# Luminescent Composite Films Based on Mechanically Strong Ladderlike Polyphenylsilsesquioxane and Oligophenyleuropiumsiloxane

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**Abstract** Nowadays organosilicon luminescent materials are of increasing interest due to the variety of their synthetic or modification techniques and application fields. Ladder polyphenylsilsesquioxanes (L-PPSQ) are a unique class of organosilicon polymers, which can be ideal matrices for the luminescent composites due to their high thermal stability, optical transparency and mechanical strength. In this work, new mechanically strong, heat-resistant, transparent and sensitive to ammonia vapor luminescent composite films based on L-PPSQ have been obtained. As the source of Europium ions oligophenyleuropiumsiloxane was used, demonstrating perfect compatibility to the matrix due to the similar nature. To improve luminescent properties of the films, new organosilicon ligands were introduced into the composites and their influence on the properties of the materials was studied. Valuable properties of described composites may allow their further application as multifunctional coatings.

Keywords Luminescent composite films; Ladder-like polyphenylsilsesquioxane; Oligophenyleuropiumsiloxane

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# INTRODUCTION

The development of luminescent materials based on organosilicon polymers is a relevant trend in modern polymer chemistry. A large body of works are devoted to the preparation of luminescent composites using polysiloxanes,<sup>[1–4]</sup> polysiloxanepolyether copolymers,<sup>[5–7]</sup> polysiloxane-polyurethane copolymers,<sup>[8]</sup> or other polysiloxane copolymers<sup>[9–11]</sup> as polymer matrices. Depending on the structure of the polymer matrix and the type of filler, such materials can have a number of specific properties, such as improved mechanical properties,<sup>[1,2]</sup> temperature sensitivity, which allows their use in luminescence thermometry,<sup>[6]</sup> pressure sensitivity,<sup>[4]</sup> self-healing,<sup>[10,12,13]</sup> they can be used in photonics,<sup>[9]</sup> as concentrators for solar cells,<sup>[5]</sup> and in other fields.

Polyphenylsilsesquioxanes (PPSQ) are a unique class of organosilicon polymers represented by a number of different structural forms of macromolecules such as polyhedral oligophenylsilsesquioxanes, statistical, superbranched, and ladder-like polyphenylsilsesquioxanes.<sup>[14]</sup>

Luminescent materials can be obtained by incorporating

organic luminophores,<sup>[15,16]</sup> salts or complexes of rare earth elements<sup>[6,17,18]</sup> into the polyphenylsilsesquioxane matrix. Polyphenylsilsesquioxanes with encapsulated Tb<sup>3+</sup> clusters can be used in optoelectronic devices.<sup>[19]</sup> Europium complexes introduced into PPSQ show extended emission lifetime.<sup>[20]</sup> The use of organic ligands is a common method to increase the luminescence intensity of lanthanide complexes.<sup>[21]</sup> One of the most versatile ligands is  $\beta$ -diketones.<sup>[22,23]</sup> Polyphenylsilsesquioxanes doped with europium complexes bearing triphenylphosphine oxide or  $\beta$ -diketone ligands show enhanced spontaneous emission or superluminescence. These materials can be used to produced high-power lasers or superluminescent diodes.<sup>[24,25]</sup> The use of organometallosiloxanes as carriers of lanthanide ions to fabricate luminescent polymer composites is also a promising approach.<sup>[8,26]</sup>

It is worth noting that most luminescent materials derived from polyphenylsilsesquioxanes have poor mechanical properties, which limits their use. However, the new synthetic approach to ladder-like PPSQ (L-PPSQ) in ammonia medium developed by us helps to obtain these polymers in high yields, with improved thermal resistance and low brittleness,<sup>[27]</sup> which makes them promising objects for use in various fields of scientific and technological activities, including the creation of composite materials. We have also demonstrated the high gas permeability of these polymers (especially for CO<sub>2</sub>)

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and the ability to separate benzene/hexane mixtures in different ratios during vacuum pervaporation.<sup>[28]</sup> Therefore, the development of a synthetic approach to L-PPSQ-based luminescent materials is promising for the further design of sensory devices that exhibit sensitivity due to both the chemosensory properties of the europium complexes and the membrane properties of the polymer matrix itself.

