

# Dendritic Oligoarylsilanes as Effective Nanostructured Luminophores for Spectral Shifters and Plastic Scintillators

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## ABSTRACT

In this work we report on synthesis and investigation of the organosilicon “molecular antennas” based on new oligoarylsilane compounds with different branching topology: dendrimers and “butterfly”-like molecules. Photoluminescence study of the new nanostructured molecules has shown an intramolecular energy transfer with the efficiency up to 99% and luminescence quantum yield up to 85%. We applied these novel nanostructured materials as luminescent additives in polystyrene for new highly effective spectral shifters and plastic scintillators (radiation detectors). Since two different luminophores are fixed properly on the nanoscale distance within the same branching molecule such a way that the efficient intramolecular energy transfer between them occurs, both the scintillating efficiency and the emitting time of the plastic scintillators are significantly improved. This lead to a new type of plastic scintillating devices based on the nanostructured organosilicon luminophores.

**Keywords:** nanostructured luminophores, oligoarylsilanes, molecular antenna, spectral shifter, plastic scintillator

## 1 INTRODUCTION

During the last years the number of light-harvesting luminescent dendrimers, which are highly branched macromolecules with monodisperse molecular weight and exact chemical structure, has increased rapidly [1]. One of the most interesting features of the dendrimers is a possibility of incorporation of different chromophores within one dendritic molecule that can lead to efficient intramolecular directional energy transfer from their peripheries to the center (the so-called “dendritic molecular antenna” effect) [2]. Albeit this effect is known since 1994, the first organosilicon molecular antennas were reported only recently [3,4]. Such molecules consist of two types of luminophores having different optical energy gaps, covalently linked to silicon atoms, which serve as branching points of the molecules. The main peculiarities of the organosilicon molecular antennas are absence of conjugation between the adjacent luminophores and efficient radiationless intramolecular energy transfer between from the luminophores with the larger optical gap

(donors) to the luminophores with the smaller optical gaps (acceptors) [5]. Close and fixed location of the luminophores connected to the same silicon atom on a distance of ca. 1-2 nm between their centers within one macromolecule are favorable for the energy transfer between them by Förster mechanism [6]. It should be noted that the organosilicon molecular antennas reported until now had the high energy transfer efficiency (87 – 97%), but rather the low fluorescence quantum yields  $Q_F$  (10 – 13%), which were determined by  $Q_F$  of the acceptors used (ter- or quaterthiophenes) [3,4]. Recently usage of a thiophene-phenylene type acceptor in a new organosilicon dendrimer allowed increasing  $Q_F$  up to 46% [7]. This was still not high enough for their applications in photonics. In this work we report the synthesis, properties and application of novel oligoarylsilane compounds with different branching topology: dendrimers and “butterfly”-like molecules, which has the intramolecular energy transfer efficiency up to 99% and luminescence quantum yield up to 85% (Fig. 1). We call them nanostructured luminophores, since they not only consist of two types of luminophores with the efficient energy transfer between them as it takes place in the dendritic molecular antennas described before [3,4], but also they possess high  $Q_F$  of 50% and more, which weakly depends on the excitation wavelength corresponding to the absorption maxima of either donor or acceptor.

As potential application of these nanostructured luminophores we suggest their usage in plastic scintillators. Typical plastic scintillator consists of polystyrene (PS) matrix with two types of luminophores molecularly distributed in it, which called activator and spectral shifter [8]. Plastic scintillators are widely used as ionizing radiation detectors [9] and when a high energy particle enters the plastic scintillator, it excites PS matrix, which emits UV light. However, the UV photons are partially captured by self-absorption in PS and are weakly detected by the photodetector, which is usually a photomultiplying tube (PMT) having maximum sensitivity in the blue spectral region. In order to overcome these problems and allow efficient detection of the excited photons by the PMT, their wavelength is shifted to the longer ones via two-step energy transfer process: 1) from PS matrix to the activator, 2) from the activator to the spectral shifter. Eventually the light emitted by the spectral shifter is detected by the PMT. However, this two-step energy transfer process in plastic

scintillators is not very efficient, since the molecules of the activator and the spectral shifter are disordered in the PS matrix. Moreover, it includes less efficient radiation energy transfer. Dendritic oligoarylsilane developed in this work can be considered as activator and spectral shifters linked into one nanostructured luminophor with very effective radiationless intramolecular energy transfer from the activator to the spectral shifter. We show in this work that their usage in plastic scintillators can increase their efficiency up to 50% as compared to the conventional one.

