} = 285 nm) gives rise to a broad emission band of the matrix (λ_{max} = 450 nm) and six narrow bands of the Eu^{3+} cation: 425 ($^5D_3 \rightarrow {}^7F_0$), 486 ($^5D_2 \rightarrow {}^7F_2$), 590 ($^5D_0 \rightarrow {}^7F_1$), 615 ($^5D_0 \rightarrow {}^7F_2$), 652 ($^5D_0 \rightarrow {}^7F_3$) and 700 nm ($^5D_0 \rightarrow {}^7F_4$). The highest intensity is found for the hypersensitive electric dipole transition $^5D_0 \rightarrow {}^7F_2$, and the high-energy transitions from high-lying excited levels $^5D_3$ and $^5D_2$ are superimposed onto the broad emission band of the matrix. The shift of λ_{excit} to 340 nm (see Fig. 3, curve *3*) results in its increase relative to the $^5D_0 \rightarrow {}^7F_2$ transition of the Eu^{3+} cation. The light energy absorbed by the film is mainly emitted as a broad band of the silica matrix, while luminescence of the europium cation appears quite moderate. One of the causes is that the existing mechanism of energy transfer from the matrix to the cation is of low efficiency. The short-wavelength emission bands at 425 and 486 nm indicate that the usually observed fast transitions from the Eu^{3+} excited states $^5D_2$ and $^5D_3$ to $^5D_0$ (followed by emission from the lowest $^5D_0$ level) are weakly manifested in the obtained structured complex. As a consequence, seldom observed direct emission from high-energy levels takes place.

The thermal stability of films was studied by UV and PL spectroscopy in the range of 100–300 °C. On heating, the intensities of the 245 and 278 nm absorption bands regularly decrease (Fig. 4) and at 300 °C, they completely disappear. Less pronounced changes are observed in the

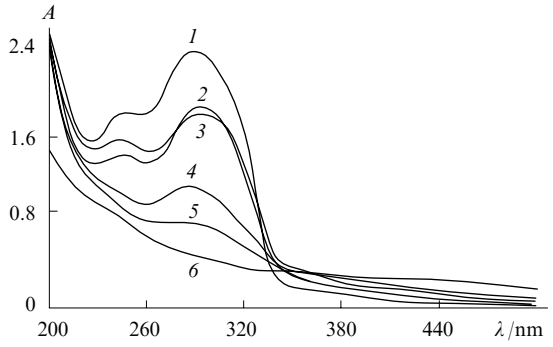


Figure 4. Variation of the UV spectrum of the film of complex **25** on a quartz substrate during heating in air.[105]
T/°C: (*1*) before heating, (*2*) 100, (*3*) 150, (*4*) 200, (*5*) 250, (*6*) 300.

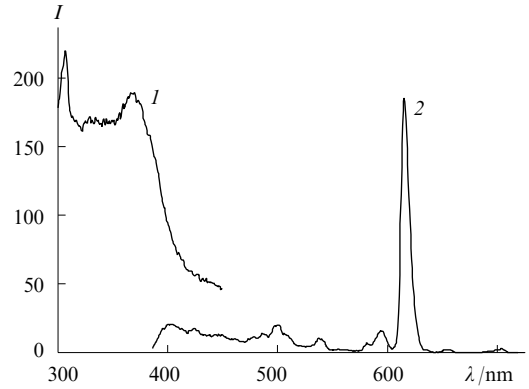
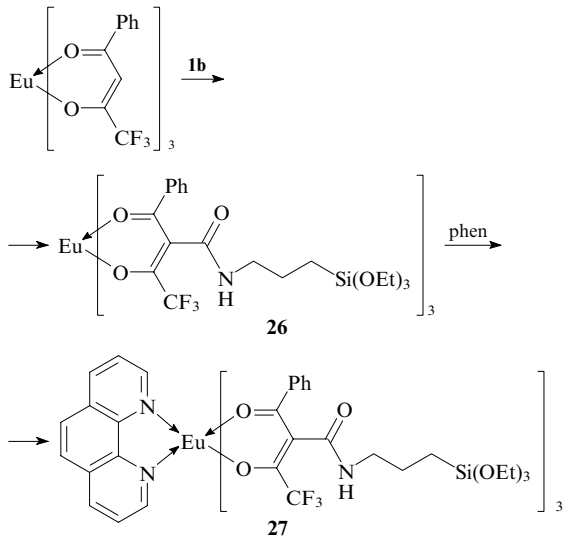


Figure 5. Fluorescence excitation (*1*, λ_{det} = 615 nm) and emission spectra (*2*, λ_{excit} = 370 nm) of the film of complex **26**.[161]
Film thickness is 134 μm.

fluorescence spectrum. As the temperature is raised to 200 °C, the emission bands of the matrix and the Eu^{3+} cation undergo only minor changes. Heating of the film to 300 °C induces a sharp decrease in the intensity of the Eu^{3+} emission bands, while the emission band of the silica matrix remains unchanged.

Benzoyltrifluoroacetone derivatives. The reaction of anhydrous europium tris(benzoyltrifluoroacetonate) with IPTES [161] affords complex **26**, which reacts with 1,10-phenanthroline (phen) to yield compound **27** (Scheme 18).

Scheme 18



Compound **26**, which is a viscous liquid, readily forms a transparent sol–gel film when cast onto a substrate. The curing time depends on the layer thickness and ranges from 5 to 20 h. Figure 5 shows the LE and PL spectra of compound **26** as a film on a quartz substrate. The LE spectrum at 615 nm detection wavelength has four bands with poorly resolved peaks at 305, 340, 370 and 470 nm. The emission spectrum for λ_{excit} = 370 nm has six narrow bands (500, 582, 594, 615, 654, 704 nm), which refer to transitions in the Eu^{3+} cation. The strongest transition is

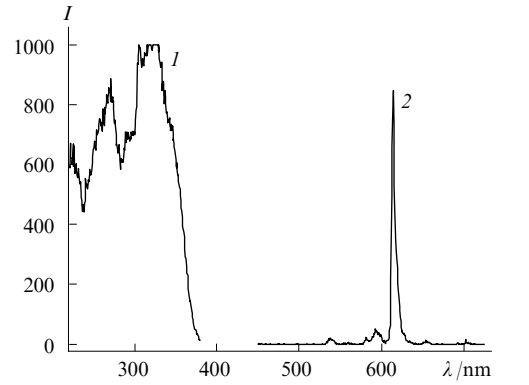


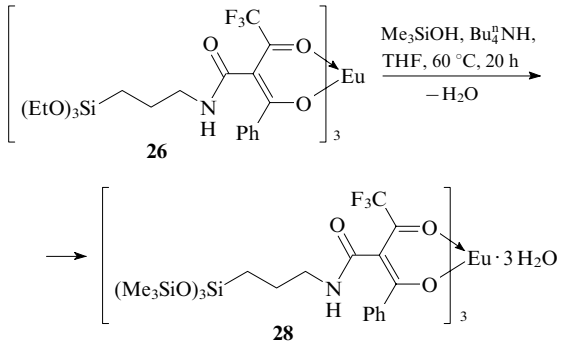
Figure 6. Fluorescence excitation (*1*, λ_{det} = 615 nm) and emission spectra (*2*, λ_{excit} = 340 nm) of complex **27** in MeCN (concentration 2×10^{-6} mol litre^{-1}).[161]

$^5D_0 \rightarrow {}^7F_2$ at λ = 615 nm. Fluorescence of the silica matrix is manifested as a broad weak band in the range from 390 to 550 nm. Figure 6 presents the PL and LE spectra of an acetonitrile solution of complex **27**.

The relative luminescence quantum yield for compound **27** calculated by comparison with the standard dye rhodamine 6G was 10%. Measurements in dilute solutions show the absence of luminescence of the organosilicon component of the complex.

For preparing transparent luminescent silicone rubbers, lanthanide complexes soluble in liquid siloxane compositions are needed. However, compounds **26** and **27** are insoluble in liquid silicones. The compatibility problem was solved [162] by replacing three ethoxy groups by trimethylsilyloxy groups, which was done by treating compound **26** with trimethylsilanol (Scheme 19). Silylated complex **28** is moderately compatible with silicone compositions, while the phenanthroline analogue is poorly soluble. Furthermore, the solubility of compound **28** in the phenyl-containing composition is higher than in the permethylated one.

Scheme 19



Liquid compositions with the complex content of up to 1.5 mass % were prepared. This gave rise to bright red-orange photoluminescence of cured films on exposure to UV light. Figure 7 shows the photoluminescence spectra of the films containing 0.5 mass % of the europium complex.

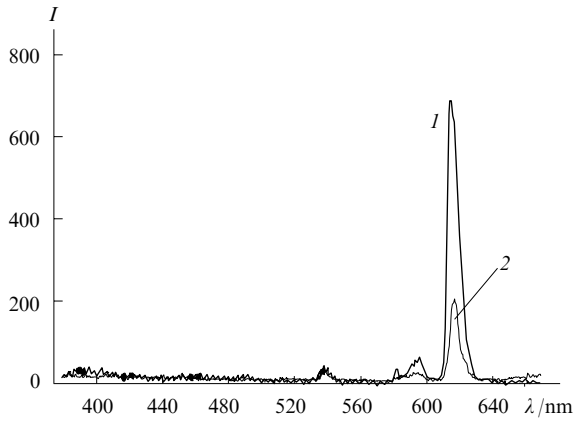
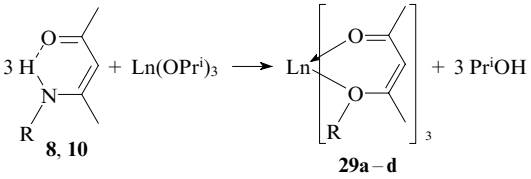


Figure 7. Photoluminescence spectra of heat (*1*) and photo cured (*2*) films doped with europium complex **28** at λ_{excit} = 340 nm.[162] Film thickness, μm: (*1*) 420, (*2*) 19.

f. Organosilicon tris(enaminoketonate) complexes of lanthanides

4-(3-Triethoxysilylpropyl)aminopent-3-en-2-one (**8**) prepared [121–123] by the reaction of acetylacetone with 3-aminopropyltriethoxysilane and its trimethylsilyloxy analogue **10** readily reacts with europium, terbium and erbium isopropoxides to give the corresponding tris(enaminoketonate) complexes **29a–d** (Scheme 20).