This work presents a new method for the preparation of composite luminescent films based on mechanically strong ladder-like polyphenylsilsesquioxanes filled with oligophenyleuropiumsiloxanes. New dibenzoylmethane-based organosilicon ligands of different structures were incorporated into the polymer matrix to increase the luminescence intensity. The composition and structure of all obtained compounds were confirmed by a number of physicochemical methods such as NMR and IR-spectroscopy, HRMS, elemental analysis. Optical, thermal, mechanical and sensory properties of the obtained materials were also studied.

# **EXPERIMENTAL**

#### Materials

High-molecular-weight ladder-like polyphenylsilsesquioxane **1** (98%) ( $M_n$ =354 kDa,  $M_w$ =1060 kDa; PDI=2.99) was synthesized by the method reported by us earlier.<sup>[27]</sup> Oligophenyleuropium-siloxane **2** (95%) was obtained by the previously described method.<sup>[26]</sup> Allyl-DBM **3** was obtained by a known procedure (98%).<sup>[29]</sup> 1,1,1,3,5,5,5-Heptamethyltrisiloxane **4** (97%) and plat-inum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (in xylene, 2% Pt) were purchased from Sigma-Aldrich. 1,1,7,7-Tetramethyl-3,3,5,5-tetraphenyltetrasiloxane **6** (98%) was purchased from ABCR. 25% Ammonia (as NH<sub>3</sub>) was purchased from PanReac. All chemicals were used as purchased. All solvents were purified before use. Dichloromethane was distilled from P<sub>2</sub>O<sub>5</sub>. Toluene was distilled from CaH<sub>2</sub>. Hexane and *o*-dichlorobenzene were distilled.

#### Synthesis

General method for the synthesis of siloxane DBM derivatives by the hydrosilylation reaction

A mixture of an appropriate hydridsiloxane, allyl-DBM **3** and Karstedt catalyst (30  $\mu$ L) in dichloromethane (30 mL) was stirred at room temperature for 24 h. Once the reaction was complete, the solvent was removed using a rotor evaporator. The residue was purified by column chromatography on silica gel (toluene:hexane=1:1).

1,1,1,3,5,5,5-Heptamethyl-3-(propylDBM)-trisiloxane (5). **5** was prepared from allyl-DBM **3** (2.50 g, 11.26 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane **4** (2.97 g, 11.26 mmol). Yield: 60%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 0.03 (s, 3H, SiCH<sub>3</sub>), 0.10 (s, 21H, SiCH<sub>3</sub>), 0.53 (t, 2H, *J*=8.1 Hz, SiCH<sub>2</sub>), 1.70 (m, 2H, CH<sub>2</sub>), 2.71 (t, 2H, *J*=8.1 Hz, CH<sub>2</sub>), 6.86 (s, 1H, COCHCO), 7.30 (d, 2H, *J*=8.0 Hz, Ar), 7.49 (t, 2H, *J*=7.8 Hz, Ar), 7.55 (t, 1H, *J*=7.4 Hz, Ar), 7.93 (d, 2H, *J*=8.1 Hz, Ar), 8.00 (d, 2H, *J*=7.0 Hz, Ar), 16.94 (s, 1H, OH). <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -0.3, 1.9, 17.3, 24.9, 39.3, 92.9, 127.1, 128.6, 132.3, 133.1, 135.7, 148.0, 185.2, 186.1. <sup>29</sup>Si-NMR (79 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -21.96, 7.21. IR (KBr, cm<sup>-1</sup>): 3065, 3032, 2957, 2931, 2900, 2862, 1608, 1559, 1540, 1506, 1487, 1414, 1301, 1258, 1227, 1184, 1051, 868, 841, 791, 763, 689, 653, 598, 509. HRMS (ESI) *m/z* Calcd.

for  $C_{25}H_{38}O_4Si_3Na$  [(M+Na)<sup>+</sup>]: 509.1997, found 509.1970. Elemental analysis Calcd. (%) for  $C_{25}H_{38}Si_3O_4$ : C, 61.68; H, 7.87; Si, 17.31; found: C, 61.49; H, 8.02; Si, 17.53.

