

Synthesis and optical properties of linear and branched bithienylsilanes

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For the first time, bithienylsilanes **1–4** containing from one to four 5-hexyl(2,2'-bithien-5-yl) fragments at the same silicon atom were obtained and their optical properties were investigated.

Thiophene and its derivatives are actively used as monomers for the synthesis of conjugated polymers and oligomers with semiconducting, photo- and electrooptical properties.¹ They were utilized as functional materials in organic light-emitting diodes (OLEDs), organic thin-film transistors (OTFTs), photovoltaics (solar cells) *etc.* Various linear,² star-shaped,³ branched and hyperbranched⁴ macromolecules, as well as dendrimers⁵ containing thiophenesilane fragments were described. Bithienylsilanes with different numbers of bithienyl fragments at a silicon atom were also reported.^{5(a),6} However, a systematic study of the influence of a polymeric chain topology on the optical properties of such compounds was not carried out. The goal of this work was to synthesise and investigate the optical properties of model linear and branched bithiophenesilanes containing from one to four bithiophenesilane fragments at the same silicon atom (Figure 1). The first compound models a terminal group, the second is an analogue of a linear polymer, while the third and fourth are branched structures, dendrimer fragments.

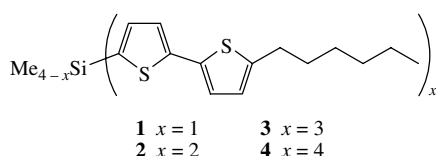
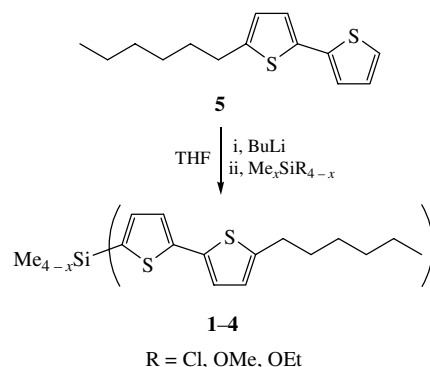


Figure 1 Structure of bithienylsilanes **1–4**.

The organolithium and organomagnesium derivatives of thiophene, which react actively with chloro- and alkoxy-silanes, could be used for the formation of the silicon–thiophene bond.⁷ In particular, the preparation of bithienylsilanes both through organolithium derivatives of 2,2'-bithiophene^{6(a)} and by the Stille coupling reaction from the corresponding organotin derivatives of thienylsilanes and bromothiophenes was described.⁸ We used a general synthetic method presented in Scheme 1.

5-Hexyl-2,2'-bithiophene **5**, which was obtained by a procedure described elsewhere,⁹ was the initial thiophene derivative since it is known that fluorescent properties in a series of oligothiophenes could be revealed starting from the bithiophene. Moreover, a hexyl group gives a good solubility to both 5-hexyl-2,2'-bithiophene and goal bithiophenesilanes. The choice in favour of the thienyllithium derivatives was governed by their higher reactivity, as compared to that of thienylmagnesium compounds.



Scheme 1 General procedure for the synthesis of bithienylsilanes **1–4**.

Compounds **1–4** were obtained by the lithiation of 5-hexyl-2,2'-bithiophene with *n*-butyllithium in a THF–hexane mixture followed by the reaction of the thienyllithium derivative formed with a corresponding functional organosilicone core. Trimethylchlorosilane, dimethyldimethoxysilane, methyltrimethoxysilane and tetraethoxysilane were used as these cores. A 20% excess of 5-hexyl-2,2'-bithiophene was used for a guaranteed substitution of all reactive groups of the polyfunctional core for the synthesis of compounds **2–4**. In accordance with the GPC data, the reaction yields were 85, 75 and 86%, respectively. In previous publications, the yields of three- and tetra-substituted thiophenesilanes were less than 10% under the usage of both organomagnesium and organolithium thiophene derivatives for the reactions with chloro- and ethoxysilanes.^{7(a)} Only tetramethoxysilane and 2-thienyllithium allowed raising the yield of tetra-thienylsilane up to 70%.^{5(a)} In this work, the most interesting result was obtained in the synthesis of tetrakis-(5'-hexyl-2,2'-bithien-5-yl)silane **4** from tetraethoxysilane in 86% yield. These data evidence the efficiency of the synthetic technique chosen, which allows us to obtain different bithienylsilane derivatives from the corresponding chloro- and alkoxy-silanes in high yields.