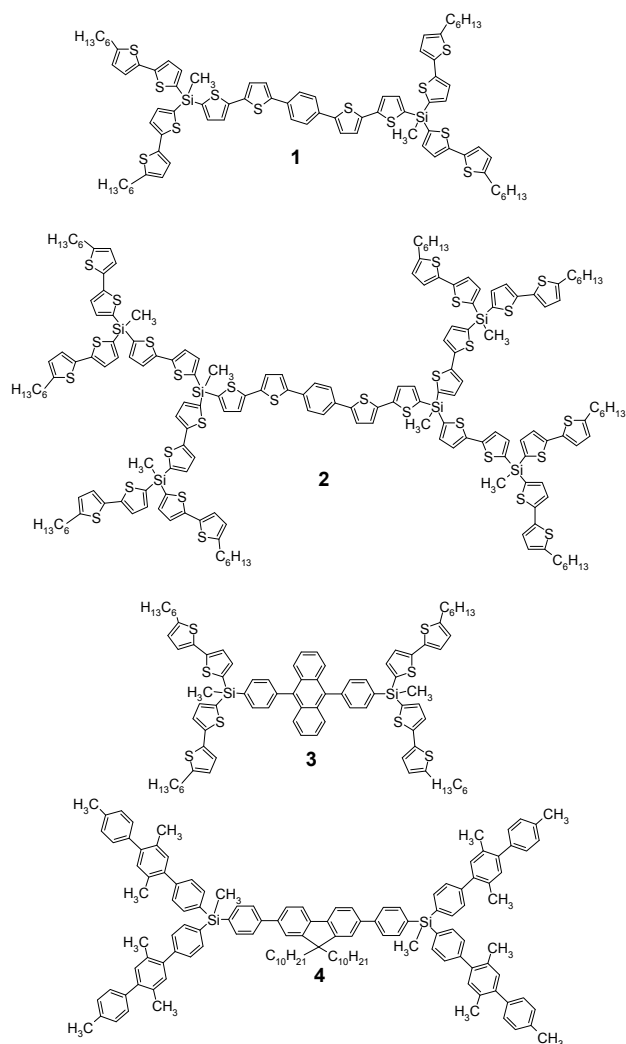


Figure 1: Dendritic oligoarylsilanes developed in this work.

## 2 RESULTS AND DISCUSSION

As can be seen from the structural formulas presented in Fig. 1, dendritic arylsilanes considered in this work can have different chemistry: they can contain oligothiophene, oligothiophene-phenylene, oligophenylene, diphenyl-anthracene, etc. However, their common features are the presence of two types of luminophores covalently linked to each other via silicon atoms and high  $Q_F$  (>50%). The

luminophor of the first type is single and located in the center of the molecule, which contain several luminophores of the second type at the periphery. Let's consider design rules for such dendritic oligoarylsilanes, their synthesis, optical properties and application in plastic scintillators.

### 2.1 Design and synthesis of dendritic oligoarylsilanes

General rules for design of a dendritic oligoarylsilane, which can serve as efficient nanostructured luminophor, are the following. First, an organic luminophor with suitable emission wavelength and high  $Q_F$  is chosen as acceptor, having lower optical band gap. Second, the other organic luminophor, luminescence spectra of which should correspond to one of the absorption bands of the acceptor, is chosen as a donor with the higher optical band gap. The donor can have significantly lower  $Q_F$  than the acceptor, but it should not be equal to zero. Third, both donor and acceptor (or their precursors) should have reactive sites suitable for organosilicon chemistry, which allows attaching several donor fragments (typically 4 or 8) to one acceptor fragment through silicon atoms. Such attachment fixes donor and acceptor fragments within one organosilicon structure on the distance of 1-2 nm between the centers of each other with the orientation favorable to intramolecular Förster energy transfer.

Synthesis of the desired dendritic oligoarylsilane starts from preparation of organosilicon precursor **A** containing reactive chlorosilane groups and a fragment of the acceptor. Coupling the donor with **A** leads to formation of monodendron **M** having at least two donors and a fragment of the acceptor. Finally, **M** reacts with bifunctional precursor **B** of the acceptor. This scheme is illustrated by the synthesis of dendritic oligoarylsilane **1** (Fig. 2). In this case the donor is 5-hexyl-2,2'-bithiophene, while the acceptor is 1,4-bis(2,2'-bithien-5-yl)benzene. Monodendron **M1** before the reaction with **B1** was transferred into its reactive organoboron derivative **M1-B-Pin**. Detailed synthetic procedure and full characterization of this oligoarylsilane is described in the Experimental section.