1,7-(PropyIDBM)-1,1,7,7-tetramethyl-3,3,5,5-tetraphenyltetrasiloxane (7). 7 was prepared from allyl-DBM 3 (0.49 g, 1.88 mmol) and 1,1,7,7-tetramethyl-3,3,5,5-tetraphenyltetrasiloxane 6 (2.10 g, 3.90 mmol). Yield: 50%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 0.01 (s, 12H, SiCH<sub>3</sub>), 0.49 (t, 4H, J=8.1 Hz, SiCH<sub>2</sub>), 1.52 (m, 4H, CH<sub>2</sub>), 2.53 (t, 4H, J=8.1 Hz, CH<sub>2</sub>), 6.85 (s, 2H, COCHCO), 7.13 (d, 4H, J=8.0 Hz, Ar), 7.30 (t, 8H, J=8.0 Hz, Ar), 7.40 (t, 4H, J=7.8 Hz, Ar), 7.50 (t, 2H, J=7.4 Hz, Ar), 7.56 (d, 10H, J=8.0 Hz, Ar), 7.87 (d, 2H, J=8.1 Hz, Ar), 8.00 (d, 2H, J=7.0 Hz, Ar), 16.96 (s, 2H, OH). <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>, δ, ppm): 0.1, 17.9, 24.8, 39.4, 92.8, 127.1, 127.2, 127.6, 128.6, 128.8, 129.9, 132.3, 133.0, 134.3, 135.7, 147.8, 185.2, 186.0. <sup>29</sup>Si-NMR (79 MHz, CDCl<sub>3</sub>, δ, ppm): -47.18, 10.08. IR (KBr, cm<sup>-1</sup>): 3069, 3049, 3026, 2955, 2926, 2859, 1958, 1895, 1818, 1770, 1606, 1531, 1486, 1429, 1381, 1303, 1254, 1227, 1184, 1124, 1057, 998, 838, 787, 767, 741, 716, 699, 577, 516, 485. HRMS (ESI) m/z Calcd. for C<sub>64</sub>H<sub>66</sub>O<sub>7</sub>Si<sub>4</sub>Na [(M+Na)<sup>+</sup>]: 1081.3798, found 1081.3778. Elemental analysis Calcd. (%) for C<sub>64</sub>H<sub>66</sub>Si<sub>4</sub>O<sub>7</sub>: C, 72.55; H, 6.28; Si, 10.60; found: C, 72.58; H, 6.35; Si, 10.55.

#### General procedure for the preparation of films L0 and L1

A solution of L-PPSQ **1** (0.9 g) for the **L0** film or a solution of L-PPSQ **1** (0.9 g) and oligophenyleuropiumsiloxane **2** (0.082 g) for the **L1** film in *o*-dichlorobenzene (10 mL) was casted onto a glass support gradually heated to 100 °C using a compact film casting machine MSK-AFA-IIID Automatic Thick Film Coater (film thickness was about 100  $\mu$ m). After complete removal of the solvent, the films were dried in a vacuum oven at 200 °C for 24 h.

**L0**: <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, *δ*, ppm): 6.03–7.90 (br. s). <sup>29</sup>Si-NMR (79 MHz, CDCl<sub>3</sub>, *δ*, ppm): -80.23, 10.30. IR (KBr, cm<sup>-1</sup>): 3400, 2921–2829, 1596, 1488, 1362, 1131–1043, 729, 700, 499.

**L1**: IR (KBr, cm<sup>-1</sup>): 3356, 2931–2849, 1593, 1502, 1371, 1143–1051, 724, 692, 501.

#### General procedure for preparation of films L2 and L3

Luminescent polymer compositions L2 and L3 were prepared similarly to films L0 and L1 from a solution of L-PPSQ 1 (0.9 g), oligophenyleuropiumsiloxane 2 (0.082 g) and ligand 5 (0.053 g, 0.11 mmol) for the L2 film or ligand 7 (0.117 g, 0.11 mmol) for the L3 film in a 1:1 molar ratio to Eu<sup>3+</sup> in *o*-dichlorobenzene (10 mL).

**L2**: IR (KBr, cm<sup>-1</sup>): 3350, 2899–2825, 1593, 1455, 1400, 1131–1034, 728, 703, 496.

**L3**: IR (KBr, cm<sup>-1</sup>): 3350, 2924–2842, 1604, 1498, 1361, 1143–1049, 728, 689, 507.

#### Characterization

<sup>1</sup>H-, <sup>13</sup>C- and <sup>29</sup>Si-NMR spectra were recorded on a Bruker Avance II spectrometer (400 MHz; Germany). Chemical shifts are reported relative to the residual proton signals of deuterated chloroform ( $\delta$ =7.25 ppm for <sup>1</sup>H-NMR,  $\delta$ =77.0 ppm for <sup>13</sup>C-NMR).