All the compounds synthesised were purified chromatographically by classical chromatography on silica gel. The structure and purity of compounds **1–4** were confirmed by ¹H NMR spectroscopy, GPC, mass spectrometry (MALDI-TOF) and elemental analysis.^{†‡}

Dilute hexane solutions of the chromatographically pure compounds were used for the investigation of spectral-lumi-

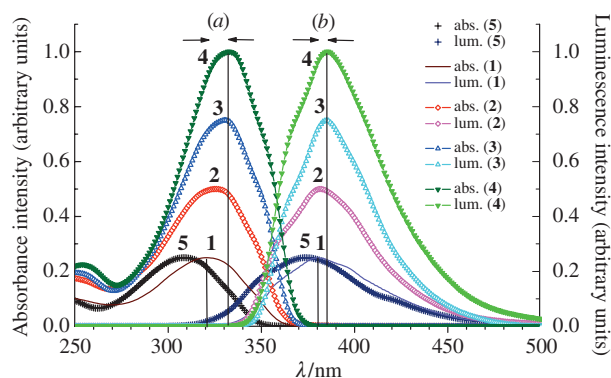


Figure 2 (a) Absorbance and (b) luminescence spectra of 5-hexyl-2,2'-bithiophene **5** and bithienylsilanes **1–4**.

nescent properties and their comparison with those of initial 5-hexyl-2,2'-bithiophene. The absorbance and luminescence spectra of these compounds are shown in Figure 2. The red shift of the absorption maximum (from 308 to 321 nm) is clearly seen when going from bithiophene **5** to bithienylsilane **1** [Figure 2(a)]. At the same time, a maximum of the luminescence spectra [Figure 2(b)] has also a long wave shift (from 374 to 381 nm). The quantum yield of luminescence increases from 1.7 (compound **5**) to 5.8% (compound **1**). As a whole, spectral-luminescent characteristics when going from bithiophene **5** to bithienylsilane **1** change in a similar manner

[†] ¹H NMR spectra were recorded using a Bruker WP-250 SY spectrometer (250.13 MHz) in CDCl₃ solutions unless otherwise stated. Mass spectra were recorded on a Bruker Daltonics Reflex-III mass spectrometer in the positive ions regime using the reflect mode with the target voltage of 20 mV. Anthracene-2,4,9-triol was used as a matrix. The samples were prepared by the dissolution of test compounds in chloroform (10^{−4}–10^{−6} mol dm^{−3}) and mixed with solution of the matrix (20 mg cm^{−3}) in chloroform in a ratio of 1:1. GPC analysis was performed on a Shimadzu instrument with a RID-10AVP refractometer and a SPD-M10AVP diode matrix as detectors using 7.8×300 mm Phenomenex columns (USA) packed with the Phenogel sorbent with a pore size of 500 Å and THF as the eluent.

Fluorescence spectra were recorded on an ALS01M scanning spectrofluorimeter with a light source (150 W arc xenon lamp), two Seya-Namioka-type monochromators and two photoelectronic multipliers. The monochromators were equipped with a concave diffraction grating of 1200 lines per mm. The scanning range of the monochromators was 200–1200 nm. The spectral widths of monochromators slits were 1–15 nm; the scanning speed was 3.75–2400 nm min^{−1}, the accuracy of wavelength setting was ±0.5 nm; the repeatability of the wavelength setting was ±0.25 nm. Two identical photoelectronic multipliers with a photocathode designed for the work in the 112–830 nm range (antimony-sodium-potassium-cesium photocathode deposited onto a magnesium fluoride window) were used for the measurements of excitation and emission intensities. A method of single photons counting on consecutive time intervals was used for the registration of low-intensity emission. A signal-to-noise ratio for a Raman scattering band of water at the excitation wavelength of 350 nm was 1000:1. The information collected was stored in a digital form and processed with corresponding software.

Data on the quantum yields *Q* of bithiophenesilanes were obtained by measuring the relative fluorescence quantum yield. The following substances were used as standards: solutions of anthracene in ethanol and hexane (*Q* = 0.30±0.04), solutions of *p*-terphenyl in ethanol and hexane (*Q* = 0.75±0.15), a solution of Rhodamine 6G in ethanol (*Q* = 0.96±0.02) and a solution of tryptophan in ethanol (*Q* = 0.14±0.06). The quantum yields of the standards were taken from the literature.¹¹ In all cases, the data presented were obtained by averaging the values calculated for all four standards. For these calculations integrals on the fluorescence spectra of the test compounds and the standards were used. Absorption spectra were measured using a Shimadzu UV-2501PC spectrophotometer. The absorbance of the solutions used for the measurements of quantum yields did not exceed 0.05 in 10 mm thick quartz cuvette. The concentrations of the solutions of bithiophenesilanes were 10^{−6} mol dm^{−3} and lower (to 10^{−8} mol dm^{−3}).

