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Synthesis and optical properties of highly luminescent phenyloxazole silane polymer

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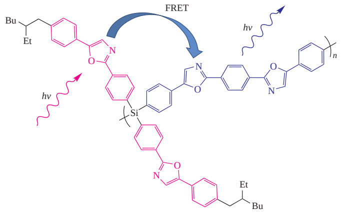
Novel comb-shaped luminescent phenyloxazole silane polymer with efficient energy transfer of the electronic excitation from the lateral donor 2,5-diphenyloxazole groups to the acceptor 1,4-bis(5-phenyloxazol-2-yl)benzene fragments in the main chain showing high photoluminescence quantum yield in the region of 400–450 nm is obtained.



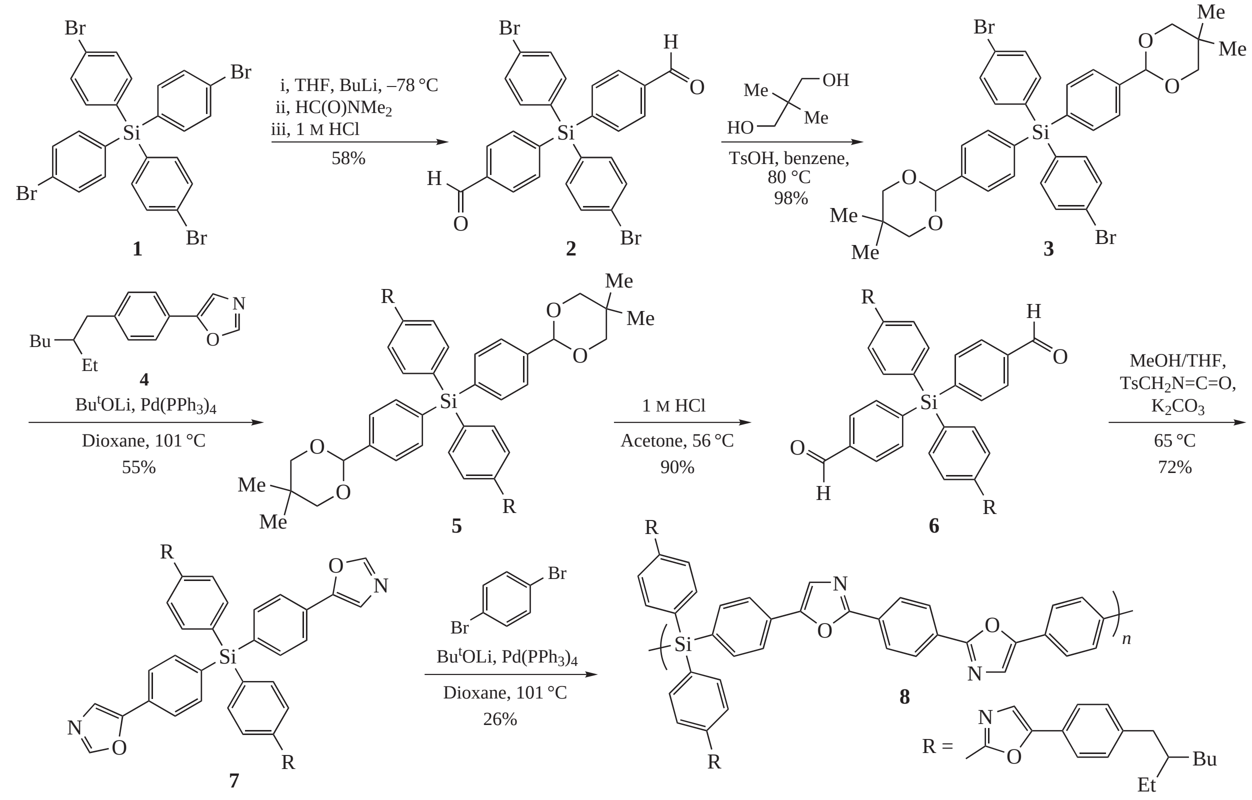
Organosilicon oligomers and polymers hold an important place among the luminescent materials.[1–4] Silicon is an effective conjugation breaker due to its electronic structure and the relatively weak π–d interactions. It allows one to create luminescent macromolecules of branched and dendritic architecture with unique characteristics.[5–9]