IR spectra were recorded on an IR spectrometer with a Fourier transformer Shimadzu IRTracer-100 in KBr pellets.

Thermogravimetric analysis (TGA) was performed by Thermoanalyzer Shimadzu DTG-60H (Japan) on samples with weight of about 5 mg at a heating rate of 10 °C/min in air. The temperature at which a weight loss of 5% was detected was considered to be the decomposition onset temperature. Mechanical properties of samples were evaluated on LLOYD Instruments LR5K Plus testing machine with 100 mm/min stretching speed.

Luminescence spectra were acquired on a Shimadzu RF-6000 spectrofluorophotometer (Japan). The UV-Vis transmittance spectra were recorded on a Shimadzu UV-1900 spectrophotometer (Japan).

# **RESULTS AND DISCUSSION**

# Synthesis

High-molecular-weight ladder-like polyphenylsilsesquioxane 1, obtained by condensation of *cis*-tetraphenylcyclotetrasiloxanetetraol in ammonia medium according to the previously developed methodology,<sup>[27]</sup> was used as a polymer matrix for the preparation of luminescent composites (Fig. 1). It should be noted that L-PPSQs are non-crosslinked polymers and therefore the materials derived therefrom can be reprocessed.

An unfilled sample **L0** was prepared based on polymer **1** to study the effect of fillers on the physicochemical properties of the final systems. **L0** was obtained as a thin, strong, transparent and colorless film with a weak blue luminescence under 254 nm excitation.

As a source of europium ions, we used oligomeric phenyleuropiumsiloxane **2** with the general formula  $[(PhSiO_{1.5})_3Eu]_m$ , which was obtained by alkaline hydrolysis of phenyltriethoxysilane in *n*-butanol followed by the reaction of the resulting alkaline intermediate with  $Eu(NO_3)_3$ ·6H<sub>2</sub>O. The presence of phenylsilsesquioxane fragments in the oligomer provides good compatibility with the polyphenylsilsesquiox-



Fig. 1 Idealized structure of L-PPSQ 1.

ane matrix and Eu<sup>3+</sup> ions distribute uniformly in the material. Such effect cannot be reached when using inorganic salts of the lanthanides.

By incorporating the oligophenyleuropiumsiloxane **2** into the polyphenylsilsesquioxane matrix, a composite containing 2 wt% of europium ions was obtained. Solutions of compounds **1** and **2** in *o*-dichlorobenzene were mixed and casted onto a glass substrate (Fig. 2). After removal of the solvent, a homogeneous colorless **L1** film was obtained in which no inclusions or phase separations were observed, indicating complete integration of the filler with the matrix. However, the luminescence intensity of this sample was low (Fig. 3).

To improve the optical performance of the tested systems, we decided to utilize the antenna effect of organic ligands, which is widely used to boost the emission of lanthanide ions.<sup>[21]</sup> In order to ensure the compatibility of the ligand with the polymer matrix material, ligands based on dibenzoyl-methane derivatives functionalized with organosilicon moieties with different substituents at the silicon atom were synthesized. Compound **5** bears only methyl substituents at the silicon atom and is a bright red liquid, and compound **7**, which contains phenyl substituents in addition to methyl, is a viscous dark orange liquid. These ligands were synthesized according to Scheme 1.

The allyl-substituted dibenzoylmethane **3**, obtained by the known procedure,<sup>[29]</sup> was subjected to hydrosilylation with heptamethyltrisiloxane **4** or tetramethyltetraphenyltetrasiloxane **6** in the presence of a Karstedt's catalyst. The reaction was carried out in dry dichloromethane in an inert atmosphere. The completion of the reaction was confirmed by the disappearance of the signal for the Si–H groups of the starting siloxanes and the appearance of new signals assigned to the propyl-dibenzoylmethane unit in the <sup>1</sup>H NMR spectrum. The target compounds were isolated and purified by column chromatography on silica gel eluting with a 1:1 toluene-hexane mixture.