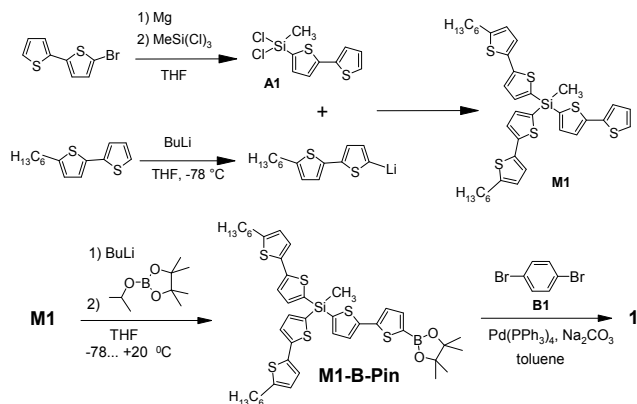


Figure 2: Synthesis of dendritic oligoarylsilane 1.

## 2.2 Optical properties of dendritic oligoarylsilanes

Since the rate constant of nonradiative energy transfer by inductive-resonance Förster mechanism is proportional

to  $\left(\frac{\bar{R}_{DA}^0}{\bar{R}_{DA}}\right)^6$ , where  $\bar{R}_{DA}$  is the distance between the

centers of the donor and acceptor fragments, and  $\bar{R}_{DA}^0$  is the critical radius of the inductive-resonance energy transfer, which, according to the Förster formula, is proportional to the overlapping integral

$\left(\int_0^\infty f_D(\nu) \cdot \varepsilon_A(\nu) \frac{d\nu}{\nu^4}\right)^{1/6}$  of the acceptor absorption

spectra  $\varepsilon_A(\nu)$  and the donor luminescence spectra  $f_D(\nu)$ , the efficiency of nonradiative energy transfer between the closely located fragments of donor and acceptor approaches to unity [6]. Thus, in the molecule of the nanostructured luminophor, several donor fragments absorb the initial short wavelength light with a high absorption cross-section and almost without any losses transfer it into specially chosen acceptor fragment having high  $Q_F$ . It leads to the effect that  $Q_F$  of the whole nanostructured luminophores is close to  $Q_F$  of its acceptor fragment under excitation into any of its absorption wavelengths, corresponding either to donor or to acceptor fragments (Table 1).

Mole- cule	Absorption		Luminescence	
	$\lambda_{\text{abs}}$ , nm	$\sigma_{\text{max}}$ , cm <sup>-2</sup>	$\lambda_{\text{lum}}$ , nm	$Q_F$ , %
1	250	3,67*10 <sup>-16</sup>	456	55
	334		456	55
	404		456	55
2	250	1,06*10 <sup>-15</sup>	456	50
	337		456	50
	404		456	55
3	261	4,60*10 <sup>-16</sup>	418	85
	332		418	80
	396		418	85
4	213	9,65*10 <sup>-16</sup>	372	78
	265		372	85
	336		372	85

Table 1: Optical properties of dendritic oligoarylsilanes.  $\lambda_{\text{abs}}$  - absorption maximum,  $\sigma_{\text{max}}$  - absorption cross-section at certain absorption band,  $\lambda_{\text{lum}}$  - luminescence maximum,  $Q_F$  - fluorescence quantum yield under excitation at certain absorption band.

## 2.3 Plastic scintillators with dendritic oligoarylsilanes as efficient spectral shifters

For determination the light output of novel plastic scintillators with dendritic oligoarylsilanes as spectral

shifters we have used a standard scintillator, containing 0.1 M p-terphenyl (PTP) and 6 mM POPOP. It has the light output of 1000 photon/MeV under its irradiation with  $\alpha$ -particles having the energy of 5.49 MeV.

Results of measurements of the amplitude spectra of scintillations, obtained under irradiation of the samples of PS scintillators, containing each 10 – 15 mM of the dendritic oligoarylsilanes, and the standard scintillator with  $\alpha$ -particles, are summarized in Table 2. The samples, containing from 10 to 15 mM of the oligoarylsilanes under irradiation with  $\alpha$ -particles give the light output from 1156 to 1281 photon/MeV that significantly exceeds the light output of the standard plastic scintillator.