to those when going from benzene to a toluene (long-wave shift of the absorbance and luminescence spectra with the increase of the quantum yield: benzene, 7%; toluene, 18%). Similar changes evidence the presence of a small σ-π conjugation between a bithiophene unit and a silicon atom. The absorbance and luminescence spectra of compounds **2–4** indicate that an increase of the number of bithiophene fragments at the same silicon atom up to two leads to a further small shift of the absorbance spectra to a long-wave area (from 321 to 325 nm). At the same time, the luminescence spectra change only slightly (from 381 to 382 nm). Both the absorbance and the luminescence spectra of compounds **3** and **4** are practically identical (Figure 2).

[‡] *Trimethyl-5-(5'-hexyl-2,2'-bithienyl)silane 1*. A 2.5 M solution of butyllithium in hexane (1.24 ml, 3.1 mmol) was added dropwise to a solution of 5-hexyl-2,2'-bithiophene (0.78 g, 3.1 mmol) in 15 ml of dry THF, keeping the temperature in the interval between −18 and 0 °C. Then, the cooling bath was removed and the temperature was allowed to rise to 0 °C. After cooling the reaction mixture again to −18 °C, a solution of trimethylchlorosilane (0.4 ml, 3.1 mmol) in 1.5 ml of absolute THF was added dropwise. After that, the cooling bath was removed and the temperature was allowed to rise to 20 °C. For isolation of the product, 100 ml of diethyl ether and 50 ml of ice water were added to the reaction mixture. The organic phase was separated, washed several times with water to pH 7 and dried over Na₂SO₄; the solvent was evaporated. As a result, 1.04 g of the substance, containing according to GPC 88% of the product, was obtained. Purification by column chromatography on silica gel (eluent, hexane) gave the pure product (0.647 g, 65%), mp 17 °C. ¹H NMR (CDCl₃) δ: 0.31 (s, 9H, SiMe), 0.88 (t, 3H, CH₂Me, *J* 6.7 Hz), 1.23–1.45 (overlapped peaks, 6H, CH₂CH₂CH₂), 1.67 (m, 2H, thiophene-CH₂CH₂, *M* = 5, *J* 7.3 Hz), 2.77 (t, 2H, thiophene-CH₂CH₂, *J* 7.3 Hz), 6.66 [d, 1H, thiophene-H(4'), *J* 3.7 Hz], 6.97 [d, 1H, thiophene-H(3'), *J* 3.7 Hz], 7.09 [d, 1H, thiophene-H(3), *J* 3.7 Hz], 7.13 [d, 1H, thiophene-H(4), *J* 3.7 Hz]. MS, *m/z*: 322 (M⁺). Found (%): C, 63.37; H, 8.26; S, 19.72; Si, 8.68. Calc. for C₁₇H₂₆S₂Si (%): C, 63.29; H, 8.12; S, 19.88; Si, 8.71.

Dimethylbis(5'-hexyl-2,2'-bithien-5-yl)silane 2 was obtained by a similar procedure from 5-hexyl-2,2'-bithiophene (1.18 g, 4.7 mmol) and dimethyldimethoxysilane (0.27 ml, 2.0 mmol). After purification by column chromatography on silica gel (eluent, hexane), the pure product was obtained (0.859 g, 78%), mp 5 °C. ¹H NMR (CDCl₃) δ: 0.63 (s, 6H, SiMe), 0.88 (t, 6H, CH₂Me, *J* 6.7 Hz), 1.23–1.45 (overlapped peaks, 12H, CH₂CH₂CH₂), 1.66 (m, 4H, thiophene-CH₂CH₂, *J* 7.3 Hz, *M* = 5), 2.77 (t, 4H, thiophene-CH₂CH₂, *J* 7.3 Hz), 6.66 [d, 2H, thiophene-H(4'), *J* 3.7 Hz], 6.98 [d, 2H, thiophene-H(3'), *J* 3.7 Hz], 7.16 [dd, 4H, thiophene-H(3),H(4), *J*₁ 3.7 Hz, *J*₂ 8.5 Hz]. MS, *m/z*: 556 (M⁺). Found (%): C, 64.70; H, 7.26; S, 23.42; Si, 5.09. Calc. for C₃₀H₄₀S₄Si (%): C, 64.69; H, 7.24; S, 23.03; Si, 5.04.

