Synthesis, photoluminescence and thermal properties of nanostructured organosilicon luminophore based on 2,2’-bithienyl and 4,7-diphenyl-2,1,3-benzothiadiazole

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Annotation. In this work, novel nanostructured organosilicon luminophore (NOL) containing four 2,2’-bithienyl donor units connected via silicon atoms to 4,7-diphenyl-2,1,3-benzothiadiazole acceptor unit was synthesized. Photophysical measurements of the NOL revealed the effect of solvents polarity on its photoluminescence quantum yield (PLQY). In THF solution the efficiency of photoluminescence was only 4%, whereas in toluene solution PLQY increased up to 76% without any changing the spectral characteristics. Under the normal conditions, the NOL synthesized is a viscous fluid, which contributes to its good solubility in various solvents. The NOL is thermostable up to 415 °C in argon atmosphere.

1. Introduction
Recently we suggested the concept of nanostructured organosilicon luminophores (NOLs) [1–3]. A NOL represents branched or dendritic organosilicon molecular antennae that is able to capture light quanta (photons) and nonradiatively transfer electronic excitation energy from the periphery to its central unit, which leads to effective light absorption in a broad spectral range and emission in a narrower region with a longer wavelength [4–7]. In the NOL two types of organic chromophores are connected to each other via silicon atoms, which break the conjugation between them and fix them specifically in the space at 1-2 nm distance necessary for efficient Förster energy transfer [6,8]. NOLs possess several advantages: absorption in a wide spectral range; 5–10 times higher absorption cross-sections than those of the best low molar weight organic luminophores; very high photoluminescence quantum yield; emission in the defined region; short luminescence lifetime. For the NOL reported in this work, 2,2’-bithiophene (2T) was chosen as a donor, like in the most previously reported NOLs. While a novel acceptor based on 4,7-diphenyl-2,1,3-benzothiadiazole (PBtdP), which is known as a strongly fluorescent dye with large Stokes shift [9-12], was used in a NOL for the first time. For increasing stability and solubility of the NOL, each of the four donor units was end-capped with n-hexyl (Hex) groups.

2. Results and Discussion

2.1. Synthesis
The synthetic strategy, which was developed previously for bithiophenesilane dendrimers and branched organosilicon macromolecules [13-15] was extended here successfully for the new NOL. The synthesis was made via palladium-mediated cross-coupling reactions widely used for the synthesis of various...
conjugated oligomers and polymers [16]. The synthetic route to the NOL is summarized in Scheme 1. A key compound for the NOL synthesis, namely, bis(5'-hexyl-2,2'-bithien-5-yl)(methyl)[4-(4,4,5,5-
tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]silane (M1), was prepared through a two-step scheme. First, bithiophenasilane monodendron (4-bromophenyl)[bis(5'-hexyl-2,2'-bithien-5-yl)]methylysilane (Hex-2T)2MeSiPhBr was obtained by the reaction between (4-bromophenyl)(dichloromethyl)ethylysilane BrPhSiMeCl2 [7] and the lithium derivative of 5-hexyl-2,2'-bithiopene in 74% yield. Second, lithiation of (Hex-2T)2MeSiPhBr followed by the treatment with 2-isoproproxy-4,4,5,5-tetramethyl-1,3,2-
dioxaborolane (IFTMDOB) lead to pinacolataborolane-functionalized monodendron M1 in 89% yield.

![Scheme 1. The synthetic scheme of the NOL.](image_url)

Finally, M1 was reacted with 4,7-dibromo-2,1,3-benzothiadiazole under Suzuki conditions to give the desired 4,7-bis{4-[bis(5'-hexyl-2,2'-bithien-5-yl)(methyl)silyl]phenyl}-2,1,3-benzothiadiazole (NOL) in 81% reaction yield (according to GPC analysis) and 63% isolated yield. The reaction was carried out until the reaction mixture no longer changed according to GPC. The monitoring by GPC using an instrument equipped with a diode array detector, which allowed recording three-dimensional chromatograms in the retention time – wavelength – signal intensity coordinates, allows to optimize the reaction time that prevents the formation of by-products. Pure NOL was isolated by column chromatography. The chemical structure and purity of all precursors and final compounds were proved by a combination of TLC, GPC, 1H-, 13C- and 29Si-NMR, MALDI-TOF MS and elemental analysis.

2.2. Optical properties of the NOL in dilute solutions

The absorption and fluorescence properties of NOLs are determined by the combination of two types of non-conjugated chromophore fragments through silicon atoms [4]. With this combination, the absorption spectrum is an additive superposition of the absorption bands of each NOL fragments. The excited state of a NOL fragment with a larger band gap (donor) is deactivated by induction-resonance transfer of the electronic excitation energy to another NOL fragment with a smaller band gap (acceptor). If the rate constant of the induction-resonance transfer is much greater than the donor fluorescence rate constant, then only the acceptor fluorescence is observed [10]. The absorption spectra were recorded using a spectrophotometer (UV-2501PC, Shimadzu) in a standard 10 mm-thick photometric quartz cuvette filled with solutions at a concentration of 10^-5 M. A scanning spectrofluorimeter ALS01M (Russia) with registration in a single photon counting mode at successive time intervals and automatic adjustment of the intensity of the emission measured was used for
registration of the photoluminescence spectra (PL) [17]. The PL excitation wavelengths were set to the absorption maxima. PL measurements were performed in 90° geometry at several optical densities in the range from 0.06 to 0.12 absorbance units in a 10 mm-thick quartz cuvette. The photoluminescence quantum yield (PLQY) was measured by comparing the integral PL intensity of 10^{-6} M diluted solutions of the NOL with the integral PL intensity of a standard as described elsewhere [18]. As the standard for measuring the PLQY, a diluted solution of 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) in cyclohexane (PLQY = 1) was used.