Composition	Concentration, mM	Light output, Photons/MeV	$\lambda_{\text{max}}$ , nm
PS + 2% (1)	10	1134	487
PS + 2% (3)	15	1281	431
PS + 2% (4)	12	1156	389
PS + 3% (4)	18	1350	389
PS + 5% (4)	30	1489	389
standard	$C_{\text{PTP}} = 100$ $C_{\text{POPOP}} = 6$	1000	425

Table 2: Composition and properties of plastic scintillators from PS matrix and dendritic oligoarylsilanes as compared to the standard plastic scintillator. The light output is measured for  $\alpha$ -particles,  $\lambda_{\text{max}}$  - maximum position in the scintillation spectra.

Since the absorption cross-section of the dendritic oligoarylsilanes in the region of luminescence of PS matrix is maximal, while in the range of their own luminescence it is minimal, increasing their concentration up to 30 – 50 M could lead to further enhancing the light output of the plastic scintillator. Indeed, under irradiation with  $\alpha$ -particles, the light output increased from 1156 Photon/MeV (for C(4) = 12 mM) up to 1489, which is 1.5 times higher as compared to the light output of the standard scintillator (1000 Photon/MeV). It should be noted that the scintillator with dendritic oligoarylsilane 4 under concentration of 30 mM has the extinction coefficient in the region of the PS emission higher than p-terphenyl under concentration of 0.1 M in the standard PS scintillator. This could be a possible reason of increasing the light output. The other reason should be related to linking of both activator and spectral shifter luminophores into one molecule of the dendritic oligoarylsilane with the effective intramolecular energy transfer from the activator to the spectral shifter.

Scintillation decay times (SDT) of the novel scintillators with dendritic oligoarylsilanes are defined by the fluorescence decay time of the acceptor, located in the center of the molecule. Comparison of the SDTs of the PS scintillator with 30 mM of 4 and the standard PS scintillator have shown that duration of the fast component of SDTs for these scintillators is 1.71 ns vs 2.41 ns, and the slow component is 13.35 ns vs 19.11 ns, respectively. Ratio of

the intensity of the fast to slow component is 1.32 vs 1.57, respectively. Therefore, both components of the SDT of the “nanostructured” PS scintillator are significantly better than those of the standard PS scintillator. Such temporal characteristics and extremely high light output of the plastic scintillators with dendritic oligoarylsilanes makes them very prospective for creation of novel plastic scintillation detectors with high temporal resolution.

### 3 EXPERIMENTAL SECTION

All reagents and solvents were purchased from Sigma-Aldrich Co. and used as it is. Synthesis of monodendrons **M1** and **M1-B-Pin** are described elsewhere [10, 7].

Synthesis of dendritic oligoarylsilane **1**: 1,4-dibromobenzene (149 mg, 0.63 mmol) was placed into a three-neck 100 mL flask equipped with a magnetic stirrer, cooler, and argon inlet. The flask was filled with Pd(PPh<sub>3</sub>)<sub>4</sub> (77 mg, 0.07 mmol) and kept under argon. Degassed solutions of **M1-B-Pin** (1.12 g, 1.34 mmol) in 30 mL of toluene and 2 M aq Na<sub>2</sub>CO<sub>3</sub> (2.0 ml, 4 mmol) were added afterwards. The mixture was heated at reflux for 20 h. After that the reaction mixture was poured into a mixture of 100 mL of water, 4 mL of 1 M HCl, and 150 mL of toluene. The organic layer was isolated, washed with water and evaporated. The crude product was purified by column chromatography on silica gel (eluent hexane - toluene, 3:1) to give pure **1** as orange solid. Yield: 0.47 g (50 %). <sup>1</sup>H NMR (DMSO/CCl<sub>4</sub>, δ, ppm): 0.88 (t, 12H, J = 6.7 Hz), 0.93 (c, 6H), 1.25-1.45 (overlapping peaks, 24 H), 1.63 (m, 8H, M = 5, J = 7.3 Hz), 2.76 (t, 8H, J = 7.3 Hz), 6.69 (d, 4H, J = 3.7 Hz), 7.05 (d, 4H, J = 3.7 Hz), 7.23 (d, 4H, J = 3.1 Hz), 7.28 (d, 2H, J = 3.7 Hz), 7.31 (d, 4H, J = 3.7 Hz), 7.34 (d, 2H, J = 3.7 Hz), 7.37 (d, 2H, J = 3.7 Hz) 7.43 (d, 2H, J = 3.7 Hz), 7.63 (s, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): -0.18; 14.07; 22.55; 28.72; 30.15; 31.52; 31.54; 123.89; 123.99; 124.36; 124.84; 125.04; 125.25; 125.92; 132.88; 133.14; 134.26; 134.29; 136.43; 137.85; 142.91; 144.35; 145.20; 145.97. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ, ppm): -25.42. Anal. Calcd. for C<sub>80</sub>H<sub>86</sub>S<sub>12</sub>Si<sub>2</sub> (%): C, 64.55; H, 5.82; S, 25.85; Si, 3.77. Found (%): C, 64.50; H, 5.60; S, 25.55; Si, 3.50. MALDI-MS: m/z 1487.62 (M + Ag)<sup>+</sup>, calculated 1488.29.