Here we describe a new luminescent organosilicon polymer, whose monomeric unit structure is organized in accordance with the principles underlying the creation of high-performance nanostructured organosilicon luminophores (NOL).[10,11] The use of two types of luminophores (donor and acceptor) with different optical bandgaps connected by the silicon atoms within a NOL makes an effective Förster energy transfer of the electronic excitation between them possible.[12] Such structures provide unique opportunities for tuning basic properties of the luminescent compounds like absorption and fluorescence spectral range, molar extinction coefficient and luminescence quantum yield. Derivatives of phenyloxazole, 2,5-diphenyloxazole (PPO) and 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP), which effectively emit light in short-wave region of the spectrum,[13] were selected as donor and acceptor luminescent fragments, respectively. However, there are no published data on such phenyloxazole-containing polymer materials apparently because of synthetic problems arising during their preparation.

In recent years, a significant progress in development of selective methods of organic synthesis, suitable for the transformation of complex functionalized molecules under mild conditions, allowed researchers to obtain a variety of chemical compounds with atomic precision.[14] One of such reactions is the direct C–H arylation of oxazoles catalyzed by transition metals.[15] On the basis of this reaction, as well as the synthesis of oxazoles from aldehyde derivatives by the van Leusen reaction,[16] we have synthesized phenyloxazole silane polymer (Scheme 1). First, dilithiated tetrakis(4-bromophenyl)silane **1** was obtained by lithiation with twofold excess of *n*-butyllithium. Then, by the reaction of this derivative with $HC(O)NMe_2$ and subsequent decomposition of the salt formed in an acidic medium, dialdehyde **2** was obtained in 58% yield after purification by column chromatography on silica gel. Since aldehydes are capable of entering into side reactions under direct C–H arylation, in the next step the carbonyl group was protected to give compound **3**. Without further purification, it was cross-coupled with 5-[4-(2-ethylhexyl)phenyl]-1,3-oxazole **4** prepared from the appropriate aldehyde by the van Leusen reaction to afford product **5** in 55% yield. Note a high rate of the direct arylation reaction, which was completed within 30 min. Removal of dioxane protection was carried out in water–acetone mixture in an acidic medium with the formation of compound **6**, which was then subjected to the van Leusen reaction leading to phenyloxazole silane **7** (yield over two steps after purification was 72%). The resulting bifunctional precursor **7** was used in the polycondensation reaction with *p*-dibromobenzene by the direct C–H arylation protocol, which afforded comb-shaped polymer **8**. To avoid the influence of the terminal groups on the optical properties, they were blocked by the addition of compound **4** and bromobenzene at the end of the reaction.

The resulting polymer **8** contained in its main chain the fragments of 1,4-bis(5-phenyloxazol-2-yl)benzene acceptor connected through silicon atoms, to each of the latter two donor fragments of 2,5-diphenyloxazole containing solubilizing 2-ethylhexyl groups being attached. This pair of luminophores (donor and acceptor) was chosen because of good overlap of the luminescence spectra of the donor and absorption spectra of the acceptor, which is a necessary prerequisite for effective intramolecular Förster energy transfer.[12]

Particular attention was paid to purification of the polymer from possible impurities, metal catalyst residues and low molecular weight oligomers since they can negatively affect the optoelectronic properties of conjugated polymers.[17] For this purpose, chelation of palladium by dithiocarbamate, its precipitation and extraction were used consecutively. According to the gel permeation chromatography (GPC) data, the polymer obtained after purification had a bimodal molecular weight distribution (MWD). This can be caused by the formation of cycles in the reaction process, which do not participate in further polycondensation. Therefore, the polymer obtained was fractionated by a preparative GPC. Figure 1 shows the GPC curves of the initial polymer and two isolated narrow fractions: high molecular weight (**P1**) and low molecular weight (**P2**). Investigation of their solutions by light



Scheme 1

scattering allowed us to determine the real values of weight-average molecular weights: M_w = 128 400 for the fraction **P1** and M_w = 15 500 for the fraction **P2** with the polydispersity index of 2.18 and 1.55, respectively. These results correspond to the weight-average polymerization degree (n_w) of 118 and 14 for **P1** and **P2** fractions, respectively, and coincide well with the GPC data obtained by calibration relative to polystyrene standards (see Table S1 in Online Supplementary Materials), which indicates a substantial flexibility of such polymer chain due to rotation of the luminophores relative to silicon atoms.