The absorption and PL spectra of diluted solutions of the NOL in toluene and in THF are presented in Figure 1. As can be seen, the spectra in these solvents are almost identical. Deconvolution of the absorption spectrum of the NOL solution in toluene to individual absorption spectra corresponding to 2,2'-bithiophene 2T (donor) and 4,7-diphenyl-2,1,3-benzothiadiazole PBtdP (acceptor) fragments showed that the NOL absorption spectrum is a superposition of the bands of these fragments (Figure 2). When excited both in the acceptor absorption band and in the preferential donor absorption band, the same spectral distribution of the PL intensity is observed. Upon excitation of the acceptor, the PL quantum yield is 10% higher than upon excitation of the donor.

Thus, the NOL investigated is a typical representative of NOL family by its absorption-fluorescent characteristics [1]. However, with almost complete coincidence of the absorption and fluorescence spectra of NOL solutions in toluene and THF, the photoluminescence quantum yields for these two solutions are different. When excited in the absorption band of the acceptor in toluene solution PLQY = 76%, while in THF solution PLQY = 4%.

Figure 3 shows the dependence of the fluorescence spectra of NOL solutions in toluene on the concentration of THF (quencher). As can be seen, with the growth of THF concentration there is a rapid quenching of the NOL fluorescence without changing the shape of the fluorescence spectrum. There are various processes of dynamic and static quenching of the fluorescence molecules [19]. Dynamic quenching is caused by random collisions between the excited molecules and the quencher molecules. In this case, the excitation energy is transferred to the quencher. In the case of static quenching, PLQY decreases as a result of exposure to the unexcited luminophore molecules. Static quenching is usually associated with the formation of non-fluorescent complexes in the ground state. The kinetics of dynamic and static fluorescence quenching is characterized by the Stern-Volmer formula:

\[
\frac{QY_0}{QY_f} = 1 + K_\cdot [T],
\]

where \(K\) – fluorescence quenching constant; \([T]\) – quenching concentration; \(QY_0\) and \(QY_f\) – photoluminescence quantum yield in the absence and presence of a quenching agent, respectively.

The dynamic quenching constant \(K = K_D\) is determined by the rate at which interacting molecules diffuse to each other. The static quenching constant is the equilibrium constant of the complexes formed.
\( K = K_{St} \). The concentration dependence of the processes of dynamic and static quenching, built in the coordinates \( \frac{QY_0}{QY_T} - 1 \) and \([T]\), can be described by a line passing through the origin.

Figure 3. PL spectra and emission images of solutions of the NOL in toluene-THF mixtures containing THF, % vol.: 0 (1); 20 (2); 40 (3); 60 (4); 80 (5); 100 (6).

Figure 4 shows the experimental dependence of photoluminescence quantum yield of the NOL on the concentration of THF in these coordinates. As one can see, the observed process of quenching NOL fluorescence by THF molecules cannot be characterized by the Stern-Vollmer formula. Therefore, it cannot be attributed to dynamic or static extinguishing processes. More detailed research is required to elucidate the mechanism of this phenomenon.

Figure 4. Experimental (red curve) and calculated by the Stern-Volmer equation (blue curve) concentration dependence of the PL quantum yield in the coordinates \( \frac{QY_0}{QY_T} - 1 \) and \([THF]\).

2.3. Thermal Behavior
Thermal properties of the NOL synthesized were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). DSC curves show only a glass transition at -8 °C, so NOL is a viscous liquid under normal conditions (Figure 5).
The thermal stability of the NOL was checked by the TGA method, which showed that it is highly thermostable – the 5% weight loss occurs only at 415 °C in argon (Figure 6). In the presence of oxygen their stability decreases - the destruction onset (5% weight loss) lies at 305 °C.

3. Conclusions
In summary, synthesis of a novel nanostructured organosilicon luminophore (NOL) containing four bithiophene fragments at the periphery and the 4,7-diphenyl-2,1,3-benzothiadiazole fragment at the center is described. The Suzuki cross-coupling reaction was controlled by GPC analysis, which allowed reducing the reaction time and preventing formation of by-products. The study of the optical properties of dilute solutions of the synthesized molecule showed that it is a typical representative of the NOL family by its absorption-fluorescent characteristics. The NOL obtained demonstrate a strong influence of the nature of solvents on the photoluminescence quantum yield. Further studies on to elucidate the mechanism of this phenomenon are currently in progress.

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