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Synthesis and properties of a new luminescent oligoarylsilane dendrimer

Marina S. Polinskaya, Oleg V. Borshchev, Yuriy N. Luponosov, Nikolay M. Surin, Aziz M. Muzafarov and Sergei A. Ponomarenko*

N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 117393 Moscow, Russian Federation. Fax: +7 495 335 9000; e-mail: ponomarenko@ispm.ru

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An oligoarylsilane dendrimer containing peripheral 2,2'-bithienyl groups and bis(2,2'-bithien-5-yl)-1,4-phenylene fragments as the central moieties of the molecule has been synthesized; it exhibited efficient intramolecular energy transfer and a high quantum efficiency of luminescence.

Over the last years, luminescent dendrimers have been studied as promising functional materials for various organic-electronic devices such as organic thin-film transistors, light-emitting diodes and photovoltaic cells (solar batteries).^{1,2} These dendrimers exhibit a so-called molecular antenna effect consisting in the ability of functional groups to absorb light and then execute nonradiative energy transfer from the periphery to the core.^{3,4} Earlier, oligothiophenesilane dendrimers containing various oligothienyl fragments and possessing luminescent properties in the UV-VIS spectral range (compounds **D1** and **D2** in Figure 1) were described.^{5–9}

The efficiencies of intramolecular energy transfer Q_{ETE} for compounds **D1** and **D2** were found to be 97 and 94%, respectively. However, their luminescence efficiencies were low (10–13%) because of the low fluorescence quantum yield Q_{F} exhibited by ter- or quaterthiophene^{8,9} acceptors used in these dendritic structures. Thiophene-phenylene oligomers demonstrated efficient luminescence both in solution and in a solid phase.^{10,11} The aim of this work was to synthesize an oligoarylsilane dendrimer **D3** containing bithiophenesilane fragments as energy donors and bis(2,2'-bithien-5-yl)-1,4-phenylene fragments as energy acceptors with a luminescence quantum yield higher than that exhibited by ter- and quaterthiophenesilane fragments and to characterize its optical properties.

The Suzuki reaction of organometallic synthesis was the key stage of the preparation of the new oligoarylsilane dendrimer. This reaction, which is well-known in the synthesis of oligo-thiophenesilane dendrimers,^{6,8,9} makes it possible to obtain the target compound almost free from higher molecular weight by-products (Scheme 1).

Bithiophenesilane monodendron $\mathbf{1}$, whose synthesis was described in detail,⁷ was used as a monofunctional starting reagent. Monodendron $\mathbf{2}$, which was prepared from compound $\mathbf{1}$ by the Kumada reaction, contained a bromophenylbithiophene fragment, whose bromine atom was then replaced by an organoboron group to yield compound $\mathbf{3}$. At the same time, for the synthesis of the



Figure 1 Organosilicon dendritic molecular antenna.



Scheme 1 Synthesis of oligoarylsilane dendrimer D3.

dendrimer of interest, methyltris(5'-bromo-2,2'-bithien-5-yl)silane 4^9 was used as the center of branching.

Monodendron 2 was obtained by the reaction of an organomagnesium derivative of compound 1 with 1,4-dibromobenzene in THF using Pd(dppf)Cl₂ as a catalyst.[†] The Grignard reagent was prepared *in situ* by the lithiation of a solution of monodendron **1** in a THF-hexane mixture with a solution of *n*-butyllithium with the following replacement of Li by MgBr using the MgBr₂·Et₂O complex. This complex was formed in situ from magnesium and dibromoethane in diethyl ether. This reaction scheme does not include the stage of preliminary bromination. According to gelpermeation chromatography (GPC), the yield of compound 2 was only 68% because of the formation of a disubstitution by-product. The organoboron derivative of oligoarylsilane monodendron 3 was obtained by the lithiation of compound 2 with BuⁿLi in THF followed by the reaction of the previously synthesized monolithium derivative with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (IPTMDOB) in 78% yield.

Dendrimer D3 was synthesized by the Suzuki reaction using trifunctional branching center 4 and a 30% molar excess of the organoboron derivative of oligoarylsilane monodendron 3 (Scheme 1). Usually, the synthesis of oligothiophenesilane dendrimers under the standard Suzuki conditions is performed using toluene as a solvent and an aqueous solution of a base (e.g., 2 M Na₂CO₃); in addition, the completeness of the process requires the boiling of the reaction mixture for 48-120 h.⁵⁻⁸ In our case, the reaction time was 27 h due to the addition of ethanol to promote the mixing of two phases (toluene-water). The moment of the termination of the reaction was determined by the cessation of the growth of the product concentration in the reaction mixture (GPC control). At the final stage, the mixture contained 58% of the target compound, which was then purified by preparative GPC. The yield of dendrimer D3 was 39%. The structures and purities of the intermediate and final compounds were confirmed by GPC, ¹H, ¹³C and ²⁹Si NMR spectroscopy and elemental analysis.#

The absorption and luminescence spectra of the dilute solutions of oligoarylsilane dendrimer **D3** in THF are presented in Figure 2. The absorption spectrum of dendrimer **D3** consists of two bands at 337 and 407 nm. A comparison to the absorption



Figure 2 Absorption and luminescence spectra of oligoarylsilane dendrimer D3.

spectra of reference compounds indicated that this spectrum is the sum of the absorption spectra of bithiophenesilane (peak 2T) and bis(2,2'-bithien-5-yl)-1,4-phenylene (peak 2T-Ph-2T) fragments. This is consistent with published data for ter- and quater-

For synthetic procedures and characteristics of compounds **2**, **3** and **D3**, see Online Supplementary Materials.