All other dendritic oligoarylsilanes under consideration were synthesized and characterized similarly.

Optical properties of dendritic oligoarylsilanes were investigated by UV-Vis absorption and luminescent spectroscopy in dilute solutions in THF using the techniques described elsewhere [3].

Plastic scintillators were prepared by co-extrusion of PS with corresponding dendritic oligoarylsilanes at different weight ratios: from 98:2 to 95:5. Samples for investigations of scintillation efficiency being round plates with the diameter of 25 mm and height of 0,2 mm were prepared by hot-pressing from the corresponding extrudates. Am<sup>241</sup> was used as a source of α-particles with the energy of 5,49 MeV. Experimental setup for measuring the scintillation efficiency was similar to those described in [11].

### 4 CONCLUSIONS

To sup up, we have successfully designed and synthesized a series of dendritic oligoarylsilanes, which can serve as efficient nanostructured luminophores, possessing high absorption cross-sections and fluorescence quantum yield from 50 to 85%. Application of them in plastic scintillators allowed increasing their light output up to 1489 Photons/MeV for α-particles, which is almost 50% higher as compared to those of the standard plastic scintillator. Novel plastic scintillators with nanostructured luminophores show faster scintillation decay times as well, which makes them prospective for high temporal resolution.

### REFERENCES

- [1] S.-C. Lo, P.L. Burn, “Development of Dendrimers: □ Macromolecules for Use in Organic Light-Emitting Diodes and Solar Cells”, *Chem. Rev.*, 107, 1097–1116, 2007.
- [2] Z. Xu, J.S. Moore. “Design and synthesis of a convergent and directional molecular antenna”, *Acta Polym.*, 45, 83-87, 1994.
- [3] Y.N. Luponosov, S.A. Ponomarenko, N.M. Surin, O.V. Borshchev, E.A. Shumilkina, A.M. Muzafarov, “The first organosilicon molecular antennas”, *Chem. Mater.*, 21, 447-455, 2009.
- [4] O.V. Borshchev, S.A. Ponomarenko, E.A. Kleymyuk, Y.N. Luponosov, N.M. Surin, A.M. Muzafarov, “Branched oligothiophenesilanes with effective nonradiative energy transfer between the fragments”, *Rus. Chem. Bull.*, 59, 797-805, 2010.
- [5] N.M. Surin, O.V. Borshchev, Y.N. Luponosov, S.A. Ponomarenko, A.M. Muzafarov, “Spectral-luminescent properties of oligothiophenesilane dendritic molecules”, *Rus. J. Phys. Chem.*, 84, 1979-1985, 2010.
- [6] T. Förster, “Zwischenmolekulare Energiewanderung und Fluoreszenz“, *Ann. Physik*, 6, 55-75, 1948.
- [7] M.S. Polinskaya, O.V. Borshchev, Y.N. Luponosov, N.M. Surin, A.M. Muzafarov, S.A. Ponomarenko, “Synthesis and properties of a new luminescent oligoarylsilane dendrimer”, *Mendeleev Commun.*, 21, 89-91, 2011.
- [8] W.R. Leo, “Techniques for nuclear and particles physics experiments: a how-to approach”, 2-nd ed., Springer, Berlin, 1992.
- [9] A. Peurrung, “Materials science for nuclear detection”, *Materials Today*, 11, 50, 2008.
- [10] Y.N. Luponosov, S.A. Ponomarenko, N.M. Surin, A.M. Muzafarov, “Facile synthesis and optical properties of bithiophenesilane monodendrons and dendrimers”, *Organic Letters*, 10, 2753-2756, 2008.
- [11] H. Nakamura, H. Kitamura, O. Shinji, K. Saito, Y. Shirakawa, S. Takahashi, “Development of polystyrene-based scintillation materials and its mechanisms”, *Appl. Phys. Lett.*, 101, 261110, 2012.