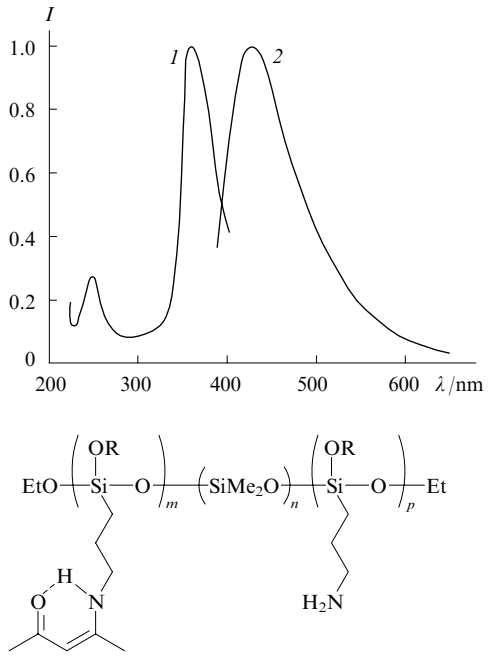
Scheme 20



R = $(CH_2)_3Si(OEt)_3$: Ln = Eu (**a**), Tb (**b**);
R = $(CH_2)_3Si(OSiMe_3)_3$: Ln = Eu (**c**), Er (**d**)

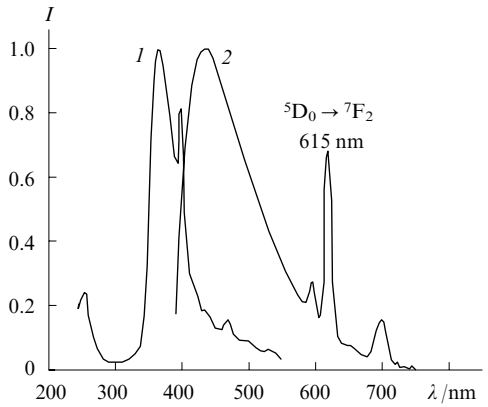
Compounds **29a**,**b** are coloured transparent viscous liquids, which are slowly hydrolyzed by atmospheric moisture. In 15–20 h after deposition on the substrate of compositions comprising one of these complexes, APTES and oligodimethylsiloxanediol $HO(SiMe_2O)_nH$ (n = 2–5), solid transparent films stable up to 150 °C with good adhesion to the glass and quartz surface are formed. Siloxanediols function as reagents that cross-link tri- and bifunctional molecules of silylated complexes by the condensation mechanism. The APTES molecules, which contain primary amino groups, serve simultaneously as the basic catalysts and as the trifunctional components together with compounds **29a**,**b**. Curing in air is accompanied by loss of mass by 20%–24% due to removal of ethanol. This gave films with metal content of 7 mass %–9 mass %. Figure 8 presents the photoluminescence excitation and emission spectra of the film formed from compound **8**, APTES and oligodimethylsiloxanediols. The LE spectrum exhibits a band at 360 nm and a low-intensity peak at 248 nm (λ_{det} = 490 nm). After excitation at 370 nm, the PL spectrum exhibits the only broad band with a peak at 427 nm.

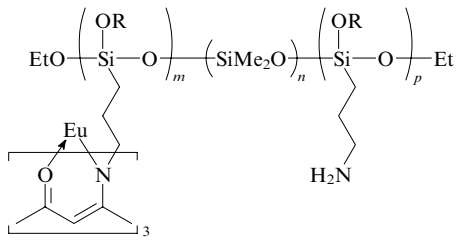
The presence of europium cation in the film changes insignificantly the pattern of the luminescence excitation spectrum (Fig. 9), despite the considerable difference in the detection wavelengths (λ_{det} = 615 nm). The photoluminescence spectrum (λ_{excit} = 370 nm) exhibits three narrow emission lines of the europium cation at 592, 615 and 697 nm caused by transitions from the excited $^5D_0$ level to three sublevels of the fundamental $^7F_1$, $^7F_2$ and $^7F_4$ multiplet. The maximum of the intense emission of the matrix (λ = 435 nm) is somewhat shifted to longer wavelengths as compared with the film devoid of the lanthanide cation.



R = Et, $SiMe_3$, Si≡

Figure 8. Fluorescence excitation (*1*, λ_{det} = 490 nm) and emission spectra (*2*, λ_{excit} = 370 nm) of the film formed from compound **8**, APTES and oligodimethylsiloxanediols.[123]





R = Et, $SiMe_3$, Si≡

Figure 9. Fluorescence excitation (*1*, λ_{det} = 615 nm) and emission spectra (*2*, λ_{excit} = 370 nm) of the film containing europium(III) cations ([Eu] = 7.9 mass %) (see the text).[123]

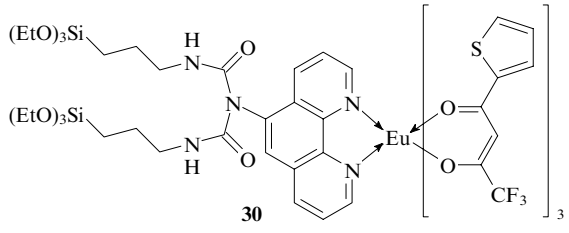
The introduction of the bulky tris(trimethylsiloxy)silyl group[163] stabilizes complexes **29c**,**d** with respect to atmospheric moisture. Hydration processes occur very slowly and consist in the insertion of a water molecule into the lanthanide coordination sphere. This feature is of considerable interest for the preparation of volatile coordination compounds of lanthanides and for increasing the solubility of these compounds in liquid siloxane compositions.

g. Insertion of lanthanide β-diketonates into the sol–gel matrix *via* functionalized neutral ligand

Lanthanide β-diketonates were inserted into organosilicate matrices using a neutral ligand, 1,10-phenanthroline, functionalized with triethoxysilyl groups. Three examples of intense luminescent sol–gel materials obtained in this way are presented below.

Complex **30** of europium thenoyltrifluoroacetonate with neutral 5-[*N*,*N*-bis(3-triethoxysilylpropyl)ureyl]-1,10-phenanthroline ligand was used[164] to prepare monolithic sol–gel glasses and to study the fluorescence spectra of the glasses. These were obtained by long-term (1 month) storage at room temperature of an ethanol solution of tetramethoxysilane, dimethyldiethoxysilane, a silylated complex and water under neutral conditions. The fluorescence spectra of glasses dried at 100 °C are similar to the spectra of solutions of the complex and europium thenoyltrifluoroacetonate.

Structure **30**

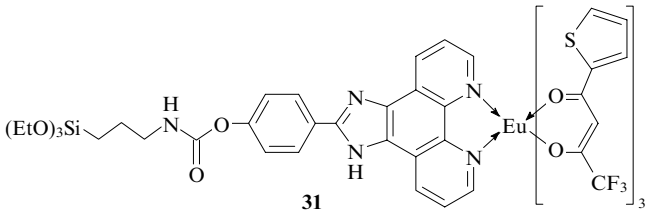


30

This complex was used to synthesize[165] mesoporous silica nanospheres containing incorporated magnetite (Fe_3O_4) nanoparticles, which produced UV-induced luminescence. The preparation method included the addition of a solution of the complex in TEOS to an aqueous colloidal solution containing magnetite nanoparticles, a surfactant (cetyltrimethylammonium bromide) and NaOH. A silicon dioxide coating is formed around the Fe_3O_4 core. This gave spherical particles of luminescent magnetic mesoporous silica with a diameter of 30 to 160 nm, a specific surface area of 850 $m^2\ g^{-1}$, a total pore volume of 0.99 $cm^3\ g^{-1}$, an average pore diameter of 2.79 nm and a wall thickness of 2.39 nm. Every particle encompasses several (1–4) magnetite cores. It is believed[165] that materials of this sort have great prospects in biotechnology and medicine as contrast reagents for magnetic resonance imaging, drug carriers, biomarkers and for enzyme immobilization.

A series of luminescent lanthanide-containing sol–gel films was prepared using 2-{4-(3-triethoxysilylpropylcarbamoyloxy)phenyl}imidazo[4,5-*f*]-1,10-phenanthroline (for example, as a part of complex **31**).[166] Sols for the formation of thin films by centrifugation were prepared from tetramethoxysilane, diethyldiethoxysilane, lanthanide thenoyltrifluoroacetonate, silylated phenanthroline, ethanol and water. The lanthanides employed included praseodymium, neodymium, samarium, europium, holmium, erbium and ytterbium. Photoluminescence in the visible (Sm, Eu) and near-IR (Pr, Nd, Ho, Er, Yb) regions was detected.

Structure **31**



31

h. Lanthanide β-diketonates in sol–gel-matrices without covalent bonding

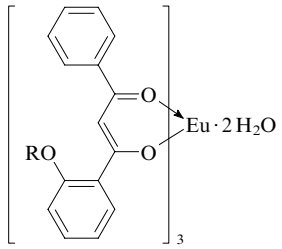
Non-functionalized β-diketones and metal β-diketonates incorporated in sol–gel matrices form no covalent bonding with the inorganic oxide network. Matthews and Knobbe[167] inserted two types of europium thenoyltrifluoroacetonate (tta) complexes, $Eu(tta)_3 \cdot 2H_2O$ and $Eu(tta)_4 \cdot pip$ (pip is piperidine), and europium chloride into silicon dioxide by acid hydrolysis of tetraethoxysilane containing a preliminarily added solution of a coordination compound or $EuCl_3$ in DMF. The sol to gel transition occurred after 9 days and the gel was slowly dried for several weeks. This was accompanied by large shrinkage and the volume of the dried gel was only 20% of the initial volume. The concentration of europium cations was 3.0×10^{18} cm^{-3}. The photoluminescence quantum yields (φ) of europium compounds $EuCl_3$, $Eu(tta)_3 \cdot 2H_2O$, and $Eu(tta)_4 \cdot pip$ in DMF solutions were 8.5%, 10.1% and

10.6%, respectively, while those in xerogels were 1.0%, 6.3% and 7.8%. The lower φ values for xerogels are attributable to partial luminescence quenching by silanol groups and crystal hydrate (especially for europium chloride) and silica gel-adsorbed water molecules.

Europium β-diketonates were inserted into the silicon dioxide matrix [168] by acid hydrolysis of a TEOS solution in methanol containing $Eu(acac)_3$, $Eu(bac)_3$, $Eu(acac)_3phen$ and $Eu(bac)_3phen$ (bac is benzoylacetone). Glasses were produced by maintaining the solutions at 60 °C for 7 days. The fluorescence excitation spectra exhibited clear-cut bands for transitions from the $^7F_0$ level to the $^5D_2$, $^5D_1$ and $^5D_0$ excited states in the europium cation. The intensity of the $^5D_0 \rightarrow {}^7F_2$ emission band for glasses with incorporated phenanthroline complexes is higher than that with complexes devoid of phenanthroline.

The covalent binding of a ligand to the silica matrix brings about an increase in the photoluminescence quantum yield.[106, 169] For the glassy xerogel obtained by co-hydrolysis of TEOS and silylated europium β-diketonate **32a**, the photoluminescence quantum yield is 2.2 times as high as that for an analogous glass in which europium complex **32b** has no covalent bonds with the silicon-and-oxygen matrix.

Structures 32

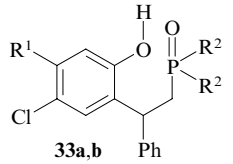


32a,b

R = $(EtO)_3Si(CH_2)_3NHC(O)$ (**a**), H (**b**)

The observed enhancement of photoluminescence is usually attributed [106, 169] to the absence or lower degree of clusterization of the complex, which prevents the concentration quenching. Fedorenko *et al.*[170] prepared ultradisperse silicon dioxide particles with incorporated europium β-diketonates by alkaline hydrolysis of aqueous ethanol solutions containing TEOS, sodium dodecyl sulfate, ammonia and europium thenoyltrifluoroacetonates of three types: (i) without neutral ligand, $Eu(tta)_3$, (ii) with phosphine oxide **33a**, $Eu(tta)_3 \cdot$(**33a**), (iii) with phosphine oxide **33b**, $Eu(tta)_3 \cdot$(**33b**).