The composite film **L2** was obtained from a mixture of solutions of compounds **1**, **2** and **5** in o-dichlorobenzene (Fig. 2) and has an equimolar ratio of ligand **5** to  $Eu^{3+}$  (the  $Eu^{3+}$  content in the material is 2 wt%). This film exhibited intense red



Scheme 1 Synthesis routes to ligands 5, 7.

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Fig. 2 General scheme for the preparation of composite films L1–L3.

luminescence when excited with light of both 254 nm and 365 nm wavelengths, due to the presence of dibenzoylmethane moiety (Fig. 3).

Composite L3 derived from polyphenylsilsesquioxane matrix 1 and oligophenyleuropiumsiloxane 2 in combination with ligand 7 (2 wt% europium in the film, ligand 7:Eu atom = 1:1) had a slight orange tint due to the presence of dibenzoylmethane. The L3 film, like L2, exhibited intense red lumines-



**Fig. 3** Images of **LO–L3** films under daylight and under 254 and 365 nm excitation.

Table 1 Composition of L0–L3 films.

Sample	Eu <sup>3+</sup> content in a sample	Ligand <b>5</b> :Eu <sup>3+</sup> ratio	Ligand <b>7</b> :Eu <sup>3+</sup> ratio
L0	-	_	-
L1	2 wt%	-	-
L2	2 wt%	1:1	-
L3	2 wt%	_	1:1

cence under 254 and 365 nm excitation.

In this way, we obtained four films, their images under daylight and under excitation at wavelengths of 254 and 365 nm are shown in Fig. 3, and their compositions are given in Table 1.

#### **Mechanical Properties**

The mechanical properties of the resultant films were investigated by the uniaxial tensile test. The stress-strain curves of the samples are presented in Fig. 4. All the obtained materials have similar stress-strain characteristics and show high Young's modulus and low elongation at break. The introduction of luminescent fillers affects the mechanical properties of the polymers as follows: compared to the starting matrix, the filled samples show a slightly higher elongation at break (up to 7.5%) and the



Fig. 4 Stress-strain curves of samples L0–L3.

Table 2 Mechanical properties of samples L0–L3.

Sample	$\sigma$ (MPa)	ε (%)	E (MPa)
LO	39.7±3.9	5.3 ± 0.5	1700
L1	35.6±3.5	$7.5 \pm 0.7$	1200
L2	40.7±4.0	$6.7 \pm 0.6$	1200
L3	40.9±4.0	7.1 ± 0.7	1500

Young's modulus decreases from 1700 MPa (**L0**) to 1500 MPa for sample **L3**, and to 1200 MPa for **L1** and **L2**. The mechanical properties of the polymers are summarized in Table 2.

In this case, the filler probably acts as a plasticizer, since there is an increase in the elongation at break compared to the values corresponding to the starting polymer matrix. This phenomenon will be studied in detail in the future. It is also worth noting that the introduction of organosilicon ligands into the system leads to an increase in the tensile strength of the resulting composites.

### **Thermal Properties**

The thermal stability of **L0–L3** films was evaluated by thermogravimetric analysis (TGA) in air in the temperature range of 50–1000 °C. The data obtained are shown in Fig. 5 and Table 3.

The introduction of metallosiloxane containing Eu<sup>3+</sup> into the polymer matrix, as is known, leads to a slight increase in the thermal stability of the samples.<sup>[8]</sup> According to the TGA data, the thermo-oxidative stability of the L-PPSQ-derived material increases when it is doped with europiumsiloxane **2** (519 °C to 568 °C). The **L3** composite containing ligand **7** is more thermally stable than the **L2** composite containing ligand **5** ( $T_d^{5\%}$  =510 and 474 °C, respectively). It should be noted that the TGA curves of the **L2** and **L3** composites show no weight loss in the temperature range corresponding to the degradation of ligands **5** and **7**, indicating strong coordination binding of the ligands to europium ions. To summarize, despite the fact that the introduction of organosilicon lig-



Fig. 5 TGA thermograms of L0–L3 samples in air.