 $^{^{\}dagger}$ Pd(dppf)Cl_ is [1,1 '-bis(diphenylphosphino)ferrocene]dichloropalladium(II).

[‡] The ¹H NMR spectra were recorded on a Bruker WP-250 SY spectrometer (250.13 MHz) using the signal of CDCl₃ (δ 7.25 ppm) as the internal standard. The ¹³C and ²⁹Si NMR spectra were recorded on a Bruker DRX500 spectrometer. The GPC analysis was performed using a Shimadzu chromatography recorder equipped with an RID-10A refractometer and an SPD-M10AVP diode bar as detectors, a Phenomenex column (USA) (7.8×300 mm) packed with Phenogel with a pore size of 500 Å; THF was used as the eluent.

In order to avoid self-absorption, the absorption and luminescence spectra were measured over the range of 200–600 nm in dilute THF solutions at concentrations of 10^{-5} – 10^{-6} mol dm⁻³. The absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer. At the same time, the luminescence measurements were carried out on an ALC01M multifunctional absorption/luminescence spectrometer, because the three-channel optical arrangement employed in its principal of functioning makes it possible to measure electronic absorption, excitation and luminescence (fluorescence and phosphorescence) spectra. High sensitivity to small concentrations of the luminescent matter was achieved by the application of the time-correlated single photon counting technique and the automatic adjustment of the measured radiation intensity.

Table 1 Luminescent spectral characteristics of dilute solutions of D1, D2 and D3 in THF.^{*a*}

Com- pound	$\lambda_{abs}/$ nm	$\frac{K_{\rm ext}}{{ m dm}^3~{ m mol}^{-1}~{ m cm}^{-1}}$	$Q_{\rm F}(\%)$	λ_{lum}/nm	$Q_{\rm ETE}$ (%)
D1	338 388	147 000 114 000	10 10	427, 450	97±3
D2	334 416	126000 138000	12 13	470, 496, 537	94±3
D3	337 407	136 000 187 000	41 46	456, 486, 523	88±3

 ${}^{a}\lambda_{abs}$ is the absorption maximum, λ_{lum} is the luminescence maximum, K_{ext} is the molar extinction coefficient, $Q_{\rm F}$ is the luminescence quantum yield, and $Q_{\rm ETE}$ is the intramolecular energy transfer efficiency.

thiophene systems with no conjugation between oligothiophene fragments connected *via* a silicon atom.^{8,9} The luminescence spectra of dendrimer **D3** excited at both 337 (absorption exhibited by the bithiophenesilane fragments) and 407 nm [absorption exhibited by the bis(2,2'-bithien-5-yl)-1,4-phenylene fragments] correspond to that of bis(2,2'-bithien-5-yl)-1,4-phenylene. At the same time, no luminescence of the bithiophenesilane fragments with a maximum at 380–400 nm was observed even during excitation in the region of the maximal absorption exhibited by bithiophene-silane (337 nm), which is indicative of the high efficiency of intramolecular energy transfer from bithiophene-silane to bis(2,2'-bithien-5-yl)-1,4-phenylene fragments.

The efficiency of intramolecular energy transfer Q_{ETE} calculated from experimental data was 88%; at the same time, the quantum yield of luminescence Q_{F} was 46%.

Table 1 demonstrates an increase in luminescence efficiency (from 10 to 13%) from ter- to quaterthiophenesilane molecules. However, in the case of the new oligoarylsilane dendrimer, a fourfold increase is observed. Meantime, the energy transfer efficiency was maximal for dendrimer **D1**, in which the donor–acceptor distance is minimal, and expectedly decreased with the length of the acceptor, since it leads to a longer distance between the donor and acceptor. The experimental data are consistent with the theoretical model, according to which energy transfer in such systems occurs by the dipole-dipole mechanism characterized by a significant dependence of $Q_{\rm ETE}$ on the donor–acceptor distance.^{9,12}

As found by TGA, the test compound is stable up to $275 \,^{\circ}$ C in the presence of oxygen or up to $390 \,^{\circ}$ C in argon, which is $90 \,^{\circ}$ C higher than in the case of the quaterthiophenesilane dendrimer.¹³

Thus, we synthesized a new oligoarylsilane dendrimer containing 2,2'-bithienyl and bis(2,2'-bithien-5-yl)-1,4-phenylene fragments in the peripheral and central parts of the molecule, respectively. The thermal and thermal oxidative stability of the compound and its optical properties were characterized. The new oligoarylsilane dendrimer is a promising material for photo- and electrooptical applications in organic electronics and photonics.

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Online Supplementary Materials

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