Structures **33**



33a,b

R^1 = H, R^2 = Me (**a**);
R^1 = Me, R^2 = 2-$MeOC_6H_4$ (**b**)

The lumonophore content in aqueous ethanol media after the synthesis was $(1-5) \times 10^{-3}$ mol litre^{-1} and the particle diameter was 280–690 nm. In the photoluminescence spectra of aqueous dispersions containing 2 to 13 g litre^{-1} of colloidal particles, most intense was the $^5D_0 \rightarrow {}^7F_2$ band (612 nm) on excitation at 350 nm. The introduction of a neutral organophosphorus ligand into the complex increased the emission intensity of colloidal dispersion.

i. Lanthanide β-diketonates in hybrids with organic polymers

The base of class I organic-inorganic hybrid materials is an inorganic network ‡ (usually silicon-and-oxide network) filled with an organic polymer.[5, 17] There are no covalent bonds between the polymer molecules and the inorganic framework but hydrogen bond contacts are significant. More elastic organic polymer imparts some strength to the brittle inorganic framework, decreases opalescence, prevents crack formation and 'leaching' of the metal cation chemically bonded to silicon atoms. In materials containing luminescent lanthanide complexes, the probability of luminescence quenching by water molecules decreases due to decrease in the concentration of water on the surface of hydrophilic silicon dioxide. Thenoyltrifluoroacetone and phenyl phenacyl sulfoxide functionalized by triethoxysilyl groups were used [108, 109] in the syntheses of europium- and terbium-containing hybrid materials of this sort.

Li and Yan [108] formed the inorganic framework at a preliminary stage, thus preparing mesoporous silica SBA-16 with covalently bonded thenoyltrifluoroacetonate groups from tetraethoxysilane, compound **34** and the surfactant Pluronic F127 (PF 127). The dried silica was impregnated with a solution of the polymer in DMF, and an ethanol solution of europium nitrate was added. The polymers used include poly(methyl methacrylate) (PMMA), poly(methacrylic acid) (PMA) and polyvinylpyrrolidone (PVP). This gave an organic-inorganic hybrid in which 'europium β-diketonate' fragments were linked through spacer groups to the silicon dioxide surface. The Eu^{3+} cations also coordinate the carbonyl groups of the organic polymer and water molecules (Scheme 21).

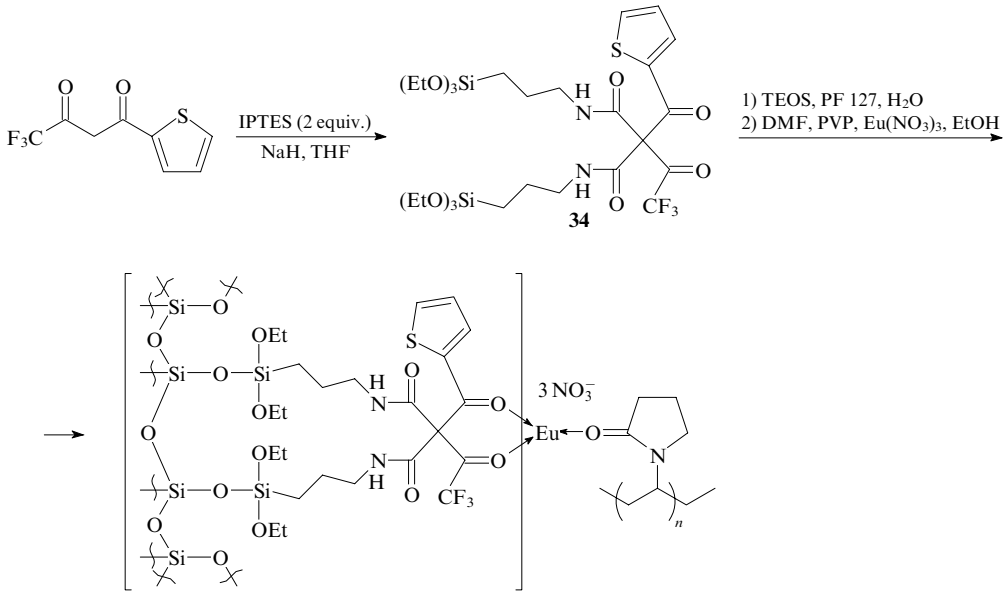
Comparative analysis of the emission spectra demonstrated that the nature of the polymer has a substantial influence on the intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ electric dipole transition band at 613 nm. This attests to changes in the local coordination environment of the europium cation on going from one polymer to another. The highest emission intensity is observed for the PVP-containing hybrid. Presumably,[108] in this case, the optimal coordination of the PVP carbonyl groups to Eu^{3+} and the highest degree of displacement of water molecules from both the metal coordination sphere and the silica surface are attained.

The assumed [108] addition of two IPTES molecules in the 3-position of thenoyltrifluoroacetone makes the general pattern of formation of the hybrid material less realistic. After the addition of isocyanate molecules, β-diketone completely loses the CH-acid properties due to the absence of a proton and cannot form the typical chelates any longer. Europium nitrate will only be able to be solvated by the carbonyl groups of the polymer and substituted β-diketone without chelation, which will considerably reduce the system stability. Also, it is known [161] that reactions of fluorinated β-diketones with IPTES are accompanied by cleavage to give urethanes.

The addition of two IPTES molecules to the sodium salt of phenyl phenacyl sulfoxide was proven by elemental analysis.[109] The formation of organic-inorganic hybrids was accomplished by hydrolysis of DMF solutions of the

‡ Class II organic-inorganic materials have strong covalent or ionic-covalent bonds between the organic and inorganic components.[5, 17]

Scheme 21



following components: TEOS, compound **7**, organic polymer, $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Eu, Tb). Polyacrylamide, PVP, PMMA and poly(ethyl methacrylate) were employed as organic polymers. The final products were obtained as monolithic blocks after storage at 80 °C for 5 days. The DMF solvent is retained in the final product, as indicated by thermogravimetric analysis (TGA) data. The mass loss starts at 170 °C and amounts to 35%–40%. The materials thus obtained demonstrate the intense cation photoluminescence of europium and terbium upon UV excitation. The lifetimes of the excited states and the emission intensity depend on the type of the organic polymer. The europium-containing organic-inorganic hybrid with PMMA has the longest lifetime (738 μs) and the highest quantum efficiency (19.6%). As in the previous case, doubly 3-substituted phenyl phenacyl sulfoxide derivative is unable to form chelates with lanthanide due to the absence of a proton.

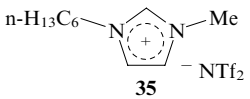
Luminescent monolithic organic-inorganic europium glasses were prepared [171] from a complex mixture of components that are cured both according to the sol–gel technique and during free radical polymerization. The sol consisting of TEOS, glycidyloxypropyltrimethoxysilane, methyl methacrylate, ethanol, water, thenoyltrifluoroacetone (or benzoyltrifluoroacetone), a neutral ligand [phenanthroline, triphenylphosphine oxide (tppo) or bipyridine] and europium chloride was cured in a plastic container at 40 °C for several days. As the catalyst for hydrolytic polycondensation, HCl was used, while free radical polymerization was initiated by benzoyl peroxide. The intensity of photoluminescence of the glasses approximately doubles if a neutral ligand is involved. The stability of the glasses to UV light was tested during 35.4 days. The highest photolytic stability was shown by the glass that incorporated the complex with tta and tppo ligands. The decrease in the luminescence intensity after 35.4 days was 44%.

Organic-inorganic hybrids can be prepared by impregnating a xerogel with a solution of the monomer and the complex followed by thermal polymerization of the monomer in the xerogel pores. For instance, in a work by Tanner *et al.*[172] microporous silica gel obtained by acid hydrolysis of TEOS was impregnated with a solution of methyl methacrylate (or ethyl methacrylate), β-diketonate $Eu(tta)_3$phen and free radical initiator (benzoyl peroxide) in DMF, and after that, MMA was polymerized by heating to 358 K. The concentration of the complex in the solution was varied from 0.05 mass % to 5.0 mass %. The organic to inorganic part ratio was from 50 : 50 to 80 : 20. The cation photoluminescence intensity was found to increase following increase in the complex concentration from 0.05% to 1.0%. According to the TGA data, the thermal stability of the PMMA–SiO_2–$Eu(tta)_3$phen composite is much higher compared with PMMA–$Eu(tta)_3$phen.

j. Lanthanide β-diketonates in ionogels

Ionogels [173] are organic-inorganic hybrids in which ionic liquids (IL) occur in the pores of the inorganic matrix (most often, silica). They can be prepared as films, powders, transparent monoliths and contain up to 80 vol.% of IL. Ionogels possess ionic conductivity, relatively high thermal stability (up to 300 °C) and a mechanical strength comparable with the strength of usual sol–gel glasses. Tetrakis(β-diketonate) derivatives of neodymium, samarium, europium, holmium, erbium and ytterbium were incorporated into the ionogels.[174, 175] The materials thus obtained were monolithic glasses composed of the organosilica matrix and IL doped with lanthanide complexes [IL is bis(trifluoromethylsulfonyl)imide 1-hexyl-3-methylimidazolium, **35**].

Structure **35**

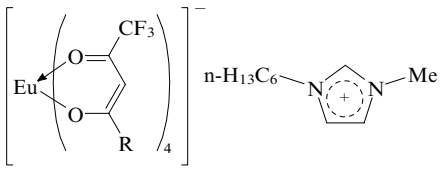


35

The organic-silica matrix was synthesized by a non-hydrolytic procedure from tetramethoxysilane, methyltrimethoxysilane, formic acid and ionic liquid **35**. After complete gel ageing (8 days), the IL was washed out by acetonitrile in the Soxhlet extraction apparatus, and the liberated gel was immediately impregnated with a solution of lanthanide complex in the same ionic liquid. Naphthoyltrifluoroacetone and thenoyltrifluoroacetone served as the β-diketonate ligands. The concentrations of the anionic complexes **36** were 0.00026–0.0033 mol litre^{-1}. Europium,

samarium and terbium sol–gel glasses show bright photoluminescence in the visible region upon UV excitation.

Structures 36



36

Ln = Eu, R is 2-naphthyl;
R is thienyl: Ln = Nd, Sm, Eu, Ho, Er, Yb

Materials containing neodymium, holmium, erbium and ytterbium cations show photoluminescence in the near-IR region. Analysis of the emission and excitation spectra attests to a quite minor influence of the organosilicate base on the lanthanide β-diketonate dissolved in an ionic liquid.