Table 3 Thermal properties of L0–L3 samples in a
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Sample	<i>T</i> d <sup>5%</sup> (°C)	Residual weight (%)
LO	519	47
L1	568	48
L2	474	46
L3	510	48

ands degrades the thermal stability of the resultant materials (most likely it can be due to the volatility of these ligands), the onset degradation temperature of the samples still remains in the high temperature range (474–510 °C). The high percentage of the mass residue is consistent with the structure of polyphenylsilsesquioxane and literature data.<sup>[30]</sup>

#### **Luminescent Properties**

The optical properties of **L0–L3** were studied in the solid state at room temperature. Fig. 6 shows the emission spectrum (left) and the fluorescence excitation spectrum (right) of the matrix **L0**, which does not contain Eu<sup>3+</sup> ions. According to the emission spectrum, fluorescence is observed in the range of 300–450 nm, with a maximum at 325 nm, which can be attributed to the emission of phenyl excimers formed in the excited state.<sup>[31]</sup> The fluorescence excitation spectrum of the solid state matrix with emission at 330 nm shows that the maximum is at 280 nm.

Fig. 7 shows the emission spectra (left) and the luminescence excitation spectrum (right) of **L1**. Under 270 nm excitation, the emission spectrum of sample showed the emission of matrix with maximum at 330 nm and five emission peaks that are characteristic of the Eu<sup>3+</sup> ions originating from the  ${}^{5}D_{0} \rightarrow {}^{7}F_{n}$  (n=0–4) transitions. Similar results were obtained for polymer films based on phenyleuropiumsiloxane molecular filler and blocksil siloxane copolymers.<sup>[8]</sup>

Fig. 8 shows the emission spectra of L2 and L3. Under UV excitation at 270 nm and 390 nm, the emission spectrum of the sample showed the low intensity emission of matrix around 300 nm (in the case of 270 nm) and five emission peaks that are characteristic of the Eu<sup>3+</sup> ions originating from the  ${}^{5}D_{0} \rightarrow {}^{7}F_{n}$  (n=0-4) transitions. The emission peak at around 590 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ) is a magnetic dipole transition, and its intensity is insensitive to the coordination environment, so this transition is used to calibrate the intensity of Eu<sup>3+</sup> luminescence spectra.<sup>[32]</sup> In this case, it is possible to compare the luminescence intensities of the transitions resulting from the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  electric dipole transition at a wavelength of about 615 nm, which is sensitive to the surrounding Eu<sup>3+</sup>. In the case of L2, a significant increase in the luminescence of this transition occurs when the excitation wavelength changes from 270 nm to 390 nm due to the coordination of Eu3+ ions with  $\beta$ -diketones fragments. However, in the case of L3, only a slight increase of this transition is observed, which can be attributed to the large size of the ligand and its steric hindrance.

Fig. 9 shows emission spectra of L1–L3 normalized to the peak at 590 nm ( ${}^{5}D_{0}\rightarrow{}^{7}F_{1}$  transition, left) and 350 nm (emission of polymer matrix, right) with excitation at 270 nm. It is possible to compare the luminescence intensity of transitions by the electric dipole  ${}^{5}D_{0}\rightarrow{}^{7}F_{2}$  transition at about 615 nm which is sensitive to the surrounding of Eu<sup>3+</sup> ion. The significant luminescence enhancement of this transition is observed in the case of L2 and L3, where  $\beta$ -diketone ligands were used for coordination with Eu<sup>3+</sup> ion. It is also possible to evaluate the general intensity of the luminescence of the polymer films L1–L3, assuming that the emission from the polymer matrix (at 325 nm) has a constant intensity. As shown in Fig. 9 (right), the highest luminescence intensity is observed for L3 doped with  $\beta$ -diketone ligand 7.

The luminescence excitation spectra of L2 and L3 in the



Fig. 6 Normalized emission (a, excitation at 270 nm) and fluorescence excitation (b, emission at 330 nm) spectra of LO in the solid state.



**Fig. 7** Normalized solid-state emission (a, normalized to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition, excitation at 270 nm) and luminescence excitation (b, emission at 330 and 615 nm) spectra of L1.





solid state with emissions at 615 nm are presented at Fig. 10. It shows that the excitation of  $Eu^{3+}$  ions occurs due to efficient energy transfer from the  $\beta$ -diketone ligands.

#### **Transparency Properties**

All the materials obtained were tested for optical transparency in the wavelength range from 200 nm to 900 nm (Fig. 11, Table 4). Fig. 11, representing the transmission spectra of the samples as a function of wavelength, shows that all films have high transparency in the visible and near infrared regions.