Study of the phase behavior at a heating rate of 20 °C min^{-1} in a nitrogen flow showed that the polymer obtained is amorphous with a glass transition temperature of 173 and 156 °C for **P1** and **P2** fractions, respectively (Figures S14 and S15). Both fractions have excellent solubility in polar organic solvents such as chloroform, toluene and THF. TGA data showed a high thermostability of the polymer obtained both in the presence of oxygen and in an inert atmosphere (nitrogen): 5% weight loss occurred at 370 and 435 °C, respectively (Figure S16). A significant difference in the weight of coke residue in the air and under nitrogen of 4 and 48%, respectively, apparently, can be related to the formation of volatile oxides in the presence of oxygen.

Optical properties of both factions of the polymer synthesized were investigated both in dilute solutions and in thin films deposited on quartz substrates by spin-coating. Figure 2 shows the spectral distribution of the decimal molar extinction coefficient $\varepsilon(\lambda)$, fluorescence and excitation spectra of **P1** and **P2** solutions in THF.

In the area of maximum absorption (336 nm), the extinction coefficient of fraction **P2** is 89.5×10^3 dm^3 mol^{-1} cm^{-1}. The spectrum of fraction **P1** is broadened and shifted relative to the spectrum of **P2** to the long wavelength range. Extinction coefficient of **P1** at a wavelength corresponding to the maximum in the absorption spectrum (338 nm) is equal to 85.2×10^3 dm^3 mol^{-1} cm^{-1}. These values correspond to the sum of the extinction coefficients of two PPO fragments at the absorption maximum and one POPOP fragment at a wavelength corresponding to the absorption maximum of the PPO in THF solution.

Fluorescence spectra of **P1** and **P2** solutions (see Figure 2) correspond to that of POPOP in THF, with a shift of 24 nm (**P1**) and 13 nm (**P2**) to the long wavelength range. The fluorescence spectrum of fraction **P1** has a slightly larger half-width than that of **P2**. The fluorescence quantum yield measured by comparison with a standard (POPOP solution in THF) for **P2** is 70±5% and for **P1** is 65±5%. Fluorescence lifetime measured by correlated photons

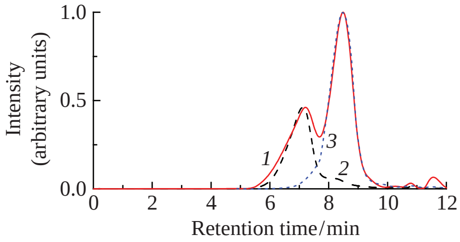


Figure 1 GPC curves for (*1*) initial polymer **8** and its fractions (*2*) **P1** and (*3*) **P2**. Phenomenex columns 300 × 7.8 mm (USA) filled with the Phenogel sorbent (particle size, 5 μm; pore size, 10^5 Å; eluent, THF; detector, diode matrix in the range of 200–800 nm) were used.

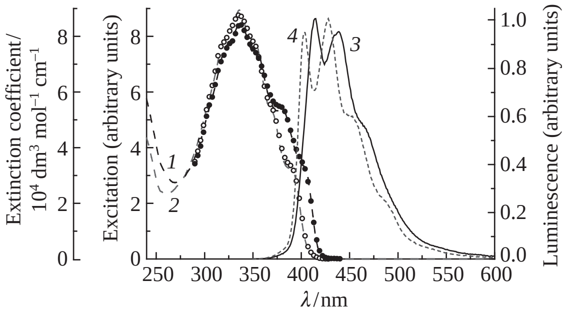


Figure 2 Optical properties of **P1** and **P2** in dilute THF solutions. Absorption spectra of (*1*) **P1** and (*2*) **P2**; fluorescence spectra of (*3*) **P1** (λ_{ext} = = 338 nm) and (*4*) **P2** (λ_{ext} = 336 nm); excitation spectra (λ_{reg} = 450 nm) of (●) **P1** and (○) **P2**. Concentration of the solutions was 10^{-5} M for absorption measurements and 10^{-6} M for luminescence measurements.

count technique was 0.99±0.02 ns for **P2** and 0.91±0.02 ns for **P1**, which correlates well with the observed decrease in values of fluorescence quantum yield upon transition from low to high molecular weight fractions.