Methyltris(5'-hexyl-2,2'-bithien-5-yl)silane 3 was obtained by a similar procedure from 5-hexyl-2,2'-bithiophene (0.9 g, 3.6 mmol) and methyltriethoxysilane (0.14 ml, 1.0 mmol). After purification by column chromatography on silica gel (eluent, hexane–toluene, 10:1) the pure product was obtained (3.69 g, 54%), mp 44 °C. ¹H NMR (CDCl₃) δ: 0.88 (t, 9H, CH₂Me, *J* 6.7 Hz), 0.92 (s, 3H, SiMe), 1.23–1.45 (overlapped peaks, 18H, CH₂CH₂CH₂), 1.66 (m, 6H, thiophene-CH₂CH₂, *J* 7.3 Hz, *M* = 5), 2.77 (t, 6H, thiophene-CH₂CH₂, *J* 7.3 Hz), 6.66 [d, 3H, thiophene-H(4'), *J* 3.7 Hz], 7.01 [d, 3H, thiophene-H(3'), *J* 3.7 Hz], 7.18 [d, 3H, thiophene-H(3), *J* 3.7 Hz], 7.27 [d, 3H, thiophene-H(4), *J* 3.7 Hz]. MS, *m/z*: 790 (M⁺). Found (%): C, 65.47; H, 7.03; S, 24.35; Si, 3.39. Calc. for C₄₃H₅₄S₆Si (%): C, 65.26; H, 6.88; S, 24.31; Si, 3.55.

Tetrakis(5'-hexyl-2,2'-bithien-5-yl)silane 4 was obtained by the similar procedure from 5-hexyl-2,2'-bithiophene (1.99 g, 8.0 mmol) and tetraethoxysilane (0.37 ml, 1.7 mmol). After purification by column chromatography on silica gel (eluent, hexane), the pure product was obtained (1.22 g, 72%), mp 50 °C. ¹H NMR (DMSO, CCl₄) δ: 0.88 (t, 12H, CH₂Me, *J* 6.7 Hz), 1.23–1.45 (overlapped peaks, 24H, CH₂CH₂CH₂), 1.66 (m, 8H, thiophene-CH₂CH₂, *J* 7.3 Hz, *M* = 5), 2.77 (t, 8H, thiophene-CH₂CH₂, *J* 7.3 Hz), 6.72 [d, 4H, thiophene-H(4'), *J* 3.7 Hz], 7.1 [d, 4H, thiophene-H(3'), *J* 3.7 Hz], 7.28 [d, 4H, thiophene-H(3), *J* 3.7 Hz], 7.37 [d, 4H, thiophene-H(4), *J* 3.7 Hz]. MS, *m/z*: 1024 (M⁺). Found (%): C, 65.33; H, 6.59; S, 25.38; Si, 2.61. Calc. for C₅₆H₆₈S₈Si (%): C, 65.57; H, 6.68; S, 25.01; Si, 2.74.

Table 1 Spectral-luminescent characteristics of dilute hexane solutions of the test compounds.

Compound	Absorbance, λ_{\max}/nm	Luminescence	
		λ_{\max}/nm	Q (%)
5	308	374	1.7±0.4
1	321	381	5.8±2.0
2	325	382	9.3±3.0
3	331	385	19.0±1.9
4	332	385	20.0±2.0

It is well known that the presence of a conjugation in the oligothiophene series is accompanied by a significant shift of absorbance and luminescence spectra to a red region.¹⁰ Therefore, a small long-wave shift observed evidences the fact that the conjugation of bithiophene fragments through a silicon atom does not take place. At the same time, changes in the spectral-luminescent properties of compounds **2–4** are characterised by two peculiarities. First, the absorbance intensity (molar absorption coefficient) increases proportionally to the number of bithiophene fragments [Figure 2(a)], that is also in favour of the suggestion about the absence of conjugation through the silicon atom. Second, when going from compound **1** to compounds **3** and **4**, a sharp increase of the luminescence quantum yield Q is observed (Table 1). The growth of Q from 5.8 to 19–20% in the absence of any remarkable conjugation through the silicon atom could be explained by the influence of 3D architecture (reciprocal orientation and distance between the bithiophene fragments) on the luminescence efficiency.

Thus, a series of bithienylsilanes **1–4** synthesised for the first time allowed us to investigate the dependence of the optical properties (absorbance and luminescence spectra and the quantum yield of luminescence) of linear and branched bithiophene-silanes on the number of thiophene fragments attached to the same silicon atom. The data obtained unambiguously show the advantages of a branched molecular structure for the development of new light-emitting materials.

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