For example, the **L0** sample, which contains no fillers, has a transparency of 84% in the 400–900 nm range. The incorporation of oligophenyleuropiumsiloxane **2** has practically no effect on either the shape of the spectrum or the transparency of the **L1** film (83% in the visible range). The transparency of these materials in the UV range is 38% and 36%, respectively, due to the absorption of light by phenyl substituents of L-PPSQ and their aggregates (Fig. 6b; Fig. 7b).



**Fig. 9** Solid-state emission spectra of L1–L3 normalized to the peak at 590 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition, a) and at 350 nm (emission of polymer matrix, b). Excitation at 270 nm.



Fig. 10 Normalized solid-state luminescence excitation spectra of L2 and L3. Emission at 615 nm.



Fig. 11 Transmission spectra of LO–L3 samples.

In the case of composite films **L2** and **L3**, the transmission spectra have a different character. Sample **L2** shows the highest transparency (89%) in the range of 400–900 nm of the tested materials, and for the sample **L3** this value is 83%. At the same time, composites **L2** and **L3** effectively absorb light in the UV range (13% and 1% transparency, respectively),

Table 4	Transparency of L	0–L3 samples in	different spectral ranges.
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Sampla	Transparency in the spectral range (%)		
Sample —	200–400 nm (UV)	400–900 nm (Vis)	
LO	38	84	
L1	36	83	
L2	13	89	
L3	1	83	

which is due to the presence of dibenzoylmethane ligands in their composition (Fig. 10). Similar  $\beta$ -diketones are often used to produce sunscreens due to their intense UV absorption.<sup>[33,34]</sup>

#### **Sensory Properties**

The sensory properties of europium complexes to acids and bases is a well-known feature that is often used in the development of sensor materials,<sup>[35–37]</sup> including those based on organosilicon polymers.<sup>[38,39]</sup>

For composite film L3, demonstrated the maximum luminescence intensity of the series obtained, the sensitivity to the ammonia vapor was investigated. The experiment was carried out as follows: the specimen of the L3 film was placed in a quartz cuvette and the initial luminescence spectrum was recorded. After that 0.05 mL of 25% ammonia was added to the cuvette and the luminescence spectrum was recorded again. The measurements have been taken every 2-4 minutes till the full saturation of the sample by ammonia vapor was registered. Fig. 12 shows the emission spectra of the sample when exposed to and after removal of ammonia vapor under 390 nm excitation. These spectra show that the luminescence intensity increases with the introduction of ammonia and reaches its maximum in 40 minutes, when full saturation takes place. At the same time, when the ammonia is removed, the intensity decreases and after 24 h the spectrum returns to the original intensity level.

The change in optical properties and the increase in luminescence intensity of europium can be associated with structural changes in the coordination sphere of europium dibenzoylmethanate, and the reversibility of this process allows the use of these films as materials with chemosensory properties.



Fig. 12 Emission spectra of the L3 sample exposed and not exposed to ammonia vapors.

# CONCLUSIONS

In this work, luminescent, thermally stable, mechanically robust, visible-transparent, and ammonia vapor-sensitive composite films were obtained. Ladder-like polyphenylsilsesquioxane, which has high mechanical strength, was used as the polymer matrix, and oligophenyleuropiumsiloxane was used as the source of europium ions. New organosilicon dibenzoylmethanebased ligands bearing different substituents were synthesized to improve the luminescence intensity. Ligand 7 containing both methyl and phenyl substituents was found to be the most compatible with the matrix. However, both composites L2 and L3 show much higher luminescence intensity compared to the ligand-free composite L1. The unique feature of these films is their non-crosslinked polymer composition, which opens the possibility of their further reprocessing; the materials can be dissolved and re-cast. The resulting films have significant mechanical properties, Young's modulus of the samples is in the range of 1200-1700 MPa. They exhibit high thermal stability in air, with degradation temperatures ranging from 474 °C to 568 °C. The transparency of the materials in the visible range is 82-84%. The L3 composite also exhibits reversible chemosensory properties. Such materials featuring valuable optical, mechanical, thermal, and sensory properties can find applications as transparent light-emitting screens, photosensitive membranes, optical filters, and can also be used to create gas-permeable sensory devices.

# **Conflict of Interests**

The authors declare no interest conflict.

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