3. Preparation of tin dioxide ionogels from tin alkoxy-β-diketonates

Semitransparent monolithic tin dioxide ionogels were prepared [176] by hydrolysis of di(*tert*-pentyloxy)di(acetylacetonato)tin on treatment with water in acetonitrile containing ionic liquid with a 1-butyl-3-methylimidazolium cation [chloride, bromide, bis(trifluoromethylsulfonylimide) and tetrafluoroborate]. Tin alkoxyacetylacetonate is the most convenient monomer for the preparation of monolithic gels due to the low rate of hydrolysis. Under the conditions used, the gel was formed after 4 days. The specific surface area of xerogels after washing out of the IL by acetonitrile varied in the range of 240–375 $m^2\ g^{-1}$, the pore diameter was 2–5 nm and the total pore volume was 0.11–0.19 $cm^3\ g^{-1}$ depending on the IL. Tin dioxide ionogels are considered [176] to be promising electrolyte materials for dye-sensitized solar cells.[177]

4. Practical applications of sol–gel materials incorporating β-diketonates

a. Optical sol–gel waveguides and light pulse amplifiers

The necessity for faster and faster data transfer calls for progress of telecommunication technologies. As information transfer media, both electrical pulses, which propagate along copper wires, and light pulses, which propagate along fibre-optic communication lines, are used. The use of light radiation instead of the electrical pulse increases the transfer rate to 10^6 bps. Optical cables consist of a transparent core and transparent cladding having lower refractive index than the core. In this case, light radiation remains inside the core and travels by long distances. Polymeric optical fibres manufactured from transparent poly(methyl methacrylates), polystyrenes and polycarbonates have proved themselves as good waveguides. They are cheaper in manufacturing and have more flexible core with easily controllable diameter as compared with inorganic glasses. In order to increase the distances by which the optical signal travels and make up for the energy losses, an optical amplifier is required.[178] In modern telecommunication facilities, light signal is transferred in the wavelength range of 1.3–1.6 μm (1300–1600 nm),[178] which coincides with the minimum absorption (maximum transmission) of quartz fibre. In 1987, light enhancement effect in quartz fibre-optic light guide doped with erbium cations was established.[179] The operation principle was based on the light amplification phenomenon at stimulated radiation and is similar to laser generation.[180] The possibility of light amplification in erbium cation-doped light guides is due to the ability of this lanthanide to emit light in the wavelength range of 1520–1570 nm,[179] which coincides with the telecommunication wavelength. Researchers who work with organic and organic-inorganic materials keep in sight the goal of solving a similar task, which can be formulated as to design an organic-inorganic hybrid or polymeric organic waveguide doped with an erbium complex capable of effective emission at wavelength of about 1500 nm and amplification effect on pumping with a semiconductor laser at 980 nm.[181] A large body of data on the production of lanthanide-doped polymers and formation of waveguides and amplifiers from them have been reported. The latest achievements in this area were analyzed in a review.[181] However, there are few examples of using sol–gel materials for this purpose.

Polymeric fibre is formed by forcing a high-viscosity polymer solution through a fine orifice (extrusion nozzle). A well known rule is employed [182] stating that the destruction of a thread flowing under pressure from a fine orifice is substantially retarded for viscous liquids as compared with the same process for low-viscosity liquids. The viscosity of a silicon dioxide sol increases upon ageing. The aged high-viscosity sol is rather rapidly transformed into a gel. This feature was used [183] for spinning a transparent optical fibre by forcing a silicon dioxide sol through a nozzle followed by gelling, ageing and drying of the fibre. This gave 20 to 200 μm sol–gel fibres doped with luminescent organic dyes with optical losses of up to 60 dB m^{-1}.

Photopolymerizing compositions have the best prospects for the design of optical integrated circuits. They can be used to form both passive (waveguides, splitters) and active (amplifiers) integrated-circuit components by means of thoroughly elaborated photolithography techniques. In the latter case, suitable photopolymerizing compositions should contain a generating component. This role can be performed by lanthanide complexes having narrow emission bands.

The design of planar optical waveguides by photolitography from sol–gel compositions consisting of TEOS, methyltrimethoxysilane and 3-methacryloyloxypropyl(trimethoxy)silane was reported.[184, 185]

Signal amplification at the telecommunication wavelength of 1550 nm in the planar optical waveguide was attained [186] by doping a sol–gel composition with erbium β-diketonate. The device was formed on a standard silicon plate. The 9 μm-thick buffer layer with a refractive index of 1.471 was deposited by a three-times immersion of the plate into a solution of the methyltrimethoxysilane sol and drying at 120 °C. The next 2 μm-thick active layer of the waveguide was formed from a solution of colloidal silica stabilized by tripropylene glycol diacrylate with particle size of 25 nm in methyldiethoxysilane containing 1.6 mass % of erbium tris(acetylacetonate) and 2.5 mass % of the photoinitiator Irgacure 819. The layer was dried at 90 °C for 15 min. The upper protecting layer of 2.5 μm thickness was deposited similarly to the buffer layer from a solution of the methyltrimethoxysilane sol. The waveguide structure was printed on irradiation of the obtained sandwich with a mercury lamp by the contact method *via* a mask. This gave a waveguide with a 2.5 cm length and 2 to 10 μm width. Amplification of the signal at 1550 nm was achieved by

diode laser pumping at 980 nm. The 2×4 μm waveguide was monomodal at 1550 nm and multimodal at 1300 nm.

b. Sol–gel materials for optical gas sensors and molecular thermometers

Boron difluoride β-diketonate linked to the surface of silicon dioxide particles *via* sulfanylpropyl(methyl)dimethoxysilane groups was proposed for the manufacture of an optical gas sensor sensitive to low concentrations of benzene, toluene and xylene (BTX) vapours in air.[187] Scheme 22 shows the preparation of the β-diketone (1-phenyl-3-tolylpropane-1,3-dione) and boron difluoride β-diketonate, fuctionalization of the latter with the organosilicon thiol and chemical binding to the surface of hydroxylated silica. The operation principle of the optical sensor is based on the ability of silica gel-immobilized dibenzoylmethane boronate (DBMB) to form exciplexes with BTX [188, 189] when they are sorbed from the gas phase. When BTX vapour appears in air, fluorescence quenching by DBMB and simultaneous build-up of exciplex luminescence are observed. The change in the photoluminescence spectrum upon sorption of BTX vapour includes a decrease in the intensity of the DBMB emission band at 425 nm and an increase in the emission intensity of the DBMB·BTX exciplex at 490–500 nm.

The sol–gel glasses based on vinyltriethoxysilane doped with europium and terbium hexafluoroacetylacetonates (hfac), $Eu(hfac)_3(tppo)_2$ and $Tb(hfac)_3(tppo)_2$ (tppo is triphenylphosphine oxide) were used [190] to develop a luminescent molecular thermometer. The colour of the luminescence of glasses varies from orange at 10 K to red at 293 K. Measurement of the photoluminescence spectra demonstrated that the efficiency of energy transfer from the terbium cation to the europium cation is appreciably temperature dependent. At low temperatures, the intensities of terbium green luminescence and europium red luminescence are approximately equal. As the temperature is raised to 293 K, the luminescence of terbium almost disappears due to the transfer of the electron excitation energy from the terbium to europium complex by the Förster mechanism.[191] Sol–gel materials doped with $(Eu/Tb)(hfac)_3(tppo)_2$ are useful as temperature sensors and thermally sensitive fibre-optic sensors.

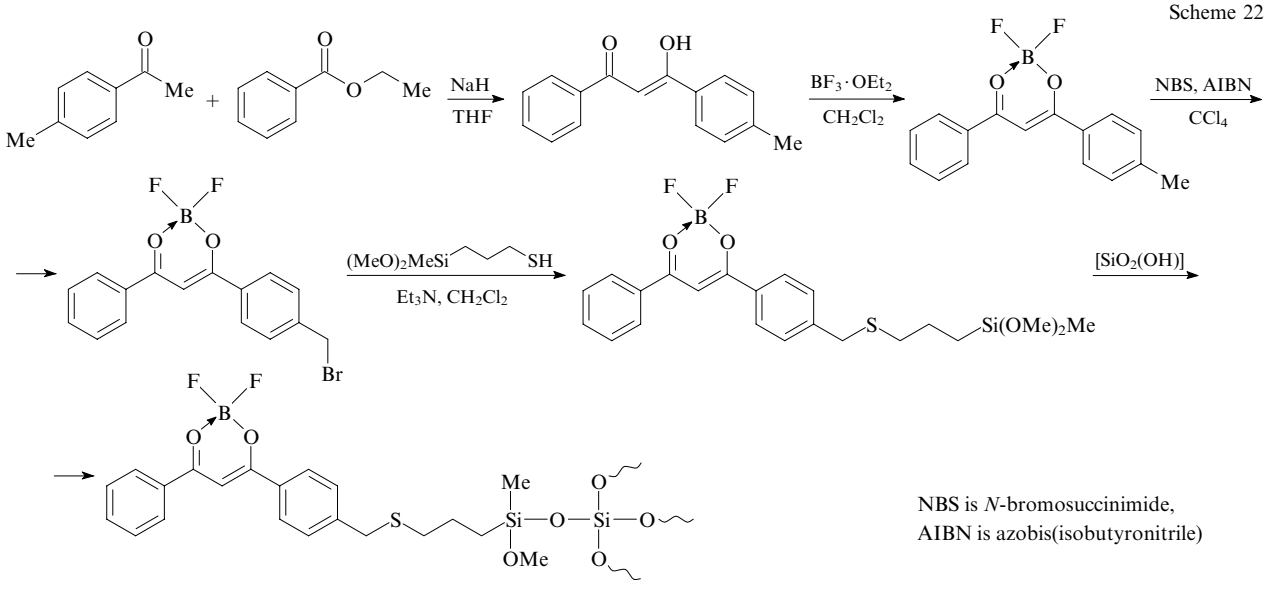
c. Preparation of micro- and mesoporous tin dioxide using β-diketones

Tin dioxide is an n-type wide-band-gap semiconductor; it finds use in photocatalysis, solar power production, as anode material in lithium cells and as a transparent conducting electrode. It is used most widely [192, 193] as a material of thin-film gas sensors for hydrogen, methane, carbon dioxide, nitrogen oxides and so on. The sensor properties depend on the thin film morphology. The SnO_2 surface has high adsorption properties and reactivity; its electrical conductivity is highly sensitive to the state of the surface. As the size of nanoparticles forming the film structure decreases, the sensitivity of the sensor substantially increases. The optimal size that ensures high sensitivity and stability of the device is considered [194, 195] to be 5–7 nm. The use of magnetron sputtering, pyrolysis of aerosols (spray pyrolysis) or chemical vapour deposition gives rise to microcrystalline layers with a small specific surface area. Deposition of solutions of tin dioxide sols obtained by hydrolytic polycondensation of tin chloride and alkoxides onto the substrate also gives thin films with insufficiently small particle size. Mixed tin chloro- and alkoxy-β-diketonates can be used to prepare highly porous tin dioxide xerogels and sols, which can be used successfully for the formation of thin films with required parameters that ensure high stability and sensitivity of sensors.

Briois *et al.*[194] studied the effect of acetylacetone additives on the hydrolysis of $SnCl_4 \cdot 5H_2O$ in ethyl alcohol at two temperatures: room temperature and 70 °C. After thermal hydrolysis, the solution was found to consist of SnO_2 nanoparticles (~2 nm size) and soluble polynuclear tin compounds. When Hacac : Sn > 2, tin β-diketonate $[Sn(acac)Cl_3(H_2O)] \cdot H_2O$ is formed; it was isolated from the solution and characterized by X-ray diffraction. The Hacac : Sn ratio in the solution affects only the rate of hydrolytic polycondensation, whereas the SnO_2 crystalline size remains roughly the same.

Nanocrystalline mesoporous tin dioxide was prepared [195] by hydrolysis of (*tert*-pentyloxy)di(acetylacetona-

Scheme 22



NBS is *N*-bromosuccinimide,
AIBN is azobis(isobutyronitrile)

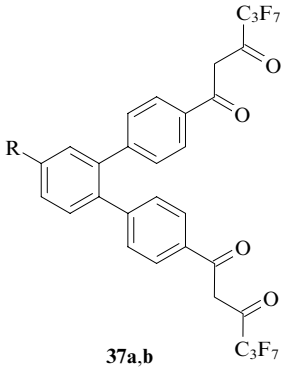
to)tin in acetonitrile followed by heat treatment at 400–500 °C. Depending on the $Sn:H_2O$ ratio and on the annealing temperature, the specific surface area of xerogels varied from 50 to 150 $m^2\ g^{-1}$, the pore size was 4.5 to 10 nm and the average particle size was 60 to 180 nm. The synthesized powders were proposed for the use as semiconductor oxide materials in dye-sensitized photovoltaic devices.[195]

The electrical conductivity of tin dioxide substantially increases[196] and becomes commensurable with the conductivity of indium–tin oxide upon doping with fluorine (3 at.%). Fluorine-containing xerogels were prepared from tin alkoxy(fluoro)-β-diketonates $Sn(OAlk)F(\beta\text{-dik})_2$, which were, in turn, synthesized[197] by disproportionation of tin dialkoxybis(β-diketonates) $(RO)_2Sn(\beta\text{-dik})_2$ and tin difluorobis(β-diketonates) $F_2Sn(\beta\text{-dik})_2$.

d. Europium β-diketonates in time-resolved fluorescence immunoassay

Time-resolved fluorescence immunoassay (TRFIA) is among the most sensitive and accurate immunoassay techniques.[198–200] It is based on detection of antigens by means of antibodies. Antibodies are labelled by a fluorescent complex and applied on the specimen. If it contains antigens, the labelled antibodies add to it to form a conjugate, which can be subsequently detected by the presence of fluorescence. Methods that use lanthanide ions, in particular, europium and terbium, have currently found the most extensive practical use for instant diagnosis of infectious diseases.[201–203] The sensitivity is increased by means of detection of 'pure' cation-centred luminescent label chemically bonded to the polypeptide chain. By the time of detection of the lanthanide cation emission, the background fluorescence of proteins, organic compounds and materials of the cell has been completely quenched. Fluorescence of the protein and organic molecules has a relaxation time of 10^{-8}–10^{-9} s, whereas the lifetime of the lanthanide excited state is 10^{-3}–10^{-6} s. This difference provides a way for complete elimination of the background luminescence and for considerable increase in the sensitivity of the method. The europium concentration determined by time-resolved fluorescence spectroscopy is 10^{-14} mol $litre^{-1}$. The use of dyes for luminescence-based diagnosis of pathological processes in the body seems less informative than the use of lanthanide complexes as probes. Europium and terbium complexes are the best and most widely used luminescent labels. A major problem associated with this method is the necessity of chemical bonding between the luminescent complex and the protein molecule. There exist quite a limited number of organic groups able to react with polypeptide chain fragments under conditions of analytical operations. Examples of using isothiocyanate derivatives and benzenesulfonyl chloride are known.[198–200] The fragments are introduced into the chelating ligand by organic synthesis techniques. A europium (or terbium) complex is either formed during the analysis of the biological specimen or is synthesized beforehand. Luminescent labels containing primary amino groups are linked to the protein molecule by means of glutaradehyde [$OHC(CH_2)_3CHO$]. By now, β-diketones and their complexes only with primary amino groups[204] and chlorosulfonic groups[205] have been obtained.

Structure **37**

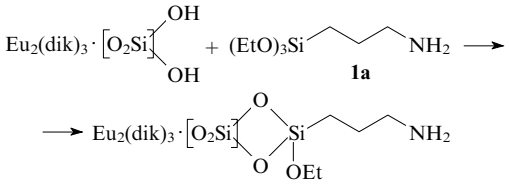


37a,**b**

R = H (**a**), SO_2Cl (**b**)

Ye and co-workers[206, 207] proposed two processes for sol–gel preparation of silica nanoparticles containing encapsulated europium β-diketonate and surface NH_2 groups. Two β-diketones were used, one without (**37a**) and one with (**37b**) a chlorosulfonic functional group. According to one process,[206] nanoparticles were formed in a microemulsion containing TEOS, H_2O (or D_2O), NH_4OH, emulsifier Triton X-100, alcohol (n-hexyl, n-heptyl or n-octyl alcohol), cyclohexane and europium β-diketonate, preliminarily synthesized from non-functionalized β- diketone. The nanoparticles thus obtained were dried and heated in a toluene solution with APTES. Thus, surface hydroxyl groups were replaced by amino groups (Scheme 23). The nanoparticle size (29–38 nm) and the lifetimes of excited states (254–296 μs) depended on the alcohol used and the type of the aqueous phase (H_2O or D_2O).

Scheme 23

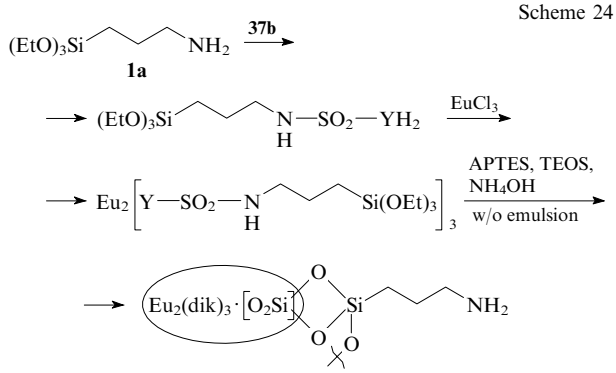


dik is deprotonated ligand **37a**

According to the second method,[207] europium β-diketonate with triethoxysilyl substituents was prepared *in situ* by the reaction of functionalized β-diketone with APTES and europium chloride. Presumably, two reactions take place: the addition of APTES at the chlorosulfonic group and the formation of europium chelate. Nanoparticles are formed in a water–oil (w/o) microemulsion, which contains APTES bonded to the fluorescent europium chelate, free APTES, TEOS, Triton X-100, n-octanol, water and cyclohexane (Scheme 24). Ammonium hydroxide was used as the catalyst. This gave stable spherical (36 nm in diameter) highly fluorescent nanoparticles with fluorescence quantum yield of 50% and a lifetime of the excited state of 370 μs.

The silica nanoparticles have amino groups on the surface through which they are linked to the protein and the protein is labelled.

Scheme 24



$YH_2 = C_6H_3[C_6H_4C(O)CH_2C(O)C_3F_7\text{-}4]_2\text{-}3,4$; dik = $YSO_2NH(CH_2)_3$

V. Conclusion

Organic-inorganic hybrid materials combine properties of both inorganic and organic components. The final material cannot surpass the components in particular characteristics. Indeed, the thermal stability of a hybrid is lower than that of the purely silica matrix; however, it is almost in all cases considerably higher than that of the organic component not incorporated in the silica framework. During recent years, lots of useful materials with enhanced characteristics have been obtained by the sol–gel technique. More and more organic compounds, oligomers and polymers are being involved in this field of technology. The information presented in this review may serve as a spectacular example of using an important class of organic compounds, β-diketones, in the sol–gel processes. The interest in this class of organic compounds is caused to a large extent by their unique properties as rather popular ligands in the coordination chemistry.

A substantial progress in the sol–gel chemistry was achieved owing to the recently discovered method for the preparation of mesoporous silicas [208] from tetraethoxysilane in the presence of surfactants. Very soon a variety of silicon, tin, titanium, zirconium and other element alkoxides and monomers $(RO)_3MR'$ functionalized by organic groups were involved in this sphere.[3–5, 17, 25–30] Considerable advances were made [209, 210] in the field of preparation of transparent sol–gel glass monoliths. Methods have been developed to avoid the main difficulties in their production — crack formation and turbidity. Practical implementation of supercritical drying extended the scope of applicability of sol–gel techniques and enabled the preparation [211, 212] of highly porous aerogels. The remarkable properties of organofluorine compounds also did not escape the attention of researchers. Currently, a substantial portion of sol–gel techniques [6–8, 213] deal with fluorinated organosilicon monomers $(RO)_3MR^F$ and $(R^FO)_3MR^F$. Phosphorus compounds are also used [35, 62, 214–216] in this area. Mixed phosphorosilicates are applied as acid catalysts and ionic conductors. Nano-sized silicate films obtained by the sol–gel technique are utilized [217] in the planar technology of manufacture of semiconductor gas sensors.

As was to be expected, most of the present data refer to silicon alkoxide derivatives, which is caused by ready availability, low cost of monomers of this class and great practical experience accumulated during more than hundred years of using alkoxysilanes. Noteworthy is the special role, in the sol–gel technology, of a carbofunctional monomer, 3-aminopropyltriethoxysilane, which is industrially manufactured by several western companies [218] and was also produced in the USSR.[219] Among the offered carbofunctional trialkoxysilanes, APTES is most readily available due to its relatively low cost. As a result of known transformations of the primary amino group, this monomer is suitable for introducing a different functional group into the organic fragment, as was demonstrated in this paper in relation to the reaction of APTES with acetylacetone [121–123] and dibenzoylmethane.[125] Direct reactions with metal chlorides [55] and carbonyls [220] provide the synthesis of metal-containing monomers.

References

1. N N Khimich *Fiz. Khim. Stekla* **30** 586 (2004) [a]
2. L L Hench, J K West *Chem. Rev.* **90** 33 (1990)
3. R J P Corriu *Angew. Chem., Int. Ed.* **39** 1376 (2000)
4. A B Wojcik, L C Klein *Appl. Organomet. Chem.* **11** 129 (1997)
5. R J P Corriu, W E Douglas, in *Silicon-Based Polymers: the Science and Technology of Their Synthesis and Applications* (Eds R G Jones, W Ando, J Choinowski) (Dordrecht: Kluwer Academic, 2000) p. 667
6. B Ameduri, B Boutevin, J J E Moreau, H Moutaabbid, M W C Man *J. Fluorine Chem.* **104** 185 (2000)
7. E Yu Ladilina, T S Lyubova, V V Semenov, A I Kirillov, D V Skamnitskii, A P Kasatkin, S A Lermontova, O N Gorshkov, M E Shenina *Fiz. Khim. Stekla* **38** 440 (2012) [a]
8. E Yu Ladilina, T S Lyubova, V V Semenov, A Yu Dolgonosova, M A Baten'kin *Vysokomol. Soedin., Ser. A* **53** 189 (2011) [b]
9. L M Khananashvili *Khimiya i Tekhnologiya Elementoorganicheskikh Monomerov i Polimerov* (The Chemistry and Technology of Organoelement Monomers and Polymers) (Moscow: Khimiya, 1998)
10. P V Ivanov, V I Maslova, N M Buzyreva, N G Mazhorova, D N Golubykh, L V Kostikova, A S Mozzhukhin, E A Chernyshev *Ros. Khim. Zh.* **42** (6) 87 (1998) [c]
11. V M Kopylov, L M Khananashvili, O V Shkol'nik, A G Ivanov *Vysokomol. Soedin., Ser. A* **37** 394 (1995) [b]
12. R J P Corriu, J J E Moreau, M W C Man *J. Sol-Gel Sci. Technol.* **2** 87 (1994)
13. M G Voronkov, E A Maletina, V K Roman *Geterosiloksany* (Heterosiloxanes) (Novosibirsk: Nauka, 1984)
14. M M Levitsky, B G Zavin, A N Bilyachenko *Russ. Chem. Rev.* **76** 847 (2007)
15. R Murugavel, A Voigt, M Ganapati, H W Roesky *Chem. Rev.* **96** 2205 (1996)
16. I B Slinyakova, T I Denisova *Kremniiorganicheskie Adsorbenty. Poluchenie, Svoistva, Primenenie* (Organosilicon Adsorbents. Synthesis, Properties and Applications) (Kiev: Naukova Dumka, 1988)
17. C Sanchez, F Ribot *New J. Chem.* **18** 1007 (1994)
18. R J P Corriu, D Leclercq *Comments Inorg. Chem.* **19** 245 (1997)
19. U Schubert *New J. Chem.* **18** 1049 (1994)
20. R J P Corriu, D Leclercq *Angew. Chem., Int. Ed. Engl.* **35** 1420 (1996)
21. M Andrianainarivelo, R Corriu, D Leclercq, P H Mutin, A Vioux *J. Mater. Chem.* **6** 1665 (1996)
22. S Acosta, P Arnal, R J P Corriu, D Leclercg, P H Mutin, A Vioux, in *Better Ceramics through Chemistry. VI (Mater. Res. Soc. Symp. Proc.) San Francisco, CA, 1994* Vol. 346, p. 43
23. A Vioux *Chem. Mater.* **9** 2292 (1997)

24. L Bourget, R J P Corriu, D Leclercq, P H Mutin, A Vioux *J. Non-Cryst. Solids* **242** 81 (1998)
25. U Schubert *J. Chem. Soc., Dalton Trans.* 3343 (1996)
26. U Schubert, N Hüsing, A Lorenz *Chem. Mater.* **7** 2010 (1995)
27. D A Loy, K J Shea *Chem. Rev.* **95** 1431 (1995)
28. D Avnir, L C Klein, D Levy, U Schubert, A B Wojcik, in *Chemistry of Organic Silicon Compounds* Vol. 2 (Eds Y Apeloig, Z Rappoport) (Chichester: Wiley, 1998) p. 2317
29. G Cerveau, R J P Corriu *Coord. Chem. Rev.* **180** 1051 (1998)
30. R J P Corriu *Polyhedron* **17** 925 (1998)
31. A D Pomogailo *Russ. Chem. Rev.* **69** 53 (2000)
32. A A Stryuchenko, E V Zakharchenko *Keramicheskie Formy v Tochnom Lit'e po Postoyannym Modelyam* (Ceramic Moulds in Precision Casting on Permanent Moulds) (Moscow: Mashinostroenie, 1988)
33. A N Bushuev, L M Terman, V V Semenov, L N Bushueva *Tekhnol. Sudostr.* (11) 40 (1988)
34. A N Fedoseev, E N Lebedev, A I Gorbunov, G A Dubrovskaya, V V Popov, M V Zaitseva *Poluchenie i Primenenie Gidrozolei Dioksida Kremniya (Obzornaya Informatsiya. Seriya 'Elementoorganicheskie Soedineniya i ikh Primenenie')* [Synthesis and Use of Hydrosols of Silicon Dioxide (Review Information. Series 'Organoelement Compounds and Their Applications')] (Moscow: NIITEKhIM, 1987)
35. V V Semenov *Lakokras. Mater. Primenenie* (7) 40 (2011) [d]
36. S A Demakhin, A G Demakhin *Selektivnye Metody Izolyatsii Vodopritoka v Neftyanye Skvazhiny* (Selective Water Shutoff in Oil Wells) (Saratov: Izd. GosUNTs 'Kolledzh,' 2003)
37. M G Miller, A S Shapatin, I V Demidov, S N Bastrikov, in *Andrianovskie Chteniya po Khimii Kremniiorganicheskikh Soedinenii* (Andrianov Reading on Chemistry of Organosilicon Compounds, Moscow, 1995) p. 83
38. E A Ryabenko *Vysokochist. Veshchestva* (1) 7 (1993)
39. P A Storozhenko, in *Teoreticheskaya, Sinteticheskaya, Biologicheskaya i Prikladnaya Khimiya Elementoorganicheskikh Soedinenii (Mater. Simpoziuma, Posvyashchennogo 90-letiyu Akad. M G Voronkova)* [Theoretical, Synthetic, Biological and Applied Chemistry of Organoelement Compounds (Proceedings of Symposium Devoted to the 90th Anniversary of the Academician M G Voronkovon), St Petersburg, 2011] p. 21
40. E P Bochkarev, N L Opolchenova, V D Savin, R I Tsanava *Vysokochist. Veshchestva* (1) 73 (1989)
41. T G Khonina, E V Shadrina, A A Boyko, O N Chupakhin, L P Larionov, A A Volkov, V D Burda *Russ. Chem. Bull., Int. Ed.* **59** 75 (2010) [*Izv. Akad. Nauk, Ser. Khim.* 76 (2010)]
42. *Meditsinskaya Khimiya i Klinicheskoe Primenenie Dioksida Kremniya* (Medical Chemistry and Clinical Application of Silicon Dioxide) (Ed. A A Chuiko) (Kiev: Naukova Dumka, 2003)
43. M G Voronkov, N N Vlasova, Yu N Pozhidaev *Appl. Organomet. Chem.* **14** 287 (2000)
44. Yu A Shchipunov, T Yu Karpenko, I Yu Bakunina, Y V Burtseva, T N Zvyagintseva *J. Biochem. Biophys. Methods* **58** 25 (2004)
45. A B Yaroslavtsev, Yu A Dobrovolsky, N S Shaglaeva, L A Frolova, E V Gerasimova, E A Sanginov *Russ. Chem. Rev.* **81** 191 (2012)
46. K Binnemans *Chem. Rev.* **109** 4283 (2009)
47. T D De Morias, F Chaput, J P Boilot, K Lahlil, B Darracq, Y Levy *C.R. Acad. Sci.: Ser. IV. Phys., Astrophys.* **1** 479 (2000)
48. T S Pozdeeva, E Yu Ladilina, V V Semenov, A A Babin, V N Burenina, G A Domrachev *Dokl. Akad. Nauk* **415** 504 (2007) [e]
49. B B Troitskii, Yu A Mamaev, A A Babin, V N Denisova, M A Novikova, L V Khokhlova, T I Lopatina *Zh. Prikl. Khim.* **82** 935 (2009) [f]
50. H-h Li, S Inoue, D Ueda, K-i Machida, G-y Adachi *Electrochem. Solid State Lett.* **2** 354 (1999)
51. T Jin, S Inoue, S Tsutsumi, K-i Machida, G-yAdachi *Chem. Lett.* 171 (1997)
52. O S Wolfbeis *J. Mater. Chem.* **15** 2657 (2005)
53. A B Seddon, in *Sol-Gel and Polymer Photonic Devices (Critical Reviews of Optical Science and Technology. CR68)*, San Diego, CA, 1999 p. 143
54. R-J Jeng, L-H Jan, R-H Lee *J. Macromol. Sci., Part A: Pure Appl. Chem.* **38** 821 (2001)
55. V V Semenov, N F Cherepennikova, M A Lopatin, L G Klapshina, T G Mushtina, S Ya Khorshev, G A Domrachev, U E Duglas, B A Bushuk, A I Rubinov, S B Bushuk *Koord. Khim.* **28** 423 (2002) [g]
56. B Darracq, F Chaput, K Lahlil, J-P Boilot, Y Levy, V Alain, L Ventelon, M Blanchard-Desce *Opt. Mater.* **9** 265 (1998)
57. D Levy *Chem. Mater.* **9** 2666 (1997)
58. K S Lam, D Lo *Appl. Phys. B: Lasers Opt.* **66** 427 (1998)
59. O A Kholdeeva, N N Trukhan *Russ. Chem. Rev.* **75** 411 (2006)
60. A D Pomogailo, A S Rozenberg, I E Uflyand *Nanochastitsy Metallov v Polimerakh* (Metal Nanoparticles in Polymers) (Moscow: Khimiya, 2000)
61. A S Sinitskii, A V Knot'ko, Yu D Tret'yakov *Neorg. Mater.* **41** 1336 (2005) [h]
62. I N Tsvetkova, O A Shilova, M G Voronkov, Yu P Gomza, K M Sukhoi *Fiz. Khim. Stekla* **34** 88 (2008) [a]
63. V M Peshkova, N V Mel'chakova *β-Diketony. Analiticheskie Reagenty* (β-Diketones. Analytical Reagents) (Moscow: Nauka, 1986)
64. P A Vigato, V Peruzzo, S Tamburini *Coord. Chem. Rev.* **253** 1099 (2009)
65. K I Pashkevich, V I Filyakova, V G Ratner, O G Khomutov *Russ. Chem. Bull. (Engl. Transl.)* **47** 1239 (1998) [*Izv. Akad. Nauk, Ser. Khim.* 1279 (1998)]
66. K I Pashkevich, V I Saloutin, I Ya Postovskii *Russ. Chem. Rev.* **50** 180 (1981)
67. O Ya Neiland, Ya P Stradyn', E A Silin'sh *Stroenie i Tautomernye Prevrashcheniya β-Dikarbonil'nykh Soedinenii* (Structure and Tautomeric Transformations of β-Dicarbonyl Compounds) (Riga: Zinatne, 1977)
68. *Problemy Khimii i Primeneniya β-Diketonatov Metallov* (The Problems of Chemistry and Application of Metal β-Diketonates) (Ed. V I Spitsyn) (Moscow: Nauka, 1982)
69. *Teoreticheskaya i Prikladnaya Khimiya β-Diketonatov Metallov* (Theoretical and Applied Chemistry of Metal β-Diketonates) (Eds V I Spitsyn, L I Martynenko) (Moscow: Nauka, 1985)
70. *β-Diketonaty Metallov* (Metal β-Diketonates) (Ed. L I Martynenko) (Vladivostok: Far Eastern Federal University, 1990)
71. S V Eliseeva, J-C G Bünzli *Chem. Soc. Rev.* **39** 189 (2010)
72. M E Sokolov, I N Arkhipova, F A Kolokolov, V A Volynkin, V T Panyushkin *Zh. Obshch. Khim.* **80** 1585 (2010) [i]
73. *Organic Reactions* (Ed. R Adams) Vol. 8 (New York: Wiley, 1954)
74. D J Otway, W S Rees Jr *Coord. Chem. Rev.* **210** 279 (2000)
75. R M Manyik, F C Frostick Jr, J J Sanderson, C R Hauser *J. Am. Chem. Soc.* **75** 5030 (1953)
76. T Sasaki, A Nakanishi, M Ohno *J. Org. Chem.* **47** 3219 (1982)
77. C Wiles, P Watts, S J Haswell, E Pombo-Villar *Tetrahedron Lett.* **43** 2945 (2002)
78. S B Meshkova, Z M Topilova, V S Matiichuk, N T Pokhodylo, I P Kovalevskaya, I M Rakipov, P G Doga *Koord. Khim.* **37** 305 (2011) [g]
79. L Li, P Cai, D Xu, Q Guo, S Xue *J. Org. Chem.* **72** 8131 (2007)
80. B Štephane *Org. Lett.* **12** 2900 (2010)
81. M Sada, S Matsubara *J. Am. Chem. Soc.* **132** 432 (2010)

82. K Sato, S Yamazoe, R Yamamoto, S Ohata, A Tarui, M Omote, I Kumadaki, A Ando *Org. Lett.* **10** 2405 (2008)
83. I S Voloshanovskii, O V Shevchenko, A S Berezhnitskaya, E A Krasnova *Ukr. Khim. Zh.* **67** 5 (2001) [j]
84. B Marciniec *Silicon Chem.* **1** 155 (2002)
85. J P English, J H Clark, J W Clapp, D Seeger, R H Ebel *J. Am. Chem. Soc.* **68** 453 (1946)
86. I E Uflyand, I A Il'chenko, A G Starikov, V N Sheinker, A D Pomogailo *Bull. Acad. Sci. USSR. Div. Chem. Sci. (Engl. Transl.)* **39** 388 (1990) [*Izv. Akad. Nauk, Ser. Khim.* 451 (1990)]
87. I S Voloshanovskii, T D Butova, O V Shevchenko *Zh. Obshch. Khim.* **69** 1504 (1999) [i]
88. I Ponticello, R L Furman *J. Polym. Sci., Part A: Polym. Chem.* **12** 985 (1974)
89. G E Southard, G M Murray *J. Org. Chem.* **70** 9036 (2005)
90. A R Katritzky, N K Meher, S K Singh *J. Org. Chem.* **70** 7792 (2005)
91. J H Olivier, J Harrowfield, R Ziessel *Chem. Commun.* **47** 11176 (2011)
92. A I Petryanina, N G Didkovskii, A V Dogadina, B I Ionin *Zh. Obshch. Khim.* **76** 1581 (2006) [i]
93. *Methoden der Organischen Chemie (Houben-Weyl) Ketone II* Bd. 7/2a, 2b, 2c (Stuttgart: Georg Thime Verlag, 1976)
94. S N Pod'yachev, S V Bukharov, I A Litvinov, V I Morozov, A T Gubaidullin, G N Nugumanova, N A Mukmeneva *Zh. Obshch. Khim.* **74** 1775 (2004) [i]
95. M Rueping, B Y Nachtsheim, A Kuenkel *Org. Lett.* **9** 825 (2007)
96. G-W Wang, Y-B Shen, X-L Wu *Eur. J. Org. Chem.* 4999 (2008)
97. J T Adams, C R Hauser *J. Am. Chem. Soc.* **67** 284 (1945)
98. F Ramirez, S B Bhatia, A V Patwardhan, C P Smith *J. Org. Chem.* **32** 3547 (1967)
99. S Komiya, A Yamamoto, T Yamamoto *Chem. Lett.* 193 (1981)
100. V V Semenov, N F Cherepennikova, L G Klapshina, I S Grigoriev, B A Bushuk, S B Bushuk, Y A Kalvinkovskaya, W E Douglas *Mendeleev Commun.* 239 (2006)
101. V V Semenov, N F Cherepennikova, I S Grigor'ev, L G Klapshina, O V Kuznetsova, M A Lopatin, B A Bushuk, S B Bushuk, Yu A Kal'vinkovskaya, V E Duglas *Koord. Khim.* **33** 70 (2007) [g]
102. E I Kostyleva, T I Rybkina, V M Kopylov, in *Teoreticheskaya, Sinteticheskaya, Biologicheskaya i Prikladnaya Khimiya Elementoorganicheskikh Soedinenii (Mater. Simpoziuma, Posvyashchennogo 90-letiyu Akad. M G Voronkova)* [Theoretical, Synthetic, Biological and Applied Chemistry of Organoelement Compounds (Proceedings of Symposium Devoted to the 90th Anniversary of the Academician M G Voronkovon), St Petersburg, 2011] p. 70
103. W Rupp, N Hüsing, U Schubert *J. Mater. Chem.* **12** 2594 (2002)
104. M Puchberger, W Rupp, U Bauer, U Schubert *New J. Chem.* **28** 1289 (2004)
105. V V Semenov, N V Zolotareva, L G Klapshina, Yu A Kurskii, M A Lopatin, G A Domrachev *Zh. Obshch. Khim.* **79** 1447 (2009) [i]
106. X Guo, H Guo, L Fu, L D Carlos, R A Sv Ferreira, L Sun, R Deng, H Zhang *J. Phys. Chem. C* **113** 12538 (2009)
107. J H Saunders, K C Frish *Polyurethanes: Chemistry and Technology* (New York: Interscience, 1962)
108. Y Li, B Yan *Dalton Trans.* **39** 2554 (2010)
109. L Guo, B Yan, J-L Liu, K Sheng, X-L Wang *Dalton Trans.* **40** 632 (2011)
110. Yu V Smirnova, Zh A Krasnaya *Russ. Chem. Rev.* **69** 1021 (2000)
111. E J Cone, R H Garner, A W Hayes *J. Org. Chem.* **37** 4436 (1972)
112. M M Khodaei, A R Khosropour, M Kookhazadeh *Zh. Org. Khim.* **41** 1477 (2005) [k]
113. A R Khosropour, M M Khodaei, M Kookhazadeh *Tetrahedron Lett.* **45** 1725 (2004)
114. L-F Zhang, S-T Yang *Zh. Org. Khim.* **45** 25 (2009) [k]
115. D H Lee, S E Park, K Cho, Y Kim, T Athar, I M Lee *Tetrahedron Lett.* **48** 8281 (2007)
116. N S Boltacheva, V I Filyakova, V N Charushin *Zh. Org. Khim.* **41** 1483 (2005) [k]
117. V G Isakova, T S Khlebnikova, F A Lakhvich *Russ. Chem. Rev.* **79** 849 (2010)
118. V I Filyakova, D L Chizhov, E F Khmara, V N Charushin *Ros. Khim. Zh.* **53** (1) 64 (2009) [c]
119. Ya F Freimanis *Khimiya Enaminoketonov, Enaminoiminov i Enaminotionov* (The Chemistry of Enaminoketones, Enaminoimines and Enaminothiones) (Riga: Zinatne, 1977)
120. A N Kudrin, V G Vorob'ev *Aminoketony* (Aminoketones) (Moscow: Meditsina, 1970)
121. V V Semenov, N F Cherepennikova, N V Melenskova, G A Domrachev, B A Bushuk, S B Bushuk, Yu A Kal'vinkovskaya, V E Duglas *Dokl. Akad. Nauk* **412** 69 (2007) [l]
122. V V Semenov, N V Melenskova, N F Cherepennikova, Yu A Kurskii, O V Kuznetsova, M A Lopatin *Zh. Prikl. Khim.* **80** 663 (2007) [f]
123. V V Semenov, N F Cherepennikova, N V Melenskova, O V Kuznetsova, B A Bushuk, S B Bushuk, Yu A Kal'vinkovskaya, V E Duglas *Koord. Khim.* **33** 550 (2007) [g]
124. M Louloudi, K Mitopoulou, E Evaggelou, Y Deligiannakis, N Hadjiliadis *J. Mol. Catal. A: Chem.* **198** 231 (2003)
125. M Louloudi, N Khad'iliadis *Ros. Khim. Zh.* **48** (4) 30 (2004) [c]
126. V Matsura, Y Guari, J Larionova, C Guerin, A Caneschi, C Sangregorio, E Lancelle-Beltran, A Mehdi, R J P Corriu *J. Mater. Chem.* **14** 3026 (2004)
127. G Qian, M Wang *Mater. Res. Bull.* **36** 2289 (2001)
128. E Yu Ladilina, T S Lyubova, V V Semenov, Yu A Kurskii, O V Kuznetsova *Russ. Chem. Bull., Int. Ed.* **58** 1023 (2009) [*Izv. Akad. Nauk, Ser. Khim.* 990 (2009)]
129. E Yu Ladilina, V V Semenov, Yu A Kurskii, O V Kuznetsova, M A Lopatin, B A Bushuk, S B Bushuk, W E Douglas *Russ. Chem. Bull., Int. Ed.* **54** 1160 (2005) [*Izv. Akad. Nauk, Ser. Khim.* 1131 (2005)]
130. E Yu Ladilina, T S Lyubova, V V Semenov, O V Kuznetsova, A I Kirillov, V I Faerman, A Yu Dolgonosova, M A Baten'kin, M A Lopatin *Russ. Chem. Bull., Int. Ed.* **59** 590 (2010) [*Izv. Akad. Nauk, Ser. Khim.* 577 (2010)]
131. W H Green, K P Le, J Grey, T T Au, M J Sailor *Science* **276** 1826 (1997)
132. V Bekiari, P Lianos *Langmuir* **14** 3459 (1998)
133. V Bekiari, P Lianos *Chem. Mater.* **10** 3777 (1998)
134. V Bekiari, P Lianos, P Judenstein *Chem. Phys. Lett.* **307** 310 (1999)
135. R Moleski, E Stathatos, V Bekiari, P Lianos *Thin Solid Films* **416** 279 (2002)
136. E Stathatos, P Lianos, U Lavrencic-Stangar, B Orel *Adv. Mater.* **14** 354 (2002)
137. T Brankova, V Bekiari, P Lianos *Chem. Mater.* **15** 1855 (2003)
138. V de Zea Bermudez, L D Carlos, M C Duarte, M M Silva, C J R Silva, M J Smith, L Assunção, L Alcácer *J. Alloys Compd.* **275–277** 21 (1998)
139. S J L Ribeiro, K Dahmouche, C A Ribeiro, C V Santili, S H Pulcinelli *J. Sol-Gel Sci. Technol.* **13** 427 (1998)
140. V de Zea Bermudez, L D Carlos, L Alcácer *Chem. Mater.* **11** 569 (1999)
141. L D Carlos, V de Zea Bermudez, R A Sa Ferreira, L Marques, M Assuncao *Chem. Mater.* **11** 581 (1999)

142. R A Sa Ferreira, L D Carlos, R R Gonsalves, S J L Ribeiro, V de Zea Bermudez *Chem. Mater.* **13** 2991 (2001)
143. K Dohmouche, L D Carlos, V de Zea Bermudez, R A Sa Ferreira, C V Santelli, A F Craievich *J. Mater. Chem.* **11** 3249 (2001)
144. L D Carlos, R A Sv Ferreira, V de Zea Bermudez, S J L Ribeiro *Adv. Funct. Mater.* **11** 111 (2001)
145. V de Zea Bermudez, D Ostrovskii, M C Gonçalves, L D Carlos, R A Sá Ferreira, L Reis, P Jacobsson *Phys. Chem. Chem. Phys.* **6** 638 (2004)
146. V de Zea Bermudez, D Ostrovskii, S Lavoryk, M C Gonçalves, L D Carlos *Phys. Chem. Chem. Phys.* **6** 649 (2004)
147. L Fu, R A Sá Ferreira, N J O Silva, L D Carlos, V de Zea Bermudez, J Rocha *Chem. Mater.* **16** 1507 (2004)
148. L D Carlos, R A Sá Ferreira, R N Pereira, M Assunçao, V de Zea Bermudez *J. Phys. Chem. B.* **108** 14924 (2004)
149. L Fu, R A Sá Ferreira, N J O Silva, A J Fernandes, P Ribeiro-Claro, I S Gonçalves, V de Zea Bermudez, L D Carlos *J. Mater. Chem.* **15** 3117 (2005)
150. C Molina, R A Sá Ferreira, G Poirier, L Fu, S J L Ribeiro, Y Messaddeq, L D Carlos *J. Phys. Chem. C* **112** 19346 (2008)
151. P P Lima, F A A Paz, R A Sá Ferreira, V de Zea Bermudez, L D Carlos *Chem. Mater.* **21** 5099 (2009)
152. S S Nobre, X Cattoën, R A Sá Ferreira, C Carcel, V de Zea Bermudez, M W C Man, L D Carlos *Chem. Mater.* **22** 3599 (2010)
153. K S Kang, J H Kim *J. Phys. Chem. C* **112** 618 (2008)
154. A Nishimura, N Sagawa, T Uchino *J. Phys. Chem. C* **113** 4260 (2009)
155. A Nishimura, S Harada, T Uchino *J. Phys. Chem. C* **114** 2568 (2010)
156. H J Im, C Willis, A C Stephan, M D Pawel, S Saengkerdsub, S Dai *Appl. Phys. Lett.* **84** 2448 (2004)
157. H Goda, C W Frank *Chem. Mater.* **13** 2783 (2001)
158. L D Carlos, R A Sa Ferreira, V de Zea Bermudez, B Julián-López, P Escribano *Chem. Soc. Rev.* **40** 536 (2011)
159. A P Silin', A N Trukhin *Tochechnye Defekty i Elementarnye Vozbuzhdeniya v Kristallicheskom i Stekloobraznom SiO_2* (Point Defects and Elementary Excitations in Crystalline and Glassy SiO_2) (Riga: Zinatne, 1985)
160. V V Semenov, N V Zolotareva, G A Domrachev, B A Bushuk, S B Bushuk *Zh. Obshch. Khim.* **79** 1948 (2009) [i]
161. V V Semenov, N V Zolotareva, M A Lopatin, G A Domrachev *Zh. Obshch. Khim.* **80** 1439 (2010) [i]
162. V V Semenov, N V Zolotareva, V N Myakov, E Yu Ladilina, E V Lapshina, M A Lopatin, I Yu Ruskol, E I Alekseeva, S R Nanush'yan *Zh. Obshch. Khim.* **82** 1458 (2012) [i]
163. V V Semenov, N V Zolotareva, B I Petrov, Yu A Efimova, G A Domrachev *Koord. Khim.* **34** 791 (2008) [g]
164. K Binnemans, P Lenaerts, K Driesen, C Görller-Walrand *J. Mater. Chem.* **14** 191 (2004)
165. J Feng, W-Q Fan, S-Y Song, Y-N Yu, R-P Deng, H-J Zhang *Dalton Trans.* **39** 5166 (2010)
166. P Lenaerts, A Storms, J Mullens, J D Haen, C Görller-Walrand, K Binnemans, K Driesen *Chem. Mater.* **17** 5194 (2005)
167. L R Matthews, E T Knobbe *Chem. Mater.* **5** 1697 (1993)
168. J Sokolnicki, K Maruszewski, W Stręk, J Legendziewicz *J. Sol-Gel Sci. Technol.* **13** 611 (1998)
169. X Guo, H Guo, L Fu, H Zhang, L D Carlos, R Deng, J Yu *J. Photochem. Photobiol. A* **200** 318 (2008)
170. S V Fedorenko, A R Mustafina, V V Skripacheva, M V Pinus, D A Tatarinov, V F Mironov, A Yu Men'shikova, K V Kholin, M K Kadirov, A I Konovalov *Russ. Chem. Bull., Int. Ed.* **60** 2222 (2011) [*Izv. Akad. Nauk, Ser. Khim.* 2180 (2011)]
171. G Qian, M Wang *J. Am. Ceram. Soc.* **83** 703 (2000)
172. P A Tanner, B Yan, H Zhang *J. Mater. Sci.* **35** 4325 (2000)
173. M-A Néouze, J Le Bideau, F Leroux, A Vioux *Chem. Commun.* 1082 (2005)
174. K Lunstroot, K Driesen, P Nockemann, C Göller-Warland, K Binnemans, S Bellayer, J Le Bideau, A Vioux *Chem. Mater.* **18** 5711 (2006)
175. K Lunstroot, K Driesen, P Nockemann, K Van Hecke, L Van Meervelt, C Goller-Warland, K Binnemans, S Bellayer, L Viau, J Le Bideau, A Vioux *Dalton Trans.* 298 (2009)
176. S Bellayer, L Viau, Z Tebby, T Toupance, J Le Bideau, A Vioux *Dalton Trans.* 1307 (2009)
177. A Hagfeldt, G Boschloo, L Sun, L Kloo, H Pettersson *Chem. Rev.* **110** 6595 (2010)
178. R Hansperger *Integrated Optics: Theory and Technology* (Heidelberg: Springer, 1982)
179. R J Mears, L Reekie, I M Jancie, D N Payne, in *Proceedings of Optical Fiber Communication Conference (OSA Technical Digest Series* Vol. 3) (Washington, DC: Optical Society of America, 1987) p. 167
180. A S Kurkov, O E Nanii *Lightwave. Rus. Ed.* (1) 14 (2003)
181. K Kuriki, Y Koike, Y Okamoto *Chem. Rev.* **102** 2347 (2002)
182. S P Papkov *Fiziko-Khimicheskie Osnovy Pererabotki Rastvorov Polimerov* (Physicochemical Fundamentals of Processing of Polymer Solutions) (Moscow: Khimiya, 1971)
183. R Gvishi, U Narang, G Ruland, D N Kumar, P N Prasad *Appl. Organomet. Chem.* **11** 107 (1997)
184. X Zhang, H Lu, M A Soutar, X Zeng *J. Mater. Chem.* **14** 357 (2004)
185. X Zhang, Z Zhao, M Qian, S Y Lee, M K Chin, X Zeng, D K Y Low, A C W Lu, P Plante *J. Cryst. Growth* **288** 176 (2006)
186. P Etienne, P Coudray, J Porque, Y Moreau *Opt. Commun.* **174** 413 (2000)
187. V A Sazhnikov, A M Muzafarov, V N Kopysov, V M Aristarkhov, Yu N Kononevich, I B Meshkov, N V Voronina, M V Alfimov *Ros. Nanotekhnol.* **7** 24 (2012) [m]
188. V A Sazhnikov, V M Aristarkhov, A G Mirochnik, E V Fedorenko, M V Alfimov *Dokl. Akad. Nauk* **437** 201 (2011) [e]
189. V A Sazhnikov, V M Aristarkhov, A A Safonov, A A Bagatur'yants, A G Mirochnik, E V Fedorenko, M V Alfimov *Khim. Vys. Energ.* **45** 347 (2011) [n]
190. Y Liu, G Qian, Z Wang, M Wang *Appl. Phys. Lett.* **86** 071907 (2005)
191. N L Vekshin *Perenos Vozbuzhdeniya v Makromolekulakh (Itogi Nauki i Tekhniki Ser.) 'Radiatsionnaya Khimiya i Fotokhimiya'*) [Transfer of Excitation in Macromolecules (Advances in Science and Engineering Series 'Radiation Chemistry and Photochemistry', Vol. 7)] (Moscow: Izd. VINITI, 1989)
192. A M Gas'kov, M N Rumyantseva *Neorg. Mater.* **36** 369 (2000) [h]
193. M N Rumyantseva, O V Safonova, M N Boulova, L I Ryabova, A M Gas'kov *Russ. Chem. Bull., Int. Ed.* **52** 1217 (2003) [*Izv. Akad. Nauk, Ser. Khim.* 1151 (2003)]
194. V Briois, S Belin, M Z Chalaca, R H A Santos, C V Santilli, S H Pulcinelli *Chem. Mater.* **16** 3885 (2004)
195. T Toupance, O Babot, B Jousseaume, G Vilaca *Chem. Mater.* **15** 4691 (2003)
196. A Gamard, B Jousseaume, T Toupance, G Campet *Inorg. Chem.* **38** 4671 (1999)
197. R Huang, L Hou, B Zhou, Q Zhao, S Ren *J. Non-Cryst. Solids* **351** 23 (2005)
198. A P Savitskii *Usp. Biol. Khim.* **40** 309 (2000) [o]
199. J-C G Bünzli *Chem. Rev.* **110** 2729 (2010)
200. V V Zherdeva, Candidate Thesis in Biological Sciences, Institute of Bioorganic Chemistry, Russian Academy of Sciences, Moscow, 2007
201. J Yuan, G Wang, H Kimura, K Matsumoto *Anal. Sci.* **15** 125 (1999)

202. Y-X Ci, X-D Yang, W-B Chang *J. Immunol. Methods* **179** 233 (1995)
203. Y Xu, Q Li *Clin. Chem.* **53** 1503 (2007)
204. V V Semenov, N V Zolotareva, G A Domrachev *Dokl. Akad. Nauk* **439** 351 (2011)[l]
205. J Yuan, K Matsumoto, H Kimura *Anal. Chem.* **70** 596 (1998)
206. Z Ye, M Tan, G Wang, J Yuan *J. Mater. Chem.* **14** 851 (2004)
207. M Tan, G Wang, X Hai, Z Ye, J Yuan *J. Mater. Chem.* **14** 2896 (2004)
208. C T Kresge, M E Leonowicz, W J Roth, J C Vartuli, J S Beck *Nature (London)* **359** 710 (1992)
209. N N Khimich, A V Zdravkov, L A Koptelova, E N Poddenezhnyi, A A Boiko *Fiz. Khim. Stekla* **35** 234 (2009)[a]
210. T I Izaak, O V Vodyankina *Russ. Chem. Rev.* **78** 77 (2009)
211. N Husing, U Schubert *Angew. Chem., Int. Ed.* **37** 22 (1998)
212. A C Pierre, G M Pajonk *Chem. Rev.* **102** 4243 (2002)
213. L B Boinovich, S N Zhevnenko, A M Emel'yanenko, R V Gol'dshtein, V P Epifanov *Dokl. Akad. Nauk* **448** 675 (2013)[l]
214. S V Klement'eva, N F Cherepennikova, V V Semenov, A I Kirillov, M A Lopatin, O V Kuznetsova, Yu A Kurskii, A A Zaitsev, L G Klapshina, V E Duglas, G A Domrachev *Russ. Chem. Bull., Int. Ed.* **56** 2214 (2007) [*Izv. Akad. Nauk, Ser. Khim.* 2138 (2007)]
215. V I Pet'kov *Russ. Chem. Rev.* **81** 606 (2012)
216. M Mehring, V Lafond, P H Mutin, A Vioux *J. Sol-Gel Sci. Technol.* **26** 99 (2003)
217. O A Shilova *Fiz. Khim. Stekla* **31** 270 (2005)[a]
218. U Deschler, P Kleinschmit, P Panster *Angew. Chem., Int. Ed. Engl.* **25** 236 (1986)
219. U F Chernyshev, Z V Belyakova, L K Knyazeva *Aminopropiltrietoksisilan (Obzornaya Informatsiya. Seriya 'Elementoorganicheskie Soedineniya i ikh Primenenie')* [Aminopropyltriethoxysilane (Review Information. Series 'Organoelement Compounds and Their Applications')] (Moscow: Scientific Research Institute of Technical and Economic Investigation in Chemical Industry, 1985)
220. V V Semenov, L G Klapshina, W E Douglas, G A Domrachev *Mendeleev Commun.* 157 (2000)

[a] — *Glass Phys. Chem. (Engl. Transl.)*
[b] — *Polym. Sci. (Engl. Transl.)*
[c] — *Mendeleev Chem. J (Engl. Transl.)*
[d] — *Russ. Coat. J. (Engl. Transl.)*
[e] — *Dokl. Phys. Chem. (Engl. Transl.)*
[f] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[g] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[h] — *Inorg. Mater. (Engl. Transl.)*
[i] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[j] — *Ukr. Chem. J. (Engl. Transl.)*
[k] — *Russ. J. Org. Chem. (Engl. Transl.)*
[l] — *Dokl. Chem. (Engl. Transl.)*
[m] — *Nanotechnol. Russ. (Engl. Transl.)*
[n] — *High Energy Chem. (Engl. Transl.)*
[o] — *Biol. Chem. Rev. (Engl. Transl.)*