Long wavelength shift and broadening of the absorption and fluorescence spectra of both polymer fractions can be due to the mutual influence of chromophore fragments of the polymer chain (POPOP) and side groups (PPO). It is obvious that the effect of such impact should be greater for the high molecular weight polymer, because in this case the nearest solvation shell of the absorbing (emitting) fragment contains more chromophore fragments of PPO and POPOP. Previously, it was shown that even molecules of bithiophene silane dendrimers, whose structures are more branched, are not kinetically rigid and are characterized by a small-scale mechanism of interactions with the external electric fields.[18]

From the data obtained it follows that Förster inductive–resonance energy transfer of the electronic excitation from the fragments of PPO (donor) to the fragments of POPOP (acceptor) occurs on both fractions of the polymer. A similar transfer of electronic excitation energy between the fluorescent fragments connected by the silicon atom was previously reported for various bithiophene silane dendrimers and NOLs based on them.[19] As can be seen from Figure 2, the fluorescence excitation spectra of diluted solutions of the polymers coincide with the spectra of their absorption. Consequently, the fluorescence quantum yield of the polymers synthesized does not depend on the excitation wavelength. This demonstrates the high efficiency of the electronic excitation energy transfer from donor to acceptor fragments of the polymer chain. Due to a strong overlap of the absorption spectra of donor and acceptor fragments, a numerical value of the energy transfer efficiency cannot be determined.

The absorption and fluorescence spectra of thin (50–70 nm) films of **P1** and **P2** polymers deposited on the quartz substrate from their THF solutions by spin-coating (Figure 3) correspond very well to the spectra of their dilute solutions in THF with a shift of 5–6 nm to the longwave length range, while the electron-vibrational structure of the spectra changes only slightly. Decrease in the intensity of a short wavelength peak in the fluorescence spectra is due to the reabsorption. The molecular nature of the spectra of thin films shows a lack of strong interaction between the chromophore fragments, which correlates well with the behavior of the polymer amorphous phase.

In conclusion, a synthesis of the new fluorescent comb-shaped phenyloxazole silane polymer has been developed. The polymer contains donor (PPO) and acceptor (POPOP) fragments separated by a silicon atom in the ratio of 2 : 1 in each monomer unit. It has a high luminescence quantum yield of 65–70% in the spectral region of 400–450 nm due to the presence of highly effective luminophores in the macromolecule structure and reveals the presence of an inductive–resonance energy transfer of the electronic excitation between the lateral donor chromophores and the acceptor luminescent fragments of the main polymer chain. Amorphous phase behavior and excellent optical properties of the polymer in thin films together with its high solubility in standard organic solvents make it posible to obtain high-quality luminescent coatings, which can be used in organic photonics and optoelectronics.

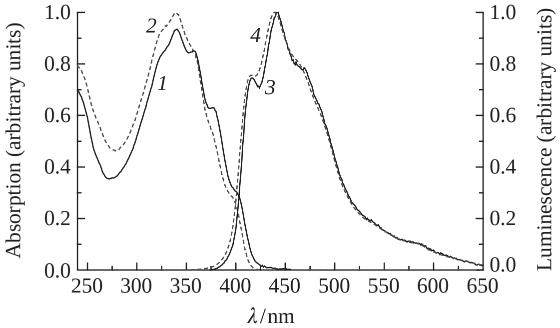


Figure 3 **P1** and **P2** thin film optical data: absorption spectra of (*1*) **P1** and (*2*) **P2**, and fluorescence spectra of (*3*) **P1** (λ_{ext} = 340 nm) and (*4*) **P2** (λ_{ext} = 343 nm).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.07